SOIL TESTING FOR PHOSPHORUS AVAILABILITY TO SOME CONIFERS IN BRITISH COLUMBIA

by

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ABSTRACT

Two complementary investigations were conducted as a preliminary study to find an adequate method for estimating "available" phosphorus (P) in British Columbia forest soils. Eight soil materials provided a range of British Columbia forest soil properties, P forms and P levels. The 12 methods evaluated were H_2O-soluble P, Truog, modified Olsen (using polyacrylamide to remove coloured organic constituents), Bray P_1 and P_2, modified Bray P_1 and P_2 (longer extraction time), modified double-acid (0.05 N HCl + 0.025 N H_2SO_4, using polyacrylamide), NH_4OAc (ammonium acetate) at pH 4.8, modified (using polyacrylamide) NH_4HCO_3-DTPA (diethylene triamine pentaacetic acid), 0.01 N HCl, and new-Mehlich. The first study investigated relationships among 12 soil test methods for estimating soil available P and 4 chemical P fractions. The 4 chemical P fractions were obtained by a modified Chang and Jackson procedure.

The second study evaluated the test methods as indices of "tree-available P" through a greenhouse pot trial with the 8 soil materials x 2 P treatment levels (P added and control) x 3 tree species (Douglas-fir, western hemlock, and lodgepole pine).

The first study revealed that most methods extract the greatest amount of P from forest floor samples (apart from a P fertilized soil) and the least from Podzolic B horizon samples. Similar to the literature, P levels obtained by a number of the methods are significantly correlated with each other. Modified Olsen values are significantly correlated with values from the greatest number of other

methods. The 4 Bray methods, modified double-acid and new-Mehlich methods yielded the next largest group of significant correlations. Water-soluble P and 0.01 N HCl values were seldom significantly correlated, and NH_4OAc(pH 4.8) values were not correlated, with other method test values.

Contrary to agricultural soils literature, only one significant correlation existed between the soil test values and P forms: NH_4OAc (pH 4.8) extraction with the Ca-P fraction. Correlations between P fractions were also not as extensive, with only reductant-soluble P and Fe-P being significantly related for all 8 soils. Across the 5 "Podzolic" soils, Ca-P and Al-P were also significantly related (negatively).

In the greenhouse study, seedling growth was best on the forest floor material, and worst on the calcareous soil material for lodgepole pine and Douglas-fir and on a Podzolic B horizon for western hemlock. All species displayed dramatic responses to P on some of the soils. In a hierarchical soil analysis screening (12 methods x 3 soils; then 3 candidate methods x 5 remaining soils) the new-Mehlich values were the most significantly correlated with foliar P concentration for all three species in the first stage. Many of the methods were significant for lodgepole pine. Modified Olsen and modified NH_4HCO_3-DTPA also appeared good for Douglas-fir, but these alkaline extractants were considered too cumbersome for routine laboratory anaysis of the study soils.

The three chosen candidate methods were new-Mehlich; 0.01 N HCl, and Bray P_1. Evaluating these methods across various groups of the 8 soils for each species (i.e. without the organic, calcareous, eluviated,

and P-fertilized soil materials in turn and in combinations) suggested that the new-Mehlich method may be best. Bray P_1 commonly did not correlate well with Douglas-fir foliar P. The 0.01 N HCl did not appear as good as it had in the preliminary screening, but did well across Podzolic horizons alone. All methods correlated poorly with western hemlock foliar P under certain conditions.

The new-Mehlich method was evaluated for the individual treatment replicates, yielding correlations with foliar P which were consistent with prior results. Correlations for the organic and eluviated soils were highly significant for all three species. For individual soils, no significant correlations existed for all but two Podzolic soil materials. However, grouped Podzolic soils yielded strong correlations for the new-Mehlich method.

The results reported here need field testing and it is recommended that the new-Mehlich and Bray P_1 soil tests still be considered together until adequate field data provide further information.

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CHAPTER 1

INTRODUCTION

Phosphorus is an essential macronutrient, required by all higher plants for normal metabolism, growth, development, maturation, and reproduction. In most ecosystems, soil phosphate represents essentially the only source for plants, atmospheric inputs being very low (Emsley 1982). The availability of soil phosphorus to plants is severely restricted by low "mobility" which is the product of many complex chemical, biological, and physical interactions. Thus, inadequate phosphorus supply to crops is a widespread agricultural problem in most parts of the world, and phosphorus fertilizer use is second only to nitrogen (Tisdale and Nelson 1975). Many soil tests have been developed to attempt to predict that amount of the soil phosphorus which is available to a given crop. No one soil P test appears to be suitable for all soils (Mattingly and Talibudeen 1967). Such soil tests must be calibrated for local soil conditions.

In forestry, a similar trend in the phosphorus problem has developed. Although P deficiences are not particularly widespread, managed pine stands in Europe, southeastern United States, and the Southern Hemisphere are often P-deficient (Baule 1973). In 1977, the total forest area fertilized with P was approximately 500,000 ha (R. Ballard 1980). The incidence of P deficiencies is expected to increase steadily on a dramatic scale with increased intensive silviculture (Pritchett 1976).

Recent investigations in the Pacific Northwest (e.g., Heilman and Ekuan 1980a) have revealed low foliar P levels in trees on some coastal forest soils. In some areas in the British Columbia interior, T. Ballard (1981) reported slight to moderate P deficiencies in some lodgepole pine (Pinus contorta Dougl.) stands (based on foliar analysis) and noted that deficiencies may be expected to increase in severity and extent following N fertilization. Similar cases may be cited for the other major timber species. With increasing intensive forest management in British Columbia the problem of P deficiencies is likely to increase. Severe N deficiency is common throughout British Columbia (T. Ballard 1983) and foliar P concentrations are known to decrease following application of N fertilizers (e.g., Otchere-Boateng 1981).

It is thought that the forest floor supplies substantially higher quantities of available P to the growing trees than the mineral soil horizons. Hence, planted tree seedlings would likely suffer from P deficiencies in some areas where logging activities or site preparation lead to (1) the removal of a significant portion of the forest floor material, and/or (2) mixing of the forest floor with mineral soil (because of increased P fixation). Exocellular phosphatase enzymes are considered responsible for P mineralization from organic matter (Ho 1979). The activity of phosphatase enzymes may be dramatically reduced by even low levels of heavy metal (e.g., Cu and Mn) pollution (Tyler 1976); such atmospheric levels may be present in British Columbia in regions with mineral ore smelters and/or concentrators, or industrial and urban centers. Concern about soil P availability therefore exists

for some species on some forest soils in British Columbia and may well be expected to substantially increase in severity and spatial extent in the near future.

However, response to P fertilization has so far not been reported in field trials in the Pacific Northwest (Heilman 1981), although some greenhouse studies using Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) and western hemlock (Tsuga heterophylla (Raf.) Sarg.) seedlings, and soils from areas believed to be P-deficient, have given excellent tree response to P treatments (e.g., Strand and Austin 1966; Heilman and Ekuan 1980a, 1980b; Curran and T. Ballard 1984). Responses to P are also noted in newly established nurseries and P fertilization is an integral part of nursery management (van den Driessche 1969). It is possible that the lack of response to applied N or P in some stands may be partially due to some unfavourable P or N interactions. (For example, application of N fertilizers (e.g., urea) to some western hemlock stands and Douglas-fir plantations in the coastal area of the Pacific Northwest (from British Columbia to Oregon) has also not increased tree growth (University of Washington, College of Forest Resources 1974; Heilman and Ekuan 1980a.)

The above discussion indicates the increasing need for an "adequate" soil test for estimating "available P" status of forest soils in British Columbia. An "available P" extraction method which is a good predictor of tree growth or tree P status in one area, may be inadequate in another locality. Thus, before a given method is used operationally in British Columbia, it must be evaluated, or calibrated, against local tree growth and/or P status.

This thesis reports on a study designed to provide a preliminary evaluation of soil test methods for estimating "available phosphorus" to forest trees in British Columbia. In the first study, methods are compared among themselves and with certain chemical phosphorus fractions. Based on the analysis of a greenhouse experiment in the second study, two methods are selected which are considered the most adequate to provide the best index of "available phosphorus" for Douglas-fir, lodgepole pine, and western hemlock. Further evaluation of the recommendations presented here must be based on field trials, which will ultimately help develop some guidelines for interpreting soil test results for operational P fertilization in British Columbia.

TERMINOLOGY

In the literature, a number of terms are used interchangeably, their use is defined here for clarity (expanded from Curran and T. Ballard 1984). The symbol "P" will refer to phosphorus. "Total P" represents the total of all soil P present. "Available P" is that fraction of the total P that is available to growing plants (e.g., usually over one growing season for agricultural crops; as yet undefined time period for British Columbia conifers). "P fractions" are quasi specific portions of the total P obtained by various extraction procedures (e.g., inorganic or chemical P fractions, and organic P fractions). "Fixed P" is a loose term referring to P bound in secondary (soil) minerals (and probably organic complexes), strongly enough that

it is not part of the available P pool. For some time, in the literature, soil P was considered as "labile P" (often analagous to available P) and "non-labile P" after Russell et al. (1954); however, these terms are now usually avoided (e.g., Larsen 1967) because it is thought that this two-compartment picture oversimplifies the problem.

LITERATURE REVIEW

Nutritional evaluation for forest trees may be investigated through soil analysis, foliar analysis, visual symptoms, fertilizer pot trials, fertilizer field trials, bioassays, and/or indicator plants (Tamm 1964; Zöttl 1973; R. Ballard 1977; Pritchett 1979). For most soil nutrients, the use of soil analysis for the assessment of nutrient availability and prediction of growth for forest trees has not been very successful (Armson 1973; van den Burg 1976; Pritchett 1979; Khanna 1981). This is not unreasonable if one considers the many other site and plant factors involved in regulating growth and nutrition. However, Pritchett (1979) notes that some success with soil P test procedures has been reported in New Zealand, Australia, southeastern United States, Netherlands, and Finland, with subsequent extensive use of soil P testing programmes in some of these countries. This successful use of soil P testing may perhaps be explained by the overwhelming importance of soil chemical factors to P mobility.

Ideas that agricultural soil tests were of little use to forestry probably stemmed from earlier work, such as that in Australia by Kessell

and Stoate (1938) and Young (1948), which found correlations with total P rather than extractable P (R. Ballard 1980). R. Ballard (1980), in his review of phosphorus nutrition and fertilization of forest trees, notes that soil tests currently used for P in forestry are generally the successful agricultural soil tests (such as the Olsen, Bray P_1 or P_2, Truog, Morgan (1941), and H_2O-soluble P). Agriculturally based soil P tests are also commonly used for nursery management (e.g., Switzer and Nelson 1956; Stoeckeler and Jones 1957; Wilde 1958; Stoeckeler and Slabaugh 1965; van dan Driessche 1969; Aldhous 1972).

Increased sophistication in nursery management and continued N and P fertilization trials indicate that a calibrated forest soil P test (or tests) for modern forest management in British Columbia is in need of development; subject areas of concern for further literature review include (1) principles of soil testing; (2) soil test objectives and criteria; (3) growth and nutrition factors beyond the scope of a chemical soil test; (4) chemical characteristics of P in soils; (5) review of soil test methods and procedural considerations; (6) correlation and interpretation of results; and (7) research needs. More specific discussions of literature relevant to experimental results will occur in the individual thesis chapters.

1. Principles of Soil Testing

Clearly, it is only the plant that can accurately determine the amount of a nutrient available from the soil (Fried and Dean 1952, Viets 1980). However, individual plants within a crop differ

physiologically. Also, a nutrient deficiency (and consequent lost productivity) has already occurred by the time plant analysis detects it, and we often wish to assess available nutrients before planting. Thus, soil testing plays an important role in providing an "index" of nutrient availability to particular crops on given soil (Viets 1980). Such soil testing involves rapid chemical analysis that is inexpensive and accurate, serving to transfer experience (gained in field, greenhouse and laboratory research) into reliable fertility predictions (Melsted and Peck 1973).

Soil testing, in one form or another, has a long history. Melsted and Peck (1973), in reviewing principles of soil testing, suggest that early search for the "principle of vegetation" actually led to the development of the science of chemistry. Modern soil testing for nutrient availability had its origins in the nineteenth century with the classical research of Liebig (1840) (Melsted and Peck 1973). Study of plant nutrition gained momentum with some major contributions from Daubeny (1845) through the concept of "active" nutrient forms and the CO_2 soil test, and Dyer (1894) in development of the citric acid soil test based on acidity studies of root sap (Kamprath andWatson 1980). Much of the soil test research early in this century focused on or included P (e.g., Russell and Prescott 1916-1917; Bray 1929; Truog 1930; Spurway 1933). Since the 1940's, soil testing has been widely accepted in agriculture as an essential tool for soil fertility management (Melsted and Peck 1973; Bertrand 1981).

Modern soil testing no longer attempts to mimic the soil-plant system but rather seeks a sound physical chemistry basis that may be

more universal (Viets 1980). Researchers working with soil tests now recognize the need to consider both "intensity" and "capacity" (Larsen 1967, Viets 1980). Intensity is a measure of nutrient present in soil solution, whereas capacity is a measure of the soil's present buffering capacity or ability to maintain the level of intensity throughout the growing season. These are important descriptive classes of soil P because they are functionally related by the solid-solution equilibria discussed later. (Olsen and Khasawneh (1980) note that a new term, quantity or quantity factor, is more appropriate to define "quantity of solid phase P that can act as a reserve" and current use of "capacity" generally describes the gradient controlling desorption, which relates "quantity" to "intensity.") In soil testing for P, the above are important considerations because soil solution concentrations of P are usually very low and must be replenished on a continuous basis during each growing season day (Barber 1962).

However, most soil tests suitable for operational soil testing programs can neither quantify intensity and capacity (Viets 1980) nor fully account for the process involved in renewal of the soil solution (Leitch _et al_. 1980), but provide some form of integration between the two. This failure of soil P tests to account for the rate (kinetics) of P migration from solid-to-solution-to-plant root is their main limitation (Leitch _et al_. 1980). However, Mengel (1982) doubts that an assessment of both intensity and P-buffering capacity would be a suitable approach for routine estimation of available P.

A number of reaction kinetics-based methods are discussed by Larsen (1967) and Venkat Reddy _et al_. (1982) (e.g., surface P, L-value,

E_t value and A-value). Detailed study of capacity is generally restricted to research involving isotopic dilution analysis (e.g., P sorption isotherms) and radio-isotope exchange (Larsen 1967). Detailed studies can characterize the "P fixing power" of a soil, which may be expected to range for very strongly acid soils in North America from about 20 to 125 tons of 20 percent superphosphate per acre-furrow slice (Brady 1974).

A sound soil testing programme consists of four phases: (1) sample collection; (2) extraction and determination of "available" nutrients; (3) interpretation of analytical resuts; and (4) making fertility recommendations (Melsted and Peck 1973). The actual soil test method employed represents only a small part of this process and is only important to the extent that it satisfies the test programme's objectives and criteria. Also, a successful programme depends at least as much on good judgements and technique throughout the process, although the actual chemical analysis employed is the popular scapegoat if things appear in error (Melsted and Peck 1973).

2. Soil Testing Objectives and Criteria for an Adequate Soil Test

Objectives for soil testing for P generally fall into one or more of three testing programme objectives (Fassbender 1980; Kamprath and Watson 1980): (1) grouping of soils into availability classes in the making of fertilizer recommendations; (2) prediction of the probability of getting a profitable response to application of P fertilizer, and (3) providing an index of the amount of available P a soil can supply.

Soil testing for operational forest fertilization with P falls into category (2) and nursery applications generally fall under (1) above.

Criteria that a good soil test for P should meet include (1) it should extract all or a proportionate part of the "available" form of a nutrient from soils with variable properties (i.e., provide an index of availability across a range of soils); (2) nutrient extraction and determination should be possible with reasonable accuracy, reproducibility, and speed; (3) the amount extracted should be correlated with growth and the response of each crop to that nutrient under various (environmental and soil) conditions; and (4) interpretation of soil data should allow grouping of soils (e.g., high, medium, low) based on field experience (calibration) with the method (after Bray 1948; Fassbender 1980).

3. Growth and Nutrition Factors Beyond the Scope of a Chemical Soil Test

Before discussing the chemical behavior of P in British Columbia forest soils, it is appropriate to bring into view the many other factors influencing growth and nutrition of forest trees.

Factors of nutrient availability relevant to soil testing have been discussed by Mengel (1982). Important factors that are generally not determined in routine soil testing, but that affect both growth and nutrition of forest trees (i.e., soil test correlation) include (with some examples from the literature): water relations (Webber 1974; Mahtab *et al.* 1972; Brockley 1981); other climatic factors, including

those influenced by slope and aspect; nutrient interactions (van Lear and Smith 1972); initial P intensity and capacity (Barrow and Shaw 1976a, 1976b, 1976c; Mengel 1982);[1] soil structure, compaction, rooting depth, parent material and pedogenic age; biological competition at all trophic levels (immobilization rate), mineralization rate, mycorrhizae (Thomas et al. 1982), tree physiology, and genetics (e.g., provenance differences).

Growth and nutrition observed for a given forest stand represent an integration of all these factors and others. Considering this, and the tremendous variability within and among many forest sites, it is amazing that many good soil testing programmes have been developed for forestry. In greenhouse studies, such as in the second part of this thesis, many of these factors are held at low variability to maximize comparison among treatments such as different soils.

4. Chemical Characteristics of Phosphorus in Soils

The chemical behavior of phosphorus in soils is as yet not well characterized. Our current state of knowledge is summed up by Bohn et al. (1979) who note that (despite intensive study that is second only to nitrogen) our ignorance of the state of soil P and our inability to increase the availability of P ranks as one of the greatest frustrations and challenges of soil chemistry. Phosphate has a high affinity for

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[1]Mengel (1982) notes that of particular concern is the dynamic changes in soil properties (such as pH and actual P-buffering power) in the actual "root depletion zone," which can significantly differ from parameters in the bulk soil.

cations (e.g., most often Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, and H^{+}) (Bohn et al. 1979) and takes part in many reactions affecting its availability, with these and other cationic species, both within the liquid phase and between the liquid and solid phase (sorption and desorption). The chemical behavior of P in soils in general will be discussed through the topics of (a) geochemistry; (b) soil solution; (c) sorption and desorption; (d) phosphate minerals; (e) and soil organic phosphorus.

a. Geochemistry of Phosphorus

Phosphorus occurs naturally almost exclusively as the highly charged cation (P^{5+}) in the complex oxyanion orthophosphate (Lindsay and Vlek 1977; Bohn et al. 1979). Phosphorus is the tenth most abundant mineral in the Earth's crust; however, the geologic P cycle turns over very slowly and new inputs to soil systems are generally very low (although these may be enough to offset leaching losses, which are also very low (Emsley 1982). Soils contain 0.02 to 0.15% P (Mengel and Kirkby 1982) which, during pedogenesis, weathers from calcium phosphates (e.g., apatite) to forms more associated with Fe and Al compounds and organic matter (Walker and Syers 1976). Organic P can represent from 20 to 80% of the total soil P (Floate 1960; Larsen 1967; Dalal 1977; Mengel and Kirkby 1982). Phosphate is biocycled by vegetation and accumulates near the surface in most soils (Floate 1960; Pierrou 1976), (where it is hence more susceptible to disturbance such as in site preparation).

b. Soil Solution Phosphorus

In the soil solution, P is present as dissociated phases of the weak acid H_3PO_4 (e.g., $H_2PO_4^-$), as complexes and in ion pairs (Taylor and Gurney 1962; Larson 1965, 1966), and complexed with organic matter (Weir and Soper 1963; Dalal 1977). Our current knowledge suggests that it is not safe to assume that even the bulk of soil solution P is always present as $H_2PO_4^-$ and HPO_4^{2-}. Soil solution P concentration (P intensity) is usually very low (e.g., 0.1 - 1.0 ppm reported by Larsen (1967) and is controlled by the heterogeneous equilibria between the liquid and solid phase.

c. Phosphate Sorption and Desorption

Since soil solution P occurs at very low concentrations, P sorption and desorption are the most important and most complex aspect of P availability (e.g., "the rate-limiting step"). Phosphate sorption may occur as "true" adsorption to surfaces, as precipitation in the form of small and poorly crystallized solids (e.g., colloids), and as some surface-associated P (Bohn *et al*. 1979). An important aspect of P desorption is that it is incongruent (Larsen 1967).

Sorption

The discussion of P sorption in the literature may apply to incidents dominated by either or all scenarios presented above (which will be discussed in turn). The quantity-intensity relationship can often be described by a Langmuir isotherm, using a series of two to five

Langmuir equations (Parfitt 1978). Sorption of P in solution may occur onto Al, Fe (and Mn) oxides and hydrous oxides at low to neutral pH, clay minerals (especially 1:1 lattice structures, which exhibit greater surface area dominated by aluminum) over a more neutral pH range, and calcium minerals (also magnesium minerals) at higher pH ranges (Parfitt 1978; Ryden and Pratt 1980).

Ryden and Pratt (1980), in reviewing P sorption surfaces for soils, stress the importance of Al and Fe hydrous oxides. Crystalline hydrous oxides (i.e., hematite and gibbsite) sorb 5 to 10 times greater P than crystalline aluminosilicates or calcium carbonate; in addition, amorphous components (such as Fe oxide gels) sorb 10 to 100 times more P than their crystalline counterparts (thus up to 1000 times more P than the crystalline aluminosilicates and calcium carbonates (e.g., Syers and Williams 1977). In British Columbia forest soils (generally weakly to moderately weathered), we may expect to find a considerable proportion of Fe and Al hydrous oxides to be amorphous, consistent with current concepts of podzolization (e.g., Farmer 1982).

Even at higher pH, amorphous hydrous oxides may reduce to minor importance P sorption by calcium carbonate, as demonstrated for calcareous soils by Holford and Mattingly (1975). The above helps to explain why many workers have found a correlation of soil P sorption capacity with extractable Al or Fe, or exchangeable Al (e.g., Sree Ramulu and Pratt 1970; R. Ballard and Fiskell 1974; Flinn _et al_. 1982). This is also true for soil test values for P (e.g., Grigg 1968; R. Ballard and Fiskell 1974; R. Ballard 1978). Also, significant

correlations between organic matter content and P adsorption suggest existence of Fe or Al chelates of high molecular weight (e.g., Weir and Soper 1963). Organic matter can also form complexes with Fe and Al compounds, reducing P sorption (Brady 1974).

Precipitation of P complexes from the soil solution is also important. Again, Al, Fe, (Mn), Ca, and (Mg) are the important constituents involved. Mengel and Kirkby (1982) note for reactions involving Ca^{2+} and Ca minerals, that (whereas desorption from Ca most likely dominates in soils rich in Al, Fe and clay minerals) precipitation apparently plays a major role in calcareous soils, poor sandy soils, and organics. Their rationale for calcareous soils is that high Ca^{2+} concentration and pH promote desorption of P (e.g., the high affinity of P for cations) and its precipitation (as calcium phosphates of low solubility); which process dominates will depend on individual soil conditions affecting soil solid-solution equilibria (e.g., HCO_3^- concentration).

Many factors affect P sorption and precipitation; these include nature of sorption sites, sorption/precipitation mechanisms, quantity and intensity relationships (i.e., capacity), reaction kinetics, and external factors such as pH. Sorption sites and mechanisms have been reviewed by Parfitt (1978). Again Fe and Al appear to be of major importance. Holford and Mattingly (1975), using naturally occurring calcium carbonate which contained 0.1 - 0.3% Fe, suggested that P sorption could be predominantly localized on the Fe sites. However, the importance of Ca^{2+} in solution reactions with P (e.g., precipitation) should not be overlooked.

Of the external factors affecting P solid-solution equlibria, CO_2 concentration, organic matter, and pH are probably of greatest importance (Larsen 1967).

Desorption

The concentration of P in the soil solution has often been conceived to be determined by sparingly soluble compounds. Larsen (1967) describes these solubility equilibria as being complex. As sorbed P increases (i.e., further saturates the P adsorption capacity) the level of P in solution (intensity) will increase to a point controlled by the solubility of some "soluble P compound." Similarly, as soil solution P (intensity) decreases, sparingly "soluble P compounds" will dissolve until the sorption complex (capacity) is saturated to a degree corresponding to the solubility of the least stable P "compounds" present.

Phosphorus concentration in acid soils is in the range of the solubilities of the Fe and Al minerals strengite and variscite and the isomorphous series between them (Larsen 1967). Similarly, P concentrations in alkaline soils are in the range of the solubilities of octacalcium phosphate and apatite. Larson (1967) notes that these relationships have led past researchers to the unfortunate conclusion that P activities could be calculated based on equilibrium with various P minerals. However, due to the complexity of factors determining soil solution P levels, the above correlation is nevertheless too crude to predict plant available P.

It is also important to be aware that Ksp values are for pure minerals (i.e., synthesized or removed from the soil environment) under standard conditions. Soil minerals are often complicated by impurities, which tend to raise the actual Ksp observed (Larsen 1967). Also, Ksp varies with pH and temperature. Therefore, some of the apparent complications in comparing concentration of P in solution with determined solubilities of pure minerals must arise out of the above simplification of reality. Also, little is known as to which P minerals are actually present and in contact with the soil solution in soils.

Perhaps the most important aspect of P mineral dissolution is that it is incongruent (Larsen 1967). The important process that may be involved is the "aging" of the P mineral formed by sorption (including precipitation). Gaitho (1978) reviewed this important character of P "fixation" and noted how, over time, P compounds formed are transformed into more stable (and thus less soluble) forms (consistent with basic thermodynamics). For example, Fe and Al phosphates may be "adsorbed" when newly formed; this represents a thermodynamically unstable form relative to amorphous forms which are in turn less stable than crystalline forms (Hsu 1982; Sims and Ellis 1983). This progression (from amorphous to crystalline structure) represents a decrease in reactivity for P (capacity for P adsorption; Sims and Ellis 1983) due to decreased surface area and probably P penetration into the internal structure. A common reference for early work on this phenomenon is Fujiwara (1950).

Clearly, the incongruence of P sorption has fundamental importance in understanding plant-available P and P minerals. Parfitt (1978)

refers to this process as involving slow reactions. Keerthisinghe and Mengel (1979) noted that "P aging" is especially rapid in calcareous soils. For Fe and Al hydrous oxides, Ryden et al. (1977) noted that most P sorption was completed in a few hours. Thus, the process of "P aging" may be expected to occur fairly soon after sorption or precipitation. Clearly, the reversibility of this process decreases with age (Tisdale and Nelson 1975).

The process of "P aging" provides an excellent basis for conceptualizing P mineral dynamics and the notion of "labile P." Many authors refer to different minerals on the surface of other more stable minerals (e.g., "mineral succession;" e.g., Larsen 1967; Parfitt 1978; Ryden and Pratt 1980). In terms of P mineral dynamics, this process means that large quantities of P minerals can exist in the soil, but not be in equilibrium with the soil solution. Soil testing for tree-available P is a very complicated undertaking because of this soil-solution interface from which "labile P" is released (and that may be expected to undergo many changes even during a portion of a single growing season).

d. Phosphate Minerals

Phosphate forms a group of minerals on its own (Larsen 1967; Lindsay and Vlek 1977). Again the usual cations Al^{3+}, Fe^{3+}, Ca^{2+}, and Mg^{2+} are the most important. Actual composition depends on the ratio of such cations, H^{+}, and P concentrations during precipitation (Larsen 1967), and perhaps "aging" (e.g., the calcium phosphate series). Due to

the tetrahedral nature of phosphate, it tends to form quite regular crystalline structures, some of which are similar to the clay minerals (Lindsay and Vlek 1977) (perhaps again representing the tendency towards more stable forms during "aging").

Identification of soil P minerals is very difficult since they apparently occur primarily in the clay-sized fraction and as very small crystals on other soil surfaces and any concentration procedures alter their forms (Larsen 1967). Mengel and Kirkby (1982) note that there have been many (unsuccessful) attempts to relate "non-labile P" to specific P minerals; a very complicated venture, considering impurities, the variety of cationic species available in a given soil, "aging", and no "real" Ksp data. A number of authors (e.g., Larsen 1967; Ryden *et al.* 1973) consider the existence of strengite and variscite unlikely; however, this should be qualified in terms of "in equilibrium with the soil solution" since these more stable minerals can exist "behind" surfaces. Of the calcium phosphates, Larsen (1967) notes that there is no reason to assume that any form other than hydroxyapatite is permanently present in slightly acid soils since other forms of apatite weather readily in acidic soils (apatites are the most significant P minerals globally).

e. Soil Organic Phosphorus

Soil organic P usually represents 20 to 80% of total P (Larsen 1967; Dalal 1977). Dalal (1977) also notes that a very significant amount of soil solution P is in organic forms that are considered only

poorly available to plants (and believed to be colloidal). Only a few soil organic P forms are presently known; these are predominantly inositol phosphates, phospholipids, and deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) (Dalal 1977).

The dynamics of soil organic P may be considered most relevant to soil testing. The soil organic system affects soil chemistry relevant to plant available P through mineralization, chelation, surface coatings, acid production and buffering, and CO_2 production. Organic matter mineralization may represent a major source of available P (e.g., Radwan and Shumway (1983) found the best extractable P correlation for hemlock growth using forest floor samples). It is now accepted that the exocellular soil phosphatase enzymes are largely responsible for P mineralization (Ho 1979). Thus, soil organic P in solution may be far more available to plants than suggested by Dalal (1977).

Chelated Al and Fe have been demonstrated as important sites for P sorption (e.g., Weir and Soper 1963). Similarly, organic matter may coat stationary Al and Fe surfaces, thereby reducing P sorption (Brady 1974). Organic acid production during decomposition in British Columbia forest soils maintains and buffers low pH conditions which are more conducive to P sorption by Al and Fe. Carbon dioxide produced during respiration can lead to increased P dissolution.

5. Review of Soil Test Methods and Procedural Considerations

The latter section, on the chemical characteristics of P in the soil, clearly indicates that there is no one single, easily extractable

form of plant-available P, such as Ca^{2+} for Ca. Phosphate undergoes many reactions, such as sorption, precipitation, and complexing with a number of soil constituents and is hence subject to many complex equilibria. Thus, there are many different P forms that differ in quantity and solubility (and hence plant availability) depending on soil and environmental conditions that may be periodic (e.g., soil solution ion activities, pH, water content) or somewhat static (e.g., texture, mineralogy, pedogenic age) in a given soil (after Leitch et al. 1980). This is why developing a soil testing programme for P is a large research undertaking.

Soil test extractants devised to index available P vary widely in their chemical nature. Release of P is mediated through the reactions of H^+ (acid solvation), OH^- (hydrolysis of cations binding P), F^- (complexing of cations binding P) and/or anions including HCO_3^-, SO_4^{-2} and organic anions such as acetate (all which contribute to anion replacement) (Thomas and Peaslee 1973; Kamprath and Watson 1980). Available P test extractants can be grouped into seven classes (expanded from Kamprath and Watson 1980) which will now be discussed in terms of physical chemistry under the larger groupings of acidic, alkaline, and near-neutral extractants:

A. Acidic Extractants

Hydrogen ions greatly increase the solubility of all Ca-P including primary Ca-P such as hydroxyapatite (Thomas and Peaslee 1973). The rate and extent of reaction depend on the hydrogen ion concentration. Al-P

and Fe-P can also be attacked, although rates become progressively slower, respectively. Hence, the order of P removal by H^+ is Ca-P > Al-P > Fe-P.

Sulfate and organic anions in acidic solution prevent readsorption of phosphate displaced by other ions (Nelson et al. 1953; Thomas and Peaslee 1973; Kamprath and Watson 1980). (Sulfate ions compete poorly with phosphates for Fe and Al (Kamprath et al. 1956) and are thus noted by Thomas and Peaslee (1973) to be important in preventing readsorption of P displaced by H^+ (which attacks primarily Ca-P).) Organic anions can also form complexes with such polyvalent cations, releasing P (Kamprath and Watson 1980). Nelson et al. (1953) note that other associated anions (i.e., NO_3^-, Cl^-) have very little effect on the extraction.

1. Dilute strong acids

Dilute strong acid extractants are generally 0.002 N to 0.5 N HCl, HNO_3 and/or H_2SO_4 of pH 3 or less. This class includes Truog (1930), double-acid ("North Carolina" or "old" Mehlich) (Nelson et al. 1953), and 0.01 N HCl in this study. Reactions occur involving strong H^+ (and SO_4^{2-} if included).

2. Dilute weak acids

Dilute weak acids include solutions of carbonic, citric, and lactic acid and/or their salts. Dilute weak acids include amonium acetate (NH_4OAc) at pH 4.8 ("University of Florida" method) used here (Breland 1957; a modification of Morgan 1941). Reactions occur involving weak H^+ and organic anions or HCO_3^-.

3. Dilute weak and strong acids

Dilute weak and strong acids usually combine the anion effects with a strong H^+ reactivity. The Egner method from Europe (Egner et al. 1960) (0.02 N Ca lactate + 0.02 N HCl) is a mixture of weak and strong acids. This was not used in this study, although the new-Mehlich method mentioned below has both weak and strong acids plus a complexing ion.

4. Dilute acid(s) plus a specific complexing ion

Addition of a complexing ion to dilute acids creates a very powerful extractant. The most common complexing ion is fluoride which forms very strong complexes with Al, thereby releasing P. Fluoride ions also specifically precipitate soluble Ca and thus extract P from more soluble Ca-P minerals such as $CaHPO_4$ (Thomas and Peaslee 1973). With the acidification, more basic Ca-P and Fe-P are also affected by the extractant. The Bray (Bray and Kurtz 1945) and new-Mehlich (Mehlich 1978) extractants are dilute acids with F^- as the complexing ion.

B. Alkaline Extractants

Alkaline extractants invariably use HCO_3^- ions which actually replace P adsorbed to surfaces of $CaCO_3$ and hydrated oxides of Al and Fe. HCO_3^- also precipitates Ca^{2+} as $CaCO_3$, further favoring P release. Thomas and Peaslee (1973) state that bicarbonate ions do not attack basic Ca-P, or Al-P and Fe-P covered with oxide coatings to any extent. (In this respect bicarbonate ions are similar to fluoride ions, although F^- reacts more vigorously and removes P unavailable to HCO_3^-.) Hydroxyl ions extract P from Al-P and Fe-P (due to hydrolysis of Al and

Fe) but have little effect on basic Ca-P (Dean 1938). Solutions of high pH can cause dispersion of organic matter.

5. Buffered alkaline solutions

These alkaline extractants are generally 0.05 M to 1 M HCO_3^- at pH 7.6 to 8.5. This class includes modified Olsen *et al.* (1954) which uses $NaHCO_3$ (Banderis *et al.* 1976) and modified ammonium bicarbonate-diethylene triamine pentaacetic acid (NH_4HCO_3-DTPA; Soltanpour and Workman 1979) methods.

C. Near-Neutral Extractants

Near-neutral extractants vary from water to dilute salts and also include the powerful isotopic exchange methods. Effects of experimental procedure, such as CO_2 build-up (and subsequent increased HCO_3^- activity) from unchecked microbial activity, may be profound due to the otherwise fairly inert reagents.

6. Water or dilute salt solutions

Water or dilute salt solutions are most commonly distilled water alone or 0.01 M $CaCl_2$. Some consider that these extractants yield an estimate of soil solution P; soil:solution ratios from saturation extract to 1:60 are in use. This class includes H_2O-soluble P used in this study. The 0.01 M $CaCl_2$ reduces the "dilution effect" (Schofield and Taylor 1955), and concentration of P in $CaCl_2$ extracts is generally one-third to one-half that of comparable water extracts (Olsen and Watanabe 1970; Soltanpour *et al.* 1974).

7. Isotopic exchange media

Ion exchange media generally work based on isotopic exchange and mass anion effect, without appreciably altering soil pH; include Cl^- saturated anion exchange resin(AER). Larsen (1967) notes that AER presents a practical integration of intensity and capacity, with minor soil chemical change, and is well correlated with plant growth. Mattingly and Talibudeen (1967) suggest that this method of evaluating P is more reliable than extraction with dilute acid or alkaline solutions (with some exceptions). Olsen and Sommers (1982) note that AER is a useful method to approximate P uptake mechanisms by roots and to measure availability of residual phosphates from fertilization. However, the AER methods were considered more time consuming than most other soil tests examined in this study.

Fractionation of Soil Phosphorus

Fractionation of soil inorganic P was initially attempted by Dean (1938). Chang and Jackson (1957) improved the initial procedure and it is their successive (i.e., one-sample) fractionation method that forms the basis of current fractionation procedures (e.g., Olsen and Sommers 1982). Some modifications and revised nomenclature include Glenn *et al*. (1959), Peterson and Corey (1966), Williams *et al*. (1967, 1971a, 1971b) and Syers *et al*. (1972). Up to six fractions may be analyzed in the initial Chang and Jackson (1957) procedure; these include soluble-P (first wash), Al-P, Fe-P, Ca-P, reductant-soluble P, and occluded-P (soils high in sesquioxides). In the modified procedure of Peterson and

Corey (1966), (which follows the re-ordering of Glenn et al. (1959) easily-soluble and loosely-bound P may be determined in the first wash (in NH_4Cl); extraction with alkaline 0.5 N NH_4F (pH 8.2) attacks only the Al-P (Chang and Jackson (1957), thus permitting determination of Al-P; 0.1 N NaOH extracts Fe-P by hydrolysis (all Al-P having previously been removed); reductant-soluble-P is extracted by dithionite and citrate which is then oxidized by $KMnO_4$ (rather than H_2O_2 called for by Chang and Jackson (1957) in this step which removes P insoluble in NH_4F and NaOH; Ca-P is then dissolved by strong acid (0.5 N H_2SO_4). A thorough review of soil P fractionation is presented by Olsen and Khasawneh (1980).

Determination of P in Soil Extracts

Typically, any soil P test procedure involves two steps: (1) extraction of P and (2) determination of P concentration in extract solution. A fast and accurate method of P determination in soil extracts is desirable. In the 1950's, four different P determination methods were in use to suit the variety of different P analyses (e.g., Jackson 1958). These methods were all based on the reduction of a molybdophosphate complex for the colorimetric determination of P in solutions based on Denigés (1920). This yields the "molybdenum blue" colour. A few methods use an unreduced vanadomolybdate phosphate complex that is yellow in colour. Stannous chloride was the initial reducing agent in the method of Denigés and was readily adopted in soil testing and used for some time (Truog and Meyer 1929; Truog 1930; Bray and Kurtz 1945; Olsen et al. 1954).

The major development to the method has been the replacement of the $SnCl_2$ reductant with ascorbic acid to produce a more stable molybdophosphate reduction. Fogg and Wilkinson (1958), in describing their experimental work on interfering ions in the colorimetric determination of P, note that Ammon and Hinsberg (1936) were the first to use ascorbic acid and go on to describe a method requiring heating. Murphy and Riley (1962) described a single-reagent ascorbic acid method for the determination of P in natural waters; their method incorporates antimony in lieu of heating and it is from their work that modern soil methods have stemmed. Watanabe and Olsen (1965) tested the Murphy and Riley method and found it to be accurate for determining soil P in water and $NaHCO_3$ extracts. Since that time, the "ascorbic acid method" has gained favour and now enjoys nearly universal acceptance. (For example, this method was proven successful for total P and the Chang and Jackson procedure by Alexander and Robertson in 1968 and 1970, and modified for use with water extractions by Omanwar and Robertson in 1969).

John (1970) modified the Murphy and Riley method and tested the new approach with regard to range in P concentration, pH, time, temperature, reagent concentrations, and interfering ions; he proved it acceptable for most commonly used P extractants. Hence (although Olsen and Sommers (1982) note that each P method has its own colorimetric method and caution the reader to follow recommended procedures) the above discussion indicates it is desirable in developing soil tests for a new area or in using proven soil tests to use the "ascorbic acid method".

Procedural Considerations

Apart from the usual care in sample collection, preparation, and laboratory precision, a number of procedural considerations are important for P extraction methods; these include soil mineralogy (e.g., percent and type of clay), soil pH, extraction solution pH buffering, soil P buffering capacity, soil: extraction solution ratio, extraction time, shaking type, filtering lag time, glassware, temperature, charcoal, microbial activity, CO_2 build-up, interfering ions, and hydrophobic samples. In addition to author comments in their individual method descriptions, the following may be noted from the literature:

Kamprath and Watson (1980) noted in their review that percent and type of clay are important for the double-acid and Bray methods, with double-acid better related to plants on soils with kaolinite and Bray better below 20% clay (e.g., Blanchar and Caldwell 1964). Soil pH and extracting solution pH buffering go hand in hand, with most dilute solutions of strong acids (e.g., double-acid) working best (although this depends on soil: solution ratio) below pH 7.0 (Kamprath and Watson 1980). The Bray methods work best on non-calcareous soils (Olsen and Sommers 1982) due to problems encountered on calcareous soils from H^+ neutralization and CaF_2 formation (Smillie and Syers 1972; Syers _et al._ 1972).

Soil P buffering capacity is also important (Barrow and Shaw 1976a, 1976b, 1976c; Mengel 1982). Barrow and Shaw (1976b) note that as P capacity increases, the initial P extracted decreases and secondary adsorption during extraction increases, yielding a significant drop in

the P extraction value (again soil:solution ratio is also important).

Soil:extractant ratio can profoundly affect the P extraction value. Dilution is most commonly manipulated in the Bray (P_1 or P_2), often to reduce effects of high clay content (Blanchar and Caldwell 1964) or high $CaCO_3$ levels (Randall and Grava 1971). Grigg (1965b), in studying potato nutrition in New Zealand found that modifying the Bray P_2 test, to 5 minutes shaking and 1:50 dilution ratio, resulted in an improved indication of the "capacity of the soil to supply P" through the entire growing season. Olsen and Sommers (1982) note that, for H_2O-soluble P, highest extract P concentrations occur with the lowest soil:solution ratios. Soil:solution ratio is an important consideration for soils that strongly resorb P during extracting. (Data obtained by the method of Olsen et al. (1954) are probably among the least altered by dilution ratios, because secondary precipitation reactions are reduced to a minimum due to the concentrations of Al, Fe, and Ca remaining at a low level in the extract, according to Olsen and Sommers (1982).) Ratios may have to be altered for organic soil, such as forest floor.

Extraction time is also an important consideration and has been discussed for the Bray P_1 by Agboola and Omueti (1980), who note, as did Bray and Kurtz (1945), that extracted P drops off after 5 minutes, due to precipitation with Al and Fe. Common observations with British Columbia soils suggest that this drop may occur more often before the 5 minute mark (e.g., data reported in Chapter 2, which indicate that, for Podzolic soils, the 5-minute extraction yielded less

than the 1-minute extraction). Regardless of extraction method, time is thus an important variable to keep consistently under control when analyzing for P.

Shaking type is yet another consideration and generally falls into two categories: rotational (e.g., "wrist-action") or reciprocal (e.g., end-to-end). Agboola and Omueti (1980) found no significant difference between stirring (analogous to swirling) and shaking for the Bray P_1 soil test, although swirling tended to extract slightly more P and they considered it to be more convenient for routine analysis. Shaking speed is also important, and generally the faster the speed the greater the extracted P (Olsen _et al_. 1954).

Filtering lag time is a consideration that is of more recent origin (many of the early methods used centrifugation or overnight settling to obtain a clear extract). Many methods recommend immediate filtering. Studying the Bray P_1 test in Nigeria, Agboola and Omueti (1980) observed that the filtering lag time effects depended on the type of extractant and the level of soil P (i.e., related to soil P buffering capacity as described by Barrow and Shaw (1976b) earlier). They concluded that, for the Bray P_1 test, filtering should be done between 5 and 15 minutes after shaking. This allows for variation between 6 and 20 minutes of actual extracting time before filtering, and the acceptability of such practice depends on local soil conditions and extractant characteristics.

New laboratory glassware is usually contaminated with arsenic (an interfering ion in the P determination procedure). Washing instructions

to overcome this problem are presented by Lavkulich (1981). Temperature can have a significant effect, generally increasing amount of P extracted as the temperature rises. Olsen et al. (1954) noted that temperature is another possible source of variation for their method and calculated that, for soils of 5 to 40 ppm P, extractable P rose 0.43 ppm for each °C from 20 to 30°C. Similar effects occur with other methods.

Charcoal should probably no longer be considered as an agent for decolouring soil extracts. Charcoal is known to adsorb P (e.g., Beaton et al. 1960), either adding to or taking from extraction values; it is also very messy to work with. Methods that formerly employed "Darco" carbon or its equivalent (e.g., Olsen et al. 1954; Soltanpour and Schwab 1977) have now been modified to use polyacrylamide as an adsorbent for coloured organic constituents in the extract solution (e.g., Banderis et al. 1976; Soltanpour and Workman 1979).

Microbial activity and CO_2 build-up (either due to microbe respiration or soil reaction) are yet two more considerations. These can lead to increased P extraction due to mineralization and HCO_3^- activity, respectively. Microbial activity may also be responsible for immobilization of P in extractions. Extraction methods that use near neutral extraction solutions and long shaking times generally employ toluene or chloroform to retard any microbial activity (e.g., Humphreys and Pritchett 1972 for H_2O-soluble P). However, one may still wish to consider that any phosphatase enzymes in the soil would most likely not be hydrolyzed in near-neutral extracts and may contribute to extraction. Extraction methods that are known to generate $CO_{2(g)}$

often call for shaking in non-stoppered flasks (e.g., Soltanpour and Schwab 1977); this prevents CO_2 build-up and consequent HCO_3^- formation which would then displace sorbed P and confound results.

A number of ions interfere with P determination in soil extracts by the ascorbic acid method. These have been studied in detail by Fogg and Wilkinson (1958) and John (1970) and the reader is directed there for detailed discussion. The ascorbic acid method developed by John (1970) after Murphy and Riley (1962) is designed rigorously to maximize utility, one aspect of which is interfering ions.

A last consideration is hydrophobic samples (e.g., after air-drying, forest floors often become hydrophobic). These may be a problem in that they are very slowly wetted, affecting especially the results of methods employing swirling for a short time period. Reciprocal shaking, longer time periods and/or greater dilution are effective means of reducing variability caused by hydrophobicity. Gaitho (1978) allowed his hydrophobic samples to sit to overnight with distilled water and then added the equivalent chemical solution to make up the reagent. However, as discussed above, a number of other sources of variability may be introduced by this practice if left unchecked (e.g., microbial activity, phosphatase activity, slow equilibrium reactions, etc.) and the practice also may not be considered convenient for routine soil analysis.

In summary, a large number of procedural considerations are important in precise soil testing for P. Interpretive usefulness of data may be limited if these considerations are not appreciated by the analyst.

6. Correlating and Interpreting the Results

In their detailed review of soil and plant testing for P, Kamprath and Watson (1980) note that correlations with extractable P may use plant growth parameters such as yield, percent yield, P uptake, and P concentration in tissues (e.g., Fitts and Nelson 1956), or estimates of labile P such as the "A" or "L" value (e.g., Larsen 1967). A basic principle of soil testing is that, under most conditions, the soil test value can be assumed to be (1) a variable independently related to crop growth and (2) a measured quantity of the nutrient level in the soil that will, or can be used to, define or express the "rate factor" (of availability) of that particular nutrient (Melsted and Peck 1973, 1977). If the above assumptions cannot be met (at some acceptable level), every other yield variable might have to be estimated before the soil test value will be of interpretive value. (In the case of NH_4^+ and NO_3^- for N, the meaning of 2 above may be less straightforward, but becomes clearer if one considers that a measured N level is inferred to express the rate of N availability.)

Simple linear correlations represent the most common statistical analyses in the literature reviewed for forest soils (e.g., Pritchett and Llewelyn 1966; Alban 1972; Baker and Brendemuehl 1972; R. Ballard 1974, 1978; Webber 1974; Kadeba and Boyle 1978; Hopmans *et al.* 1978a; Banerjee and Chand 1975; Lea *et al.* 1980; Tiarks 1982; and others). These studies have used yield, P uptake and/or foliar P concentration as the plant variable.

Kamprath and Watson (1980) reviewed numerous studies that demonstrate quantitative relationships between nutrient concentration in plant tissue and plant growth, including foliar P concentration in pine species (e.g., Terman and Bengtson 1973; R. Ballard and Prichett 1975a). In-depth reviews on principles and problems of foliar analysis (Leaf 1968; Armson 1973; Zöttl 1973; Everard 1974; Morrison 1974; van den Driessche, 1974) suggest good utility for soil test correlations. Foliar analysis is now a common basis of nutrient status diagnosis for forestry in British Columbia (e.g., T. Ballard 1981; T. Ballard and Carter 1983).

Some simple data manipulations may be used to improve soil test correlations. Bremer (1984), evaluating the Olsen and Bray P_1 methods for agriculture in the British Columbia interior, found better correlations when the log of the soil test value was used. This is presumably due to the fact that growth response to a nutrient tends to the asymptotic. Percentage yield and/or percentage of maximum "plant P" may also improve results, although not in Bremer's (1984) case.

A major consideration affecting soil test correlations for forestry is the initial soil sampling. Trees root across a variety of genetic soil horizons, and variability in tree root distribution and soil variability complicate sampling. There are differing reports in the literature on successful sampling schemes. R. Ballard (1980) noted that the surface layer of soil is generally better correlated in literature reports (e.g., Alban 1972; R. Ballard and Pritchett 1975b). However, other studies report improved success by considering the lower solum

(e.g., Kessel and Stoate 1938) and/or averaging P for the rooting zone (e.g., MacDougall 1984). Webber (1974), studying correlation with soil test P for Douglas-fir on Vancouver Island, found that consideration of either the upper or entire solum did not effect the results appreciably. Clearly the results vary with the site and this demonstrates the importance of each of the four phases of soil testing discussed earlier. R. Ballard (1980) notes that the sampling problem may be expected to become more acute with stand age (e.g., forest floor complications), suggesting a relationship with the most successful studies reported in the literature having involved young stands.

Interpretation of soil test data follows the same general practices as agriculture except that R. Ballard (1980) notes that the actual soil test values used as interpretation thresholds are usually lower for forest trees than for agricultural crops.

7. Research Needs

Topics for investigation in developing a calibrated soil test for a region include (after Melsted and Peck 1973; FAO 1980) (1) the significant chemical forms of the nutrient in the soils of the area; (2) suitability of extractants for accurately and rapidly measuring (indexing) the available nutrient forms (including an evaluation of "operability" for routine laboratory use); (3) pot trials including the expected range of local soil conditions for initial screening of P extractants based on the best and most consistent correlations with plant growth and/or nutrient status; (4) fertilizer trials in the field

(crop responses monitored for varying rate and method of fertilizer application and further soil test screening and calibration for response prediction capability); and (5) methodological refinement type research (e.g., field sampling techniques, etc.). Generally, the first three topics represent the initial background research and the latter two represent at first background and then ongoing research.

Leitch et al. (1980) note that, when working up and testing a chemical soil test, it is necessary to work with soil samples of known crop response and which give a range in crop responses (i.e., the local range in soil conditions). Therefore, in developing a soil testing programme for P for forestry in British Columbia we require initial background research on: (1) the significant chemical forms of P in British Columbia forest soils; (2) the extractants most adequate to index available P in British Columbia forest soils; and (3) pot trials on a suitable range of British Columbia forest soils for initial screening of P extractants.

THESIS OBJECTIVES

The main objective of this thesis is to find an adequate method (or methods) for estimating the forest soil P which is "available" to Douglas-fir, lodgepole pine, and western hemlock growing in various kinds of British Columbia forest soil materials, using greenhouse pot culture. The objective will be accomplished by a preliminary study that will evaluate the following specific objectives:

a. identify significant inorganic P fractions in a variety of British Columbia forest soil materials,

b. investigate correlations among results obtained by various soil test methods,

c. evaluate relationships between the soil test results and the abundance of chemical P forms,

d. determine which soil test method (or methods) gives the best relationship with the P status of British Columbia conifers, and

e. evaluate test methods for routine laboratory analysis.

Objectives a, b, and c will be addressed in Chapter 2. "Amounts and Correlations of Extractable Phosphorus Obtained by 12 Methods and Chemical Phosphorus Fractions from Fractionation."

Objective d is the fundamental objective of Chapter 3. "Greenhouse Evaluation of Methods to Estimate Phosphorus Availability to Douglas-fir, Lodgepole Pine, and Western Hemlock."

Objective e is addressed through both Chapters 2 and 3, with final concluding remarks in Chapter 3.

CHAPTER 2

AMOUNTS AND CORRELATIONS OF EXTRACTABLE PHOSPHORUS OBTAINED BY 12 METHODS AND CHEMICAL PHOSPHORUS FORMS FROM FRACTIONATION

INTRODUCTION

In British Columbia, soil testing for phosphorus (P) in forest soils is in the early stages of development. Many methods exist in the literature for characterizing soil P availability to agronomic species (Olsen and Sommers 1982). However, no one P soil test may be considered universal; each new region or crop in a region requires a soil test that is "adequate" for the local soil-plant conditions of interest. Forest soils represent a generally wider range of chemical properties of importance to soil testing for P (such as pH, organic matter content, P forms and P level) than most managed agricultural systems. In evaluating soil tests for adaptation to forestry, the existence of various chemical P forms, and of relationships of these with soil available P test values, will be of interest across the range of expected soil conditions.

In developing a calibrated soil test for a region, two initial topics for investigation identified by Melsted and Peck (1973) and the FAO (1980) are (1) the significant chemical forms of the nutrient in the regional soils, and (2) the suitability of various extractants for measuring the available nutrient forms. It is of interest how well the

many various soil P test results are correlated with chemical P forms and with the results of other soil tests. Such information serves an important role in providing valuable insight on soil P chemistry in local soils and in enabling investigators to view the results in the perspective of a familiar soil test method. Accordingly, the objectives of this Chapter are to (a) identify significant inorganic P fractions in a variety of British Columbia forest soil materials, (b) investigate correlations among results obtained by various soil test methods, and (c) evaluate relationships between the soil tests and the abundance of chemical P forms.

The significant chemical forms of P in soil are usually evaluated through a fractionation procedure. The soil inorganic P fractionation procedure, initially attempted by Dean (1938) and improved by Chang and Jackson (1957), forms the basis of some current methods (e.g., Olsen and Sommers 1982). Some modifications and revised nomenclature include Glenn et al. (1959), Peterson and Corey (1966), Williams et al. (1967, 1971a, 1971b) and Syers et al.(1972). The Ca-P fraction commonly dominates total inorganic P in soils that are relatively young and the Al-P and Fe-P fractions are generally dominant in more weathered soils (Williams et al. 1967; Walker and Syers 1976).

Extractants of "available P" can be grouped into seven classes (1) Dilute strong acids; (2) Dilute weak acids; (3) Dilute, mixed weak and strong acids; (4) Dilute acid(s) plus a complexing ion; (5) Buffered alkaline solutions; (6) Water or dilute salt; or (7) Isotopic exchange media (e.g., anion exchange resin--not studied here). Numerous studies

have reported test values and correlations for various P extraction methods; however, only a few of these report on regional forest soils (e.g., Gaitho 1978; Radwan and Shumway 1983) or on British Columbia agricultural soils (e.g., John 1971, 1972; Bremer 1984).

Correlations between soil test values and P fractions are of interest, in developing a soil testing programme, for relating the various extractants to nutrient forms and for comparison with results from other soils. Many studies have correlated the amount of P extracted by soil tests with various chemical P forms from Chang and Jackson type fractionations. Data reviewed by Kamprath and Watson (1980) indicate that, for a wide range of soils (including some British Columbia soils studied by John 1972), results obtained by the Olsen (buffered alkaline) and Bray P_1 (dilute acid with complexing ion) methods were primarily correlated with the Al-P fraction; whereas P extracted by dilute strong acids(Truog, double-acid) was correlated with the Ca-P fraction in soils high in Ca-P and with Al-P in soils low in Ca-P. All fractionation studies noted have involved agricultural soils and (in addition to meeting the specific objectives) it is of interest if the above relationships extend to forest soil conditions.

MATERIALS AND METHODS

Eight forest soil materials were selected from coastal and interior British Columbia to represent a range of forest soil conditions such as pH (3.65 to 7.60 in H_2O), texture (sand to silt loam), parent materials,

P forms and P levels (Table 1). The selected soil materials represented some Podzolic, Brunisolic, and Regosolic forest soil materials of southern and central British Columbia. The soil samples were air-dried and sieved (< 2 mm). Available P was estimated by 12 P extraction methods (Table 2), and four chemical P fractions (Al-P, Fe-P, reductant-soluble P (Red-P), and Ca-P) were extracted by the Chang and Jackson (1957) procedure as modified by Peterson and Corey (1966). Measurement of P in all soil extracts was by ascorbic acid reduction of a phospho-molybdate complex (Murphy and Riley 1962) as described for soil extracts by Watanabe and Olsen (1965). Color intensity was read on a Gilford Stasar II at 700 nm. Modified Olsen and modified NH_4HCO_3 - DTPA were also read at 880 nm with a red filter on a Bausch and Lomb Spectronic 20, to reduce error from effervescence, by increasing the light path length through the solution. Readings at 880 mm with a red filter are preferred; as the Gilford lacks this capability, readings at 700 mm are used as an alternative (Murphy and Riley 1962). The Gilford is more efficient to use because of its flow-through capability and low sample volume requirement.

Data analysis was performed on the University of British Columbia computing system. Simple linear correlations formed the basis of the data analysis, with Spearman rank correlation coefficients calculated as a check and recorded in Appendix 4. (With small sample size normality assumptions are considered to play a greater role for significant parameters (Dr. Malcolm Greig personal communication).[2]

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[2]Head Analyst, Statistical Analysis, University of British Columbia Computing Center.

Table 1. Summary of Study Soils

Symbol	Name (This Study)	Horizon Used	pH H_2O	pH $CaCl_2$	Texture[1]	Sampling Location	Notes
EL	Eluviated	Ae	3.65	3.15	LS	UBC Research Forest	Ae horizon from Orthic Humo-Ferric Podzol developed in glacial drift dominated by acid-igneous materials.
AP	Ap horizon	Ap	4.35	4.20	MSL	UBC Research Forest	Scarified surface horizon from Orthic Humo-Ferric Podzol developed in glacial outwash dominated by granitic clasts.
CM	P-fertilized	Ap	4.65	4.40	SL	Campbell River Nursery	P-fertilized nursery soil on Vancouver Island, made by mixing various soil materials.
CU	Non P-fertilized	Ap	5.00	4.60	LS	Campbell River Nursery	Unfertilized, newly scarified nursery soil (Humo-Ferric Podzol developed in glacial outwash).
FF	Forest floor	(F) H	3.75	3.30	-	University Endowment Lands	Western Hemlock forest floor (Orthic Humimor[2])
MI	Memekay	Bf	4.90	4.60	SiL	North of Campbell River	Orthic Humo-Ferric Podzol developed in marine clay.
CA	Calcareous	Ck	7.60	7.20	SiL	North of Lillooet (Pavilion Lake)	Calcareous Orthic Regosol developed in limestone Colluvium, displays apparent Fe deficiencies in conifers in the field[3].
TS	Tsus	Bf	5.15	4.80	S	East of Prince George (Tsus Creek)	Orthic Humo-Ferric Podzol developed in glacial outwash, displays apparent Fe deficiencies in conifers in the field[3].

Notes: [1]Hand Texture (M = mucky).
[2]Klinka *et al.* 1981.
[3]Soil CA is from Site 5 in Majid (1984); TS from Site 1.

Table 2. Available Phosphorus Methods Tested[1]

Method	Extraction Solution	Soil/Sol'n (g/ml)	Shaking Time[2] (min.)	Shaking Type
1. H_2O-soluble P (Humphreys and Pritchett, 1972)	H_2O + $CHCl_3$	1:10	960	reciprocal
2. Truog (1930)	0.002 N H_2SO_4 buffered with $(NH_4)_2SO_4$ - pH 3.0	1:200	30	reciprocal
3, 3A.[3] Modified Olsen (Banderis et al. 1976)	0.05 M $NaHCO_3$ - pH 8.5 (Polyacrylamide instead of carbon black)	1:20	30	reciprocal
4. Bray P_1	0.03 N NH_4F + 0.025 N HCl - pH 2.7	1:10	1	rotational
5. Modified Bray P_1	0.03 N NH_4F + 0.025 N HCl - pH 2.7	1:10	5	rotational
6. Bray P_2	0.03 N NH_4F + 0.1 N HCl - pH 1.5	1:10	1	rotational
7. Modified Bray P_2	0.03 N NH_4F + 0.1 N HCl - pH 1.5	1:10	5	rotational
8. Double-acid (Nelson et al.)	0.05 N HCl + 0.025 N H_2SO_4	1:5	5	reciprocal
9. NH_4OAc at pH 4.8 (Breland 1957)	1 M NH_4OAc adjusted with acetic acid pH 4.8	1:10	5	reciprocal
10, 10A.[3] Modified NH_4HCO_3 - DTPA Solantanpour and Workman (1979)	1 M NH_4HCO_3-DTPA pH 7.6	1:2	15	reciprocal
11. 0.01 N HCl	0.01 N HCL	1:10	5	rotational
12. New-Mehlich (Mehlich 1978)	0.02 N NH_4Cl + 0.2 N HOAc + 0.015 N NH_4F + 0.012 N HCl - pH 2.5	1:10	5	reciprocal

[1] Detailed descriptions appear in Appendix 1.
[2] All extractions were filtered immediately through Whatman No. 42 Filter paper (No. 40 for modified Olsen).
[3] Phosphorus determined in all extracts by ascorbic acid reduction of phosphomolybdate complex and read at 700 nm (880 nm for 3 and 10, 700 nm for 3A and 10A).

RESULTS AND DISCUSSION

Phosphorus Forms

Phosphorus forms obtained through fractionation varied considerably among the soils (Table 3). The Podzolic horizons (TS, MI, CU and including the scarified AP, and P-fertilized CM soils) were dominated by the Al-P and Fe-P fractions and yielded high amounts of P (in the order of 300 to 800 ppm total for sum of all four fractions). The CA soil (although yielding a total sum of fractionated P of about 265 ppm), was dominated by the Ca-P fraction. The FF and EL soils yielded much less summed P from all fractions (under 100 ppm and under 10 ppm respectively) and both contained primarily Al-P.

Observations for the Podzolic soil materials agree with results of previous studies on agricultural soils in western Canada (e.g., John 1971). It appears reasonable that most of the P bound by organic matter would be detected in the first step of fractionation, which involves NaOH. The EL soil appears extremely low in P, which is not unreasonable, considering that all but acid-resistant primary minerals have been eluviated from this material in the course of soil development.

Extractable Phosphorus

All available P extractants (except the Troug, Bray P_2, double-acid and the NH_4OAc at pH 4.8) yielded highest test values, among unfertilized soil materials, with the FF. The double-acid and Bray P_2

Table 3. Summary of Phosphorus Extraction and Fractionation Data for the Study Soils[1]

Method	Soil							
	FF	EL	TS	CM	AP	MI	CU	CA
	ppm P							
1. H_2O-soluble P	128.0	1.5	.6	.1	0.0	0.0	.2	.5
2. Truog	40.0	2.0	16.0	50.0	10.0	2.0	3.0	50.0
3. Mod. Olsen *et al.* (880 nm)[3]	22.5	2.3	14.5	38.0	11.5	.5	6.5	12.0
3A. Mod. Olsen *et al.* (700 nm)	56.8	8.1	17.5	54.8	20.8	3.5[4]	4.8	31.1
4. Bray P_1 - 1 min.	51.0	7.0	50.0	84.0	30.0	2.0	16.0	.5
5. Bray P_1 - 5 min.	59.0	8.8	36.0	61.0	20.0	2.0	11.5	.5
6. Bray P_2 - 1 min.	53.0	7.8	71.0	127.0	49.0	3.3	29.0	0.0
7. Bray P_2 - 5 min.	60.0	9.0	64.0	109.0	35.5	2.3	23.0	.5
8. Double-acid	32.0	4.8	34.0	54.5	12.0	1.3	8.5	4.4
9. NH_4OAc at pH 4.8	38.3	.6	2.8	7.1	2.9	1.1	2.3	95.0
10. Mod. NH_4HCO_3-DTPA (880 nm)[3]	18.4	.7	5.8	17.8	2.1	.7	.6	16.9
10A. Mod. NH_4HCO_3-DTPA (700 nm)	33.2	N.V.[2]	5.9	13.5	3.7	1.8	N. .	12.0
11. 0.01 N HCl	32.0	1.3	2.2	1.3	.5	.2	.2	1.8
12. New-Mehlich (1978)	32.0	3.0	13.5	32.5	5.0	2.1	5.0	26.0
FRACTIONATION								
Al - P	86.5[4]	3.6	208.0	409.0	477.3	267.5	114.0	26.0
Fe - P	0.0	0.0	304.5	153.5	134.0	164.8	54.3	0.0
Reductant-soluble P	1.8	2.3	176.8	71.0	46.5	110.5	60.8	7.8
Ca - P	4.0	2.0	76.8	55.5	25.3	42.8	77.0	230.3

[1]Data represents means of duplicate analyses.

[2]N.V. = no value attained, due to operational difficulties, in two separate attempts.

[3]All other determinations made at 700 nm.

[4]Data represents one determination.

extractants yielded highest unfertilized soil test values with the Podzolic TS soil. The Troug and NH_4OAc at pH 4.8 yielded highest P with the calcareous CA soil. The P-fertilized CM soil yielded higher soil test results than FF with the Truog, Olsen (880 nm), all Bray methods, modified double-acid and new-Mehlich methods. For the FF, H_2O-soluble P was the highest and for the CA, NH_4OAc at pH 4.8 was the highest. The NH_4OAc at pH 4.8 extracted very little P from the eluviated EL soil and Podzolic MI and CU, as did modified NH_4HCO_3-DTPA. The 0.01 N HCl and H_2O extracted little P from all soils but FF.

The Bray P_2 (1 minute shake) and Bray P_1 (1 minute) almost invariably yielded the highest and second highest extractable P, respectively, for the Podzolic and eluviated soil materials (TS, CM, AP, CU and EL). For the Bray methods, the 1-minute was always higher than the 5-minute version except for the eluviated EL, organic FF, and often the calcareous CA, where the opposite was true. All Bray methods extracted very little P from the CA (amounts similar to H_2O-soluble P).

High P test results for the FF are consistent with other reports for British Columbia forest floors (Gaitho 1978; Carter 1983). (Along with the very high value for H_2O-soluble P, this suggests the importance of the forest floor as a major pool of available P in forest ecosystems.) The strongly acidic Bray P_2 extractant would be expected to preferentially dissolve Al-P and Fe-P, over organically bound P, in a Podzolic Bf horizon such as TS.

Both the NH_4OAc at pH 4.8 and new-Mehlich solutions effervesced the most with the calcareous CA soil, yielding fairly high P concentrations;

perhaps the reaction involved acetate, since acetic acid was present in both. However, the strong acidic extractants (i.e., Bray P_2) did not extract much P from this soil. High Truog P for CA is consistent with the presence of Ca-P in a slowly soluble form released in longer shaking. Extracts filtered very slowly for NH_4OAc at pH 4.8 and Truog, prolonging effective extraction time. In comparison, Bray methods yielded much lower P for CA, most likely due to H^+ neutralization and CaF_2 formation (Smillie and Syers 1972; Syers et al. 1972; Olsen and Sommers 1982), and possibly also due to shorter extraction time.

Those methods which yielded higher P for the P-fertilized CM over the organic FF preferentially release easily soluble P, and include strongly alkaline solutions with HCO_3^- (modified Olsen method), and strongly acidic extractants with F^- (Bray and new-Mehlich methods) or SO_4^{2-} (Truog and double-acid methods). The Olsen method has been shown to act on Ca-P to a similar degree as Bray P_1 (Kamprath and Watson 1980).

Time of extraction has been proven very important in Bray extractions (Bray and Kurtz 1945; Agboola and Omueti 1980). Extracted P generally declines after 1 or 5 minutes due to resorption. (The Miller and Axley (1956) test uses H_2SO_4 instead of HCl in the Bray P_1 reagent; this most likely cuts down on P resorption through SO_4^{2-} activity.) The NH_4OAc at pH 4.8 and modified NH_4HCO_3-DTPA extracted little from the eluviated EL, because of soil acidity and low P status. The Modified NH_4HCO_3-DTPA employs a narrow soil:solution ratio which may also explain low extraction values with MI and CU due to very low soil pH (perhaps a wider ratio would have been better). The 0.01 N HCl has no active anion

to prevent resorption of P or to aid in P release to the extracting solution, explaining the commonly low test values.

Correlations Among Extractable Phosphorus Obtained by Various Methods

Soil test values obtained by a number of the methods are significantly correlated (Table 4). Modified Olsen (700 nm) values are significantly correlated with the greatest number of values from other methods: Truog, all Bray methods, double-acid, modified NH_4HCO_3-DTPA and new-Mehlich. All four Bray method modification results are significantly correlated with each other and those from the double-acid method. Bray P_1 5-minute data are significantly correlated with new-Mehlich data. Modified NH_4HCO_3-DTPA values are also significantly correlated with 0.01 N HCl extractable P. Values obtained from NH_4OAc at pH 4.8 were not correlated with any values obtained by other methods.

Olsen extractable P is commonly correlated with Bray extracted P and results from other acidic P methods with SO_4^{2-} or F^- since they all extract P forms similarly (Kamprath and Watson 1980). Similar correlations among Bray P_1, Olsen, Truog and new-Mehlich values have been observed for other British Columbia forest soil materials by Gaitho (1978). Olsen and Bray soil test values have also been demonstrated very significantly correlated with each other for British Columbia agricultural soils by John (1972).

Spearman rank correlation coefficients (Appendix 4-1) agree with results discussed.

Table 4. Correlation Coefficients for the Relationships Among Soil Phosphorus Test Values Obtained From 12 Extraction Methods[1]

P Extraction Method	1.	2.	3.	3A.	4.	5.	6.	7.	8.	9.	10.	10A.[1]	11.
1. H_2O-soluble P													
2. Truog	.3439												
3. Mod. Olsen *et al.* (880 nm)[3]	.2973	.7891*											
3A. Mod. Olsen *et al.* (700 nm)	.6085	.8829**	.8953**										
4. Bray P_1 - 1 min.	.2829	.5008	.9123**	.7308*									
5. Bray P_1 - 5 min.	.5633	.5361	.8775**	.8211*	.9500***								
6. Bray P_2 - 1 min.	.0957	.4428	.8895**	.6361	.9795***	.8703**							
7. Bray P_2 - 5 min.	.2339	.4914	.9107**	.7060	.9979***	.9334***	.9871***						
8. Double-acid	.2750	.5760	.9264***	.7516*	.9851***	.9388***	.9573***	.9867***					
9. NH_4OAc at pH 4.8	.2373	.6945	.1204	.3925	-.2387	-.1403	-.3041	-.2537	-.1483				
10. Mod. NH_4HCO_3-DTPA (880 nm)[3]	.5104	.9807***	.7901*	.9274***	.5318	.6190	.4402	.5153	.6054	.6601			
10A.[1] Mod. NH_4HCO_3-DTPA (700 nm)	.9169*	.6356	.5171	.8401*	.3798	.6446	.1992	.3421	.4083	.3812	.7890		
11. 0.01 N HCl	.9981***	.3790	.3240	.6326	.3061	.5831	.1169	.2573	.3049	.2623	.5432	.9289**	
12. New-Mehlich	.5191	.9666***	.8643**	.9624***	.6444	.7161*	.5591	.6277	.7008	.5653	.9877***	.7977	.5515

*,**,***Significant at the 5, 1 and 0.1% levels, respectively
[1]N = 8 except for 10A (mod. NH_4HCO_3-DTPA) where N = 6

Correlations of Extractable Phosphorus with Phosphorus Fractions

Only one significant r value exists in the correlation matrix (Table 5). This is NH_4OAc at pH 4.8 which correlates significantly at the $\alpha = .05$ level with the Ca-P fraction obtained from the modified Chang and Jackson procedure. This may be explained by the apparent affinity of this extractant for basic Ca-P as demonstrated by previous discussion of the CA data.

These observed results for the 8 forest soil materials tested are contrary to numerous studies in the literature (Chang and Juo 1963; Shelton and Coleman 1968; Tripathi *et al.* 1970; Zubriski 1971; John 1972; Susuki *et al.* 1963; Ahmed and Islam 1975; Cajuste and Kussow 1974). Data from the literature indicate that, for a wide range of primarily agricultural soils, Olsen and Bray P_1 extractable P values are primarily correlated with the Al-P fraction, whereas dilute acid extractants (Truog, double-acid) are related to the Ca-P fraction in soils high in calcium and to the Al-P fraction in other soils.

In studying British Columbia agricultural soils, John (1972) found soil test values from the Olsen, Bray P_1 and double-acid methods to be correlated with P forms as above. Results here follow general trends as discussed above, but are not significant, partially due to the very wide range of soils tested in this one study. The existence of relationships among extractable P and P forms is primarily of interest in a forest soil P testing programme if it occurs across this range of soil properties. However, examining the correlations across Podzolic soil horizons only (without CA, EL, FF; Appendix 2) does not substantially

Table 5. Correlation Coefficients for the Relationships Between Extractable Phosphorus and Phosphorus Fractions[1]

Available P Method	P Fraction			
	Al-P	Fe-P	Red-P	Ca-P
1. H_2O-soluble P	-.2672	-.3822	-.3878	-.3337
2. Truog	-.0087	-.1939	-.2854	.4676
3. Mod. Olsen *et al.* (880 nm)[3]	.3863	.1413	-.0087	-.0040
3A. Mod. Olsen *et al.* (700 nm)	.1511	-.1642	-.3076	.0149
4. Bray P_1 - 1 min.	.4971	.3990	.2498	-.2988
5. Bray P_1 - 5 min.	.3153	.2059	.0783	-.3811
6. Bray P_2 - 1 min.	.5953	.4718	.3174	-.2503
7. Bray P_2 - 5 min.	.4969	.4145	.2729	-.2779
8. Mod. Double-acid	.3926	.3907	.2660	-.1972
9. NH_4OAc at pH 4.8	-.4577	-.4988	-.4767	.7809*
10. Mod. NH_4HCO_3-DTPA (880 nm)[3]	-.0750	-.2337	-.3107	.3476
10A. Mod. NH_4HCO_3-DTPA (700 nm)	-.4976	-.6326	N.S.[2] -.6050	-.1719
11. 0.01 *N* HCl	-.2784	-.3642	-.3735	-.3061
12. New-Mehlich (1978)	.0266	-.1597	-.2594	.2679

*Significant at 5% level
[1]N = 8 except 10A where N = 6
[2]N.S. = not significant (N = 6) at $\alpha = .10$
[3]All other P determinations made at 700 nm.

improve results from those reported above, with respect to the literature observations.

Spearman rank correlation coefficients (Appendix 4-2) disagree with the results discussed in that no significant correlations (at $\alpha = .05$) exist. Therefore, although many more observations are required to test for normality, it is suggested from both correlations that, for study soils, test results are generally not correlated with P forms from a Chang and Jackson type fractionation.

Correlations Among Phosphorus Fractions

Across all eight study soils only the Fe-P and Red-P fractions are significantly correlated (Table 6a). For Podzolic soil horizons only (i.e., without CA, EL, FF) the above correlation holds true and also, Al-P is significantly and negatively correlated with Ca-P (Table 6b). These results are consistent with, but less extensive than those of John (1972), Pratt and Garber (1964), and Westin and Buntley (1966). Their studies also found significant correlations ($\alpha = .01$ level) between Red-P and Al-P and negative correlation between Ca-P and Fe-P.

The negative correlation between Ca-P and Al-P is due to the relationship between Ca-P and Al-P in the soil (i.e., relative to pH). Most previous studies used a narrower range of soils; the fact that more correlations exist across a subset of study soils (Table 6b) suggests that poor correlations here are again partly due to the wide range of soil properties selected for investigation.

Table 6 - Correlation Coefficients for the Relationships Among Phosphorus Fractions.

6A. Correlations Across all 8 Soils (N=8)

		Fe-P	Red-P	Ca-P
Al-P		.5952	.4006	-.2781
Fe-P	.0179		.9549***	-.1003
Red-P	-.4166	.8922+		-.0245
Ca-P	-.8269+	.1886	.4848	
	Al-P	Fe-P	Red-P	

6B. Correlations Across Podzolic Soil Horizons[1] (N=5)

+,*** significant at 10, and 0.1% levels, respectively.

[1]Without FF(organic), CA(calcareous), EL(eluviated).

Spearman rank correlation coefficients (Appendix 4-3) agree with the results discussed.

CONCLUSIONS

The British Columbia forest soils tested present a variety of amounts and distributions of P forms obtained from a Chang and Jackson type fractionation. This suggests diverse soil chemistry relative to P availability to forest trees. This indicates that either a soil test method capable of extracting P from all important P forms, or more than one kind of soil test method, will be required for soil testing for P availability to forest soils in British Columbia.

The twelve soil P extraction methods tested vary greatly in their ability to extract P from the various study soils. (However, the limited scope of this study does not warrant discarding any methods prior to the greenhouse analysis involving forest trees.) Almost all methods extract more P from forest floor than unfertilized mineral soils, suggesting the importance of the forest floor as a reservoir of available P in forest soils.

On British Columbia forest soils, test methods yield correlated results similar to reports in the literature reviewed. However, on British Columbia soils, P forms (fractionated by a modified Chang and Jackson procedure) do not appear as well correlated among themselves or with soil P test values as in the literature for agricultural soils. This suggests somewhat different P chemistry in British Columbia forest

soils relative to agricultural soils, which is consistent with the fact that a wide range of soil conditions was tested. Spearman rank correlation coefficients (Appendix 4) present no major discrepancies with the simple linear correlations presented in the text, improving confidence in the results.

CHAPTER 3

GREENHOUSE EVALUATION OF METHODS TO ESTIMATE PHOSPHORUS AVAILABILITY TO DOUGLAS-FIR, LODGEPOLE PINE, AND WESTERN HEMLOCK

INTRODUCTION

Objectives for a forest soil testing programme for P fall into all three categories defined by Fassbender (1980) and Kamprath and Watson (1980): (1) Grouping soils into availability classes for making fertilizer recommendations (e.g., nursery soils as discussed by van den Driessche 1969); (2) predicting probability of a profitable response to fertilization; and (3) providing an index of P supplying capacity of a soil.

In British Columbia, soil testing for P in forest soils is in the early stages of development. Preliminary and on-going research are the fundamental basis to a reliable soil testing programme (Melsted and Peck 1973; Leitch et al. 1980). Topics for investigation include (after Melsted and Peck 1973; FAO 1980): (1) significant chemical forms of P across the range of soils; (2) suitability of P extractants for accurately and rapidly indexing P across the range of soils; (3) pot trials, including the expected range of soil conditions, for initial screening of P extractants based on the best and most consistent correlations with seedling growth or P status; (4) fertilizer trials in the field (responses to varying rate and method of fertilizer

application for each species and further soil test screening and calibration for response prediction capability); and (5) methodological type research (e.g., field sampling techniques, etc.). All five topics above represent preliminary research whereas the last two should also be of an on-going nature and are just as important to a successful soil testing programme as choosing the proper method.

The previous chapter reported on research investigating amounts and relationships among soil P forms and soil P extracted by various methods (1 and part of 2 above); this chapter reports on a greenhouse study designed to provide an initial screening of soil test methods for P in British Columbia forest soils (3 and part of 2 above). The specific objective of this Chapter is to identify the test method (or methods) giving the best relationship with foliar P concentration, through an initial screening based on pot trials with Douglas-fir, lodgepole pine and western hemlock. Further evaluation of the suitability of the soil test methods for routine laboratory analysis of British Columbia forest soils will also be addressed. Final selection and calibration of a suitable soil test method for P will depend upon field fertilizer trials (4 above).

Criteria that an "adequate" forest soil test for P should meet include (after Bray 1948; Fassbender 1980): (1) it should extract all or a proportionate part of the available form(s) of P from soils with variable properties (i.e., provide an index of availability across the expected range of soils); (2) P extraction and determination should be possible with reasonable accuracy, reproducibility, and speed; (3) the

amount extracted should be correlated with the growth and response of each tree species to P under various (environmental and soil) conditions; and (4) interpretation of soil data should allow grouping of soils (e.g., high, medium, low) based on field experience with the method.

In Western Canada, currently developed soil P testing programmes for agricultural crops employ the Olsen method ($NaHCO_3$ at pH 8.5, Olsen et al. (1954)), the Bray P_1 method (0.025 N HCl + 0.03 N NH_4F, Bray and Kurtz 1945) and the Miller and Axley extractant (0.03 N H_2SO_4 + 0.03 N NH_4F, Miller and Axley 1956) (Leitch et al. 1980). In British Columbia, the Bray P_1 method is dominantly used along with some recent use of the Olsen for certain (e.g., calcareous) soil conditions (Bertrand 1981; Bremer 1984). The Bray P_1 test has traditionally been used in British Columbia forest nursery management (van den Driessche 1969; 1981); however, nursery soils do not present the complete range of British Columbia forest soils for which evaluations may be desired.

EXPERIMENTAL DESIGN

This study involved a greenhouse pot trial with 8 soils x 2 P levels (P added vs. control) x 3 tree species (lodgepole pine, Douglas-fir, western hemlock) x 4 replications arranged in a randomized block design according to soils. The 8 soils (Table 1) represented a range of British Columbia forest soil conditions of interest in soil testing for P (organic [FF], scarified [AP, CU], Podzolic B [MI, TS],

eluviated [EL], calcareous [CA], and P-fertilized [CM] soil materials).

The P treatments were designed to enhance interpretations of study results; in effect, they enabled comparisons for soils which differ only in P levels, in a sense doubling the scope of the experiement without requiring the collection of double the number of soils. To be meaningful for purposes of interpreting data from soils which are not fertilized with P, the P added in this study was to resemble native soil P, rather than conventional, soluble fertilizer P.

The mixture represented a range of P forms (strengite, taranakites, colloidal Al-P and tribasic Ca-P) which are thought to occur naturally in soils or closely resemble naturally occurring soil phosphates. The amount applied was approximately equivalent to 100 kg /ha for both the organic and the mineral soil materials. In studying sources of P for slash pine, R. Ballard and Pritchett (1975b) found that strengite was not nearly as effective, but that potassium taranakite was just as effective as normal fertilizer sources.

On a weight basis, because of bulk density differences, the fertilizer addition to the organic material was greater than to the mineral soil material. This was considered appropriate because of the substantially higher extractable P level in organic material (Table 3). Good resolution of the difference between treated and untreated soil would require a relatively large addition. Gaitho (1978), studying similar British Columbia forest soils with two exotic conifer species, used fertilizer P treatments of 20 and 200 ppm P (i.e., approximately 40 and 400 kg P/ha). He found that both treatments yielded results

differing from the control, so in this study, 100 kg P/ha was expected to yield useful results.

Twelve agricultural soil test methods for "available" P were selected based on previous local experience with agriculture and forestry (John et al. 1967; van den Driessche 1969, 1981; John 1971, 1972; Gaitho 1978; Leitch et al. 1980; Bertrand 1981) and forestry literature (Switzer and Nelson 1956; Stoeckler and Jones 1957; Wilde 1958; Stoeckler and Slabaugh 1965; Pritchett and Llewelyn 1966; Alban 1972; Baker and Brendmuehl 1972; Humphreys and Pritchett 1972; R. Ballard 1974, 1978; Webber 1974; Kadeba and Boyle 1978; Hopmans et al. 1978; Lea et al. 1980; Tiarks 1982). Soil test methods chosen (Table 2) covered 5 of the 7 classes of soil P extractants defined in the literature review and Chapter 2.

Use of foliar P concentrations (rather than P uptake or some measure of yield) was considered to be the most reliable plant criterion for soil test correlations because of substantial variability in seedling development between and within soils. Foliar P has commonly been used with good success in the literature (e.g., Terman and Bengston 1973; R. Ballard and Pritchett 1975a, 1975b; MacCarthy and Davey 1976 and others). The soil test methods were screened on the basis of the criteria presented in the introduction.

Soil samples were initially analyzed as composites of treatment replicates, with foliage samples analyzed individually. Simple linear correlations formed the basis of the data analysis to enable comparison with the literature. Spearman rank correlation coefficients were

calculated to improve confidence in the simple linear correlations. Analysis of variance and covariance were performed to evaluate some factor effects on the final soil analysis with replication.

Screening of test methods was by a hierarchical approach involving first three, then five soils. Three soils (FF, EL and TS), representing the extreme ranges of the study soils with reasonable seedling growth (high organic matter, highly eluviated, and high sesquioxide content, respectively) were analyzed with all 12 methods. Based on these initial results, the three most promising methods were selected and tested further on the remaining five soils (AP, MI, CM, CU and CA). The apparently most promising method was then analyzed for the individual treatment replicates to provide an assessment for each individual soil type. The overall results were considered in the final recommendations.

MATERIALS AND METHODS

Large quantities of soil samples were obtained from selected locations in coastal and interior British Columbia (Table 1). These soil samples were air dried, screened to remove coarse fragments larger than about 5 mm and homogeneous subsamples placed in plastic pots to a standard volume (with all replicates of a single soil type kept at a constant weight).

Potassium taranakite, ammonium taranakite, strengite, and colloidal aluminum phosphate were prepared according to procedures described by Taylor _et al_. (1960) and Taylor and Gurney (1961). Tribasic calcium

phosphate was obtained as a commercially available reagent chemical. A phosphate mix was then formulated as follows:

8.00 g strengite (16.5% P)	=	1.32 g P
14.27 g K-taranakite (18.5% P)	=	2.64 g P
13.62 g NH_4-taranakite (19.4% P)	=	2.64 g P
26.76 g colloidal Al-P (14.8% p)	=	3.96 g P
21.41 g tribasic Ca-P (18.5% P)	=	3.96 g P
84.06 g total	=	14.52 g P

In P-treatment pots, the phosphate mixture additions were 285 mg (about 50 mg P) per kg of mineral soil and 2300 mg (about 400 mg P) per kg of organic soil (roughly equivalent to P fertilization at 100 kg/ha). The phosphate mixture was then mixed thoroughly into the soil materials which, along with the control pots, were then watered to a weight corresponding to "field capacity" (previously determined for each soil by means of a porous-plate tension-table device). Pots were then covered with plastic film and re-watered daily until soil water content had remained near "field capacity". (This procedure was necessary because some of the soils, particularly the forest floor samples, had become hydrophobic on air-drying.)

Several seeds were then sown in each pot and the film replaced until germination appeared complete. The pots were placed on the greenhouse benches at random, subject to natural plus 12 hours of fluorescent and incandescent light per day. Watering with tap water was done daily during hot weather, less frequently when cooler. To facilitate reasonable growth and P demand by the seedlings, a macro-nutrient (except P) fertilizer solution was prepared based on Swan (1966) and added in lieu of watering on a few occasions.

Seedlings were harvested 13 months after germination and dried at 70°C until the foliage was dry (12 to 18 hrs). (Douglas-fir needles were stripped prior to drying, lodgepole pine and western hemlock afterwards.) Foliage samples were ground until uniformly fine and digested by a modified Parkinson and Allen (1975) wet oxidation procedure (T. Ballard 1981; T. Ballard unpublished data)[3]. Total P was determined on a Technicon Autoanalyzer II.

Following harvesting, the greenhouse soils were air dried and sieved (< 2 mm). Forest floor samples were ground in a Waring blender. Extraction methods used to extract available P were detailed in Chapter1 (Table 2). Measurement of P in all soil extracts was by ascorbic acid reduction of a phospho-molybdate complex (Murphy and Riley 1962) as described for soil extracts by Watanabe and Olsen (1965). Samples were read on a Gilford Stasar II at 700 nm. Modified Olsen and modified NH_4HCO_3 - DTPA were also read at 880 nm with a red filter on a Bausch and Lomb Spectronic 20.

Data analysis was performed on the University of British Columbia computing system.

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RESULTS AND DISCUSSION

Operational Evaluation of Tested P Extractants

The two alkaline-based P extractants (Modified Olsen and modified NH_4HCO_3-DTPA) were very cumbersome, and therefore undesirable for routine laboratory testing of the study soils. The HCO_3^- and OH^- ions in these extractants react with organic matter, causing foaming and organic matter dispersion that often results in dark soil extracts and precipitation upon acidification for P determination. Persistent effervescence of some samples complicates spectrophotometer readings and often necessitates use of more time-consuming apparatus. Both these methods are recommended for alkaline soils (Olsen *et al.* 1954; Soltanpour and Schwab 1977); however, their wide ranging success (including the use of the Olsen test on British Columbiaagricultural soils) was reason for their inclusion in this study.

Seedling Growth

Generally, the organic FF displayed the best seedling growth for all the species, the calcareous CA the worst for Douglas-fir and lodgepole pine and the Podzolic CU the worst for western hemlock. This demonstrates the importance of the forest floor as a nutrient reservoir in British Columbia forest soils. All species displayed a dramatic response to P treatment on at least some soils which is in agreement with other greenhouse studies from the region (e.g., Heilman and Ekuan 1980a). Response to P was most dramatic for western hemlock and least

for lodgepole pine. Westen hemlock growth and survival were poor on a number of the mineral soils. Low biomass precluded obtaining western hemlock foliar P data for all replicates of CU with P added and three replicates of CU without P. Necrosis of lodgepole pine foliage on the calcareous CA soil precluded meaningful foliar analysis. Clearly, other nutritional and environmental factors have affected growth.

Correlations of Extractable P with Foliar P Concentration

In the preliminary analysis of all 12 methods, the amount of P extracted by the various methods (Appendix 3) again followed the observations of Chapter 2. Correlations of soil extractable P with foliar P, by species, varied (Table 7); almost all methods were significant at $\alpha = .05$ for lodgepole pine, but new-Mehlich was the only one significant at $\alpha = .01$. The new-Mehlich was also the only one significant for western hemlock (at $\alpha = .20$) and was significant for Douglas-fir at $\alpha = .05$. The 0.01 N HCl and modified Olsen were significant for Douglas-fir at $\alpha = .20$ and for lodgepole pine at $\alpha = .05$. Modified NH_4HCO_3-DTPA also showed well, being significant for lodgepole pine at $\alpha = .05$ and for fir ($n = 5$) at $\alpha = .05$. In the overall correlation (no strata, to test a method's adequacy across all three species, Table 7) almost all methods were significant at $\alpha = .10$, but new-Mehlich and modified Olsen were the only ones significant at $\alpha = .05$; modified NH_4HCO_3-DTPA and 0.01 N HCl were significant at $\alpha = .10$.

In the selection of three candidate methods for further analysis, the operational limitations of modified NH_4HCO_3-DTPA and modified Olsen

Table 7 - Correlation Coefficients for the Relationship Between Soil-Extractable Phosphorus and Foliar Phosphorus for 12 Methods and 3 Soils

Species	n	1 H_2O sol. p	2 Truog	3 Mod. Olsen (380 nm)	3A Mod. Olsen (700 nm)	4 Bray P_1	5 Mod. Bray P_1	6 Bray P_2	7 Mod. Bray P_2	8 Double Acid	9 NH_4OAc at pH 4.8	10 Mod. NH_4HCO_3 DTPA	11 0.01 N HCl	12 new-Mehlich
Lodgepole Pine	6	.7987^{+}	.8704*	.8901*	.8441*	.8287*	.8665*	.5064	.8682*	.8669*	.8623*	.8984*	.8757*	.9313**
Western Hemlock	6	.3885	.4306	.4382	.4289	.3248	.4848	-.0490	.3725	.3411	.4334	.5508	.5342	.6224^{-}
Douglas-fir	6	.2582	.5583	.6451^{-}	.5700	.3896	.5229	-.0820	.4488	.3812	.5771	.9268[1]*	.6525^{-}	.8548*
All	18	.3557^{-}	.4247^{+}	.4685*	.4666^{+}	.3316^{-}	.4091^{+}	.0197	.3648^{-}	.3250^{-}	.4051^{+}	.4609^{+}	.4388^{+}	.5592*

$^{-}$, +, *, ** Significance at 20, 10, 5 and 1% levels, respectively.
[1] N = 5 For modified NH_4OAc with Douglas-fir due to effervescence.

ruled out their further consideration. Thus, the methods chosen for further analysis were new-Mehlich, 0.01 N HCl because of their apparent "good" correlations with foliar P, and the "standard " Bray P_1 (1 minute shake) because of its current widespread use. (Bray P_1 was significant overall at $\alpha = .20$ and for lodgepole pine at $\alpha = .05$). The Bray P_2-1 minute shake appeared considerably different from the other Bray methods. Re-extraction confirmed this relationship (Appendix 4-5).

The three chosen methods are quite similar chemically (which helps to confirm the screening results), all being acidic extractants, with Bray P_1 and new-Mehlich having a complexing ion (F^-), and 0.01 N HCl being of similar acidic strength. The new-Mehlich also has the organic anion acetate which may be expected to aid in improving the consistency of results through anion replacement, both preventing P readsorption during extraction (Nelson et al. 1953; Thomas and Peaslee 1973), and releasing P by forming complexes with polyvalent cations (Kamprath and Watson 1980).

It is not surprising that many of the proposed methods were significantly correlated with lodgepole pine since many studies in the literature report significant correlations for pine species with various methods (e.g., Pritchett and Llewelyn 1966; Alban 1972; Humphreys and Pritchett 1972; R. Ballard 1974, 1977; R. Ballard and Pritchett 1975a, 1975b; Gaitho 1978; Kadeba and Boyle 1978; Tiarks 1982; MacDougall 1984; and others). Gaitho (1978) in a greenhouse study with Pinus patula on three British Columbia forest soil materials (Bf, Ah, LFH) found that all extraction methods tested (Truog, Olsen, Bray P_1, Modified Bray P_1,

new-Mehlich) yielded significant correlations with P uptake.

Many of the methods which appear inadequate (in addition to the modified Olsen and modified NH_4HCO_3-DTPA) have acted predictably. (Such methods were included in the study based on experience in the literature with other soils.) H_2O-soluble P represents an estimate of soil solution P (intensity) (Humphreys and Pritchett 1972; Olsen and Sommers 1982) and might be expected to yield very low levels on strongly P-fixing soils. (Low test levels may be considered unacceptable, regardless of correlation strength, due to increased potential error and, perhaps, limited opportunity for mathematical manipulation such as logarithms.) The Truog (1930) extractant is a non-buffered dilute solution of strong acid which (although perhaps similar to some root environments) might be expected to be slow at dissolving Al-P and even slower for Fe-P.

Bray soil test methods have been noted to extract P forms that are unavailable to plants (Grigg 1965a); perhaps this explains poor correlations with the stronger, Bray P_2 methods. Local soils commonly yield less Bray extractable P in 5 minutes shaking (Chapter 2) than in 1 minute. Therefore, since all soils vary in their P buffering capacity, one might expect to find the results of the best correlation with the lesser extraction time and the weaker Bray extractant.

The double-acid method has been noted to be satisfactory on soils under pH 7.0 (Kamprath and Watson 1980). The NH_4OAc at pH 4.8 method is derived from the Morgan (1941) reagent which has been noted by Kamprath and Watson (1980) to be the least effective (of the P soil tests they

discussed) for a wide range of soils. However, this would have been an advantageous reagent because Klinka et al. (1980) found the most successful method for extracting soil cations for forest productivity studies in southwestern British Columbia was NaOAc at pH 4.8; perhaps NH_4OAc at pH 4.8 would serve both purposes.

It is important to note that, although a given P extraction method may not be satisfactorily correlated with foliar P concentration in this study, it may still be significantly correlated with other growth and nutrition parameters. Examples of this from the literature on pine species include identification of sites that will respond to fertilization (Hopmans et al. 1978; Tiarks 1982) and prediction of growth on unfertilized sites (R. Ballard 1974). However, the data in this study provide no alternative to use of foliar P for this purpose.

Spearman rank correlation coefficients (Apendix 4-4) agree with results discussed above, with one major exception. The 0.01 N HCl is the only method significantly correlated with western hemlock foliar P concentration at $\alpha = .20$, suggesting perhaps a strong curvilinear type of relationship (Dr. George Eaton, personal communication)[4]. The presence of significant correlations with both statistical methods for the new-Mehlich and 0.01 N HCl favoured their selection. The Bray P_1 was chosen over two others because of current use in forestry (and

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despite differences in rank correlations, Truog, Bray P_1, and NH_4OAc at pH 4.8 were similarly correlated in Table 7) suggesting the Bray P_1 to be desirable.

Overall Comparison of the Three Candidate Methods

Correlations of soil extractable P with foliar P, by species, were performed across all eight soils and various subgroups of the eight soils (Table 8). Across all eight soils, new-Mehlich appeared best overall, always significant at $\alpha = .01$ or less; Bray P_1 was next, being better than new-Mehlich for lodgepole pine, and similar to new-Mehlich for western hemlock, but significant only at $\alpha = .05$ for Douglas-fir. The 0.01 N HCl did not appear as good as these other two methods in any case ($\alpha = .05$ or more). In an overall correlation, across all three species and eight soils, both the new-Mehlich and Bray P_1 were significant at $\alpha = .001$ (with new-Mehlich somewhat higher). The 0.01 N HCl was significant at $\alpha = .05$. A modification of the new-Mehlich (rotational shaking) was tested and compared favourably with the results reported for new-Mehlich, extracting slightly more P (Appendix 4-7).

The results of the rest of the correlations (Table 8) suggest that the new Mehlich method is the most universal soil test for P, for the study soils and species. This relationship holds true without FF, AP, CU and CA (in turn and in groups) and EL data alone. Bray P_1 appears better where only the calcareous soil (CA) and the eluviated EL are removed for purposes of correlation. (However, Bray P_1 did not generally correlate well with Douglas-fir.) Looking at only the

Table 8 - Correlation Coefficients for the Relationships Between Soil-Extractable Phosphorus and Foliar Phosphorus for 3 Candidate Methods and 8 Soils

Soils	Species	n	Bray P_1	0.01 N HCl	New-Mehlich
All	All	45	.5242***	.3192*	.5582***
All	Lodgepole pine	14	.8418***	.5630*	.7486**
All	Western hemlock	15	.6789**	.5018*	.6633**
All	Douglas-fir	16	.5398*	.4110	.8221***
All but CA	Lodgepole pine	14	.8418***	.5630*	.7486**
"	Western hemlock	13	.6026*	.5190+	.7291**
"	Douglas-fir	14	.7583**	.4474	.8458***
All but CU, CA	Lodgepole pine	12	.8461***	.5550+	.7443**
"	Western hemlock	12	.5986*	.5125+	.7278**
"	Douglas-fir	12	.7413**	.4073	.8273***
All but FF	Lodgepole pine	12	.7801**	.4588	.8068**
"	Western hemlock	13	.5606*	.5514+	.6094*
"	Douglas-fir	14	.5005+	.5598*	.8725***
All but FF, CA	Lodgepole pine	12	.7801**	.4588	.8068**
"	Western hemlock	11	.4440	.7832**	.7996**
"	Douglas-fir	12	.7672**	.5242+	.8830***
All but FF, AP	Lodgepole pine	10	.7963**	.5145	.8757***
"	Western hemlock	11	.5891+	.5324+	.5916+
"	Douglas-fir	12	.5117+	.5795*	.8980***
All but FF, AP, CA	Lodgepole pine	10	.7963**	.5145	.8757***
"	Western hemlock	9	.4638	.7846*	.8004**
"	Douglas-fir	10	.7871**	.5518+	.9194***

Table 8 continued...

Table 8 continued

Soils	Species	n	Bray P_1	0.01 N HCl	New-Mehlich
All but EL	Lodgepole pine	12	.8900***	.5709+	.7395**
"	Western hemlock	13	.9208***	.5518+	.7519**
"	Douglas-fir	14	.5464*	.3785	.8013***
All but EL, CA	Lodgepole pine	12	.8900***	.5709+	.7393**
"	Western hemlock	11	.8994***	.5780+	.8298**
"	Douglas-fir	12	.8360***	.4183	.8294***
All but FF, EL, AP	Lodgepole pine	8	.9053**	.9076**	.8789**
"	Western hemlock	9	.8980**	-.3199	.5419
"	Douglas-fir	10	.5229	.7321*	.8979***
All but FF, EL, AP, CA	Lodgepole pine	8	.9053**	.9076**	.8789**
"	Western hemlock	7	.8573*	.9057**	.8228*
"	Douglas-fir	8	.9325***	.9597***	.9190**
All but CM	Lodgepole pine	12	.7982**	.7242**	.8028**
"	Western hemlock	13	.5960*	.6353*	.6690*
"	Douglas-fir	14	.2768	.5755*	.8055***
All but CM, CA	Lodgepole pine	12	.7982**	.7242**	.8028**
"	Western hemlock	11	.5063	.6526*	.7405**
"	Douglas-fir	12	.6029*	.6736*	.8475***

+, *, **, *** significance at 10, 5, 1 and 0.1% levels, respectively.

Podzolic soil horizons TS, MI, CM and CU (i.e., without FF, AP, EL, CA), 0.01 N HCl was the method yielding most significance for all three species (although Bray P_1 and new-Mehlich were also significant at $\alpha = .05$ or less). However, without the operationally P-fertilized CM, and without CA, new-Mehlich is the most significant for all three species ($\alpha = .01$ or less).

The results with the modified new-Mehlich method are very similar to the comparison between stirring (similar to swirling) and reciprocal shaking made by Agboola and Omueti (1980) for Bray P_1 and another NH_4F extractant. The authors found that, although not statistically significant, stirring tended to extract slightly more P and they considered stirring more adaptable to rapid routine analysis. However, with hydrophobic samples there can be problems with getting consistent wetting from swirling. Reciprocal shaking still appears better for this reason, along with increased risks of error associated with other alternatives for hydrophobic samples, as discussed in the literature review.

It is interesting that the Bray P_1 method appears to be not very well correlated with Douglas-fir foliar P status in a number of instances. Current soil testing programs for forest nursery management in British Columbia employ the Bray P_1 method (van den Driessche 1980, 1981). A much narrower range of soils is involved in the nurseries and the Bray P_1 test seems well correlated with Douglas-fir across the more similar Podzolic horizons.

The 0.01 N HCl did not perform well and this, along with the fact that it extracts quite low amounts of P from a number of study soils

(making the method more susceptible to error), suggests that the method should not be considered further.

Spearman rank correlation coefficients (Appendix 4-6) agree with results discussed above, except that Bray P_1 is the method that is commonly the least significantly correlated with foliar P concentration and 0.01 N HCl appears better than discussed. This evaluation supports the choice of the new-Mehlich method for further testing, because it gives the best relationship with plant P status for both correlation methods.

Further Evaluation of New-Mehlich

Correlations of soil extractable P with foliar P, by species, across all eight soils were consistent with prior results (Table 9), with the new-Mehlich being significant for all three species at $\alpha = .001$. Overall correlations, for all species and all soils and groups thereof, were all significant at $\alpha = .001$. Also of interest in this section are correlations by species for each of the individual soils. Correlations with foliar P on FF and EL were significant at $\alpha = .01$ or less, for all three species. Only two other significant correlations existed among the remaining six soils: AP was significant (at $\alpha = .01$) with Douglas-fir and MI with lodgepole pine. The remaining soils without correlations represent some calcareous and Podzolic horizons of British Columbia.

Strong correlations with plant P status indicate a useful analytical method. However, a limited range of soil P data may yield a

Table 9 - Correlation Coefficients for the Relationships Between Soil Phosphorus Extracted by the New-Mehlich Method and Foliar Phosphorus for all Treatment Replicates.

Soil	Species	n	r
All	All	176	.5169***
All but CA	All	162	.5679***
All but FF	All	152	.6173***
All but EL, CA	All	145	.5180***
All	Lodgepole pine	56	.7485***
All	Western hemlock	56	.4942***
All	Douglas-fir	64	.7406***
FF	Lodgepole pine	8	.9763***
FF	Western hemlock	8	.9456***
FF	Douglas-fir	8	.9183***
AP	Lodgepole pine	8	.4555
AP	Western hemlock	8	.3395
AP	Douglas-fir	8	.9621**
MI	Lodgepole pine	8	.8862**
MI	Western hemlock	8	-.2155
MI	Douglas-fir	8	.5831
CM	Lodgepole pine	8	.3918
CM	Western hemlock	6	.2928
CM	Douglas-fir	8	.1767
EL	Lodgepole pine	8	.8569**
EL	Western hemlock	15	.8035**
EL	Douglas-fir	8	.9885***
TS	Lodgepole pine	8	.0590
TS	Western hemlock	4	.4948
TS	Douglas-fir	8	.4949
CU	Pine	8	.5909
CU	Western hemlock (too few cases for analysis)		
CU	Douglas-fir	8	.2540
CA	Lodgepole pine	0	N/A
CA	Western hemlock	6	.4110
CA	Douglas-fir	8	.4491

+,*,**,***significant at the 10, 5, 1 and 0.1% levels respectively.

weak correlation, obscuring a real relationship. Consequently, the absence of a strong correlation does not necessarily mean that a method is not useful for evaluating available P. (For most of the Podzolic horizons, there was little difference in P test values between P-treated and control samples.) It is important to recall from Table 8 that the new-Mehlich method was very well correlated with plant P status across groups of Podzolic horizons that provided the necessary variation to provide a correlation analysis.

It is not surprising that the new-Mehlich method is not well correlated with foliar P concentrations on the calcareous CA soil. In soil testing for white clover in New Zealand, Holford (1980) noted that the new-Mehlich method extracted excessive (non-labile) P at pH > 6.0. (The new-Mehlich method has been found significantly correlated with foliar P for Pinus patula by Gaitho (1978) and Lea et al. (1980).)

Regarding the Podzolic horizons, the fact that the new-Mehlich method may not be significantly correlated with foliar P both agrees and contrasts with other findings for British Columbia Podzolic horizons. John (1971) in studying British Columbia agricultural soils, was not able to get any significant soil test correlations with Olsen or Bray P_1 on Podzolic horizons. However, Gaitho (1978) found significant correlations, using three P levels, with Pinus patula on the Bf horizon he studied, with all 5 methods he tested and noted that new-Mehlich may be the best index of available P in Podzolic horizons (based also on the most significant correlation with Cupressus lusitanica seedling P uptake). However, Gaitho (1978) also noted that the new Mehlich was not

significant for Pinus patula on an Ap horizon, consistent with this study.)

In evaluating soil test methods on New Zealand soils high in sesquioxides, Grigg (1968) found that the degree of correlation with rye grass yield was proportional to a soil test's ability to extract Al and Fe phosphates from surfaces; he rated Olsen > Bray P_1 > Bray P_2 > Truog, in this regard. However, John's (1971) study employed both Olsen and Bray P_1 to no avail. The record of Bray P_1 in British Columbia forest nurseries suggests that it should be included in further analyses of this kind.

Spearman rank correlation coefficients (Appendix 4-8) agree with the results discussed (although only western hemlock is significant on FF and EL). The analysis of variance (Appendix 4-9) revealed a significant soil x tree species x P level interaction which complicates interpretation (Hicks 1973), and interpretation may be considered beyond the scope of current soil testing programme objectives. The analysis of covariance (Appendix 4-10) displays less significant factor contributions as would be expected when a covariate accounts for variation in the yield variable, however this is also complicated by the same interaction yielding the same conclusion regarding interpretation. Similar variance analyses for the previous phases of this experiment, which have no replication, would require use of the soil x tree species x P level interaction as the error term, yielding a "conservative" analysis (Dr. George Eaton, personal communication)[5]

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that, due to the interaction noted above, may again be considered beyond the scope of the objectives.

CONCLUSIONS

In agreement with the second chapter in this thesis, the twelve soil P extraction methods tested vary greatly in their ability to extract P from the various study soils but almost all extract the most from the forest floor (apart from the P fertilized soil). Test methods with alkaline extraction solutions do not appear feasible for routine laboratory analysis of British Columbia forest soils.

This preliminary study suggests that the new-Mehlich and Bray P_1 test methods appear the most adequate (in that order) for soil testing for P in British Columbia forest soils. Detailed analysis results for the new-Mehlich are inconclusive for some individual soils and it is possible that the method may prove inadequate on some Podzolic and calcareous horizons. However, across groups of Podzolic horizons the new-Mehlich method was very well correlated with plant P status. Clearly, there is need for further background research involving field trials. It is recommended that the two candidate methods still be considered together in further research on developing a soil P test programme for forestry in British Columbia. (The new-Mehlich may afford greater utility since it was developed to extract various nutrient cations in addition to P.)

With some modification of the 0.01 N HCl method (enabling extraction of more P to lessen the significance of laboratory error), it may prove viable for use with Podzolic B horizons if the two proposed methods (or modifications of them) are found to be unacceptable on these soils. In field trials on calcareous soils, reinstatement of one of the alkaline based extractants might be considered to provide an alternative if the new-Mehlich and Bray P_1 again appear inadequate under these soil conditions.

CHAPTER 4

THESIS SUMMARY AND CONCLUSIONS

Based on this study, involving a range of British Columbia soil conditions for lodgepole pine, western hemlock and Douglas-fir, the following conclusions can be made regarding the status of P in British Columbia forest soils, P fractions in British Columbia forest soils, soil test methods, and correlations of soil test values with tree P status.

The forest floor has the highest index of P availability among unfertilized soil materials (indicating its reported importance in P cycling). Soil P test methods vary greatly in their ability to extract P from the range of British Columbia forest soils studied. Although results in Chapter 2 revealed that a number of soil test methods yield results correlated with each other, only a few yielded results well correlated with foliar P status of trees in Chapter 3.

British Columbia forest soils generally present a wider range of soil conditions than most agricultural comparisons. A more diverse cross-section of soil P chemistry is suggested for the forest soils by the results that P fractions are not as well correlated with each other or with soil P test values, as reported in the literature for agricultural soil comparisons.

Soil test methods involving with alkaline extracting solutions are not feasible for routine laboratory analysis of nutrient status in the

range of British Columbia forest soils studied. This is due to operational difficulties resulting from organic matter dispersion, and effervescence of sample extracts.

This study suggests that, of the methods tested, the new-Mehlich and Bray P_1 methods are the most promising (in that order) for soil testing for P in British Columbia forest soils for the three tree species studied. Detailed analysis of the new-Mehlich is inconclusive for individual soils and it is possible that this method may prove inadequate on a restricted range of Podzolic horizons. The new-Mehlich appears excellent for the organic and eluviated soils and was very well correlated with foliar P across groups of Podzolic soils.

The three species varied in their depletion of extractable P from the soil (Appendix 3), with Douglas-fir appearing to yield the lowest soil test values and lodgepole pine the highest, on most soils tested. Despite this, the new-Mehlich method appears capable of indexing P availability to each of these species. The Bray P_1 method does not appear as well correlated with Douglas-fir. Results for western hemlock (which may be considered less conclusive due to poor growth on mineral soils) provide the same recommendation of methods for future research.

There is the need for further research, particularly field trials, to calibrate more promising methods. It is recommended that the new-Mehlich and Bray P_1 methods be considered (in that order) for further evaluation. If problems on Podzolic horizons actually become apparent, other methods (e.g., 0.01 N HCl) are recommended. It is recommended that further soil test evaluation on calcareous soils consider reinstatement of one of the alkaline-based soil P extractants.

A consideration for future soil testing on British Columbia forest soils is the possible lack of currently tested methods to correlate well with plant P status on a restricted range of Podzolic horizons. Correlation tests over a wider range of soil extractable P values is recommended.

It is recommended that future fertilization trials with P use the new-Mehlich and Bray P_1 methods for soil testing, unless special conditions (e.g., calcareous soils) suggest that alternatives are desirable.

The poor growth of western hemlock on mineral soil, as demonstrated here and in the field, may be considered a topic of great interest and importance.

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APPENDIX 1: ANALYTICAL METHODS

INDEX

Note: References cited are listed in the Literature Cited Section. Phosphorus determination reagents for the "ascorbic acid method" are not described in this section (see John 1970). Watanabe and Olsen (1965) was followed in the results reported in this thesis.

A. Notes on P Standards, Duplication, Filtering, Hydrophobic Samples

P Standards: These were prepared for each extraction method as follows:

Reagents: Stock 100 ppm P solution - dissolve 0.4393 g of oven dry monobasic potassium phosphate (KH_2PO_4) in distilled water, dilute to 1 litre (Olsen and Sommers, 1982). (Stored in refrigerator.)

P Working Standards - pipette 0,1,2,3,4,5,7 and 10 ml stock 100 ppm P solution in 100 ml volumetric, make to volume with extracting solution. (These represent 0-10 ppm P.) Store in refrigerator (record P determination absorbance values to verify standard concentrations over time).

Duplication: All blanks and one third of the samples analyzed on the greenhouse soils were duplicated to verify precision in the laboratory determinations. Pre-greenhouse soil samples representing the soils being analyzed were also run in duplicate. Most duplications were very close to one another. This "double duplication" (samples and reference samples duplicated) provided insight on variability between and within analysis batches for all extraction techniques. All standards were duplicated in the P determination step to further verify laboratory precision.

Filtering: This study incorporated 9 cm filter paper (Whatman #42) for extractions of 20 to 25 mls, based on previous experience in the laboratory. In many cases larger filter paper (i.e. 11 cm)

would have been better. This is noted in the following method descriptions along with further recommendations regarding faster filter paper in some instances.

Hydrophobic Samples: A number of the dried soil samples, particularly the FF samples, displayed hydrophobicity and did not wet up well with the extracting solutions during the extracting times involving swirling (rotational shaking). Some studies have allowed hydrophobic soils to sit overnight in distilled water and then make them up to an equivalence of the normal extracting solution strength (Gaitho 1978). However, perhaps stronger agitation (reciprocal shaking) may be more appropriate.

P EXTRACTION METHOD NO.1 - H_2O-soluble P

ORIGINAL METHOD: Humphreys and Pritchett (1972)[1]

Procedure Followed:

1. Weigh 5g soil into container
2. Add 50 ml distilled H_2O
3. Add 5 drops chloroform ($CHCl_3$ to check microbial activity
4. Shake for 16 hrs (960 min.)
5. Filter
6. Refilter if not clear
7. P determination volumes:

   Std - 2ml
   FF - 2ml
   AP,TS,CM,CU,EL,MI - 20 ml
   CA-8 ml

Extracting Solution: Distilled H_2O with 5 drops $CHCl_3$ per sample
- pH: — not determined

Soil:Solution Ratio: 5g:50ml

Container: 125 ml plastic bottle

Shaking - type: reciprocal
- time: 16 hrs (960 min.)

Filter Paper: Whatman #42
Size: 15 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

4. "equilibrating" for 16 hrs stated in original method - we have inferred shaking
5. original method does not mention filtering

Comments/References

Inconveniences Noted:

Minor-very slow filtering; perhaps use Whatman #40 (may be worthwhile to consider centifuging or use of 0.05% polyacrylamide).

Calculation: ppm P soil = (ppm solution - ppm blank*) $\left[\frac{50\text{ ml}}{5\text{g}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml aliquot}}\right]$

*also subtracted ppm color blank for dark and/or large volumes (PA)

Reagents: (P-determination: see page 1-14)

Extracting Solution: Distilled H_2O - 5 drops $CHCl_3$ added to each individual extraction prior to shaking.

[1] Original method for the procedure followed; many researchers have studied H_2O-soluble P.

P EXTRACTION METHOD NO.2 - Truog (1930)

ORIGINAL METHOD: Truog (1930)

Procedure Followed:

1. Weigh 1 g soil into container
2. Add 200 ml ext. solution
3. Shake for 30 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   AP,CU,EL,MI,TS - 20 ml
   CA,CM,FF - 8 ml

Extracting Solution: 0.002 N H_2SO_4

- pH: 3.0

Soil:Solution Ratio: 1 g:200 ml

Container: 250 ml plastic bottle

Shaking - type: reciprocal
- time: 30 minutes

Filter Paper: Whatman #42
Size: 15 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 1 g instead of "2 g"
2. 200 ml instead of "400 ml"
4. refilter if not clear instead of "discard filtrate until it comes through perfectly clear"

Comments/References

1 g:200 ml is a common substitution for 2 g:400 ml

Inconveniences Noted: Large extract volumes

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}) \left[\frac{200 \text{ ml}}{1 \text{ g}}\right] \left[\frac{2 \text{ ml std.}}{x \text{ ml sample}}\right]$$

Reagents:

Stock Solutions: 1.0 N H_2SO_4 - add 28.7 ml conc. H_2SO_4 to about 300 ml of distilled H_2O; make up to 1 litre. Check normality by titrating a portion against a standard alkali.

Extracting Solution: Dilute 4 ml 1.0 N H_2SO_4 to 2 litres. Adjust pH of solution to pH 3.0 by adding 3 g of $(NH_4)_2SO_4$ or K_2SO_4 per litre of solution.

P EXTRACTION METHOD NO.3A - Modified Olsen

ORIGINAL METHOD: Olsen et al. (1954), modified by Banderis et al. (1976)

Procedure Followed:

1. Weigh 2.5 g soil into container
2. Add 50 ml extracting solution
3. Shake for 30 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 10 ml
   CU,CM,FF,MI,TS - 5 ml
   AP,CA,EL - 10 ml

Extracting Solution: 0.5 M $NaHCO_3$ with polyacrylamide
- pH: 8.5

Soil:Solution Ratio: 2.5 g:50 ml

Container: 125 ml polyethylene bottle

Shaking - type: reciprocal
- time: 30 minutes

Filter Paper: Whatman #40
Size: 15 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2.5 g instead of 5 g
2. polyacrylamide in extract solution rather than Darco carbon

Comments/References

Banderis et al. (1976)

Inconveniences Noted:

Major-procedure is difficult because of the need for color blanks, because of efferverscence when acid added to reduce pH to 5.0 and precipitation upon acidification.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{blank} - \text{color blank}) \left[\frac{50\ \text{ml}}{2.5\ \text{g}}\right]\left[\frac{10\ \text{ml std}}{x\ \text{ml sample aliquot}}\right]$$

Reagents:

Stock Solutions:
1. 0.5 M $NaHCO_3$
2. 0.05% aqueous polyacrylamide solution (BDH chemicals - MW > 5×10^6, No. 29788-3N).

Extracting Solution:
1. Add 5 ml 0.05% aqueous polyacrylamide per litre of 0.5 M $NaCHO_3$.
2. Adjust pH to 8.5 with NaOH.
3. Add mineral oil to avoid exposure of solution to air.
4. Store in a polyethylene container (may be stored over one month, but pH must be checked before use).

P EXTRACTION METHOD NO.3 - Modified Olsen

ORIGINAL METHOD: Olsen et al. (1954) modified by Banderis et al. (1976)

Procedure Followed:

3. Shake for 30 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 10 ml
   CU,CM,FF,MI,TS - 5 ml
   AP,CA,EL - 10 ml

Extracting Solution: 0.5 M $NaHCO_3$ n

Container: 125 ml polyethylene bottle

Shaking - type: reciprocal
- time: 30 minutes

Filter Paper: Whatman #40
Size: 15 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Bausch and Lomb
- wavelength: 880 nm

Modifications from Original Method

1. 2.5 g instead of 5 g
2. polyacrylamide in extract solution rather than Darco carbon

Comments/References

Banderis et al. (1976)

Inconveniences Noted:

Major-procedure is difficult because of the need for color blanks, because of fizzing when acid added to reduce pH to 5.0 and precipitation upon acidification. Also, standards are not linear.

Calculation:

ppm P soil = (ppm soil by using linear regression, assuming linearity to 3 ppm)

Reagents:

Stock Solutions:
1. 0.5 M $NaHCO_3$
2. 0.05% aqueous polyacrylamide solution (BDH chemicals - MW > 5 x 10^6, No. 29788-3N).

Extracting Solution:
1. Add 5 ml 0.05% aqueous polyacrylamide per litre of 0.5 M $NaCHO_3$.
2. Adjust pH to 8.5 with NaOH.
3. Add mineral oil to avoid exposure of solution to air.
4. Store in a polyethylene container (may be stored over one month, but pH must be checked before use).

P EXTRACTION METHOD NO.4 - Bray P_1: 1 min. shake

ORIGINAL METHOD: Bray and Kurtz (1945)

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 1 minute exactly
4. Filter immediately
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   CM,FF,TS - 1 ml
   AP,CA,CU,EL,MI - 2 & 4 ml

Extracting Solution: 0.03 N NH_4F + 0.025 N HCl
- pH: 2.7

Soil:Solution Ratio: 2.00 g/20 ml

Container: 50 ml Erlenmeyer flask (pyrex)

Shaking - type: hand swirling
- time: 1 min. exactly

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2 g instead of 1 g
2. 20 ml instead of 7 ml
3. handswirling instead of stoppered swirling - common lab methodology
4. filtered instead of allowed to settle

Comments/References

Not all laboratories use the same proportions or shaking time (Olsen and Sommers 1982)

Stirring (analogous to swirling) recommended for operational use in Nigeria by Agboola and Omueti (1980)

Filtering mentioned by Bray and Kurtz (1945)

Whatman #42 called for in Olsen and Sommers (1982)

Inconveniences Noted:

None observed for study soils. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}\left[\frac{20\text{ ml}}{2\text{ g}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

Reagents: (Color development: see page 1-14)

Stock Solutions: 1.0 N NH_4F: Dissolve 37 g NH_4F in distilled water, make to a volume of 1 litre. Store in polyethylene bottle.
0.5 N HCl: Dilute 40.4 ml conc. HCl to a volume of 1 litre.

Extracting Solution: Add 30 ml 1.0 N NH_4F and 50 ml 0.5 N HCl to distilled water, make to a volume of 1 litre. This will keep in glass bottle for over 1 year.

P EXTRACTION METHOD NO.5 - Bray P_1: 5 min. shake

ORIGINAL METHOD: Bray and Kurtz (1945)

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 1 minute exactly
4. Filter immediately
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   CM, FF, TS - .5 & 1 ml
   AP, CA, CU, EL, MI - 2 & 4 ml

Extracting Solution: 0.03 N NH_4F + 0.025 N HCl
- pH: 2.7

Soil:Solution Ratio: 2.00 g/20 ml

Container: 50 ml Erlenmeyer flask (pyrex)

Shaking - type: rotational
- time: 5 min. exactly

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2 g instead of 1 g
2. 20 ml instead of 7 ml
3. open swirling instead of stoppered swirling - common lab methodology
4. filtered instead of allowed to settle

Comments/References

Not all laboratories use the same proportions or shaking time (Olsen and Sommers 1982)

Stirring (analogous to swirling) recommended for operational use in Nigeria by Agboola and Omueti (1980)

Filtering mentioned by Bray and Kurtz (1945)
Whatman #42 called for in Olsen and Sommers (1982)

Inconveniences Noted:

None observed for study soils. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}\ \frac{[20\ \text{ml}]}{2\ \text{g}}\frac{[\ 2\ \text{ml std}\ ]}{\text{x ml sample aliquot}}$$

Reagents:

Stock Solutions: 1.0 N NH_4F: Dissolve 37 g NH_4F in distilled water, make to a volume of 1 litre. Store in polyethylene bottle.
0.5 N HCl: Dilute 40.4 ml conc. HCl to a volume of 1 litre.

Extracting Solution: Add 30 ml 1.0 N NH_4F and 50 ml 0.5 N HCl to distilled water, make to a volume of 1 litre. This will keep in glass bottle for over 1 year.

P EXTRACTION METHOD NO.6 - Bray P_2: 1 min. shake

ORIGINAL METHOD: Bray and Kurtz (1945)

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 1 minute exactly
4. Filter immediately
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   CM, FF, TS - .5 & 1 ml
   AP, CA, CU, EL, MI - 2 & 4 ml

Extracting Solution: 0.03 N NH_4F + 0.10 N HCl
- pH: 1.5

Soil:Solution Ratio: 2.00 g/20 ml

Container: 50 ml Erlenmeyer flask (pyrex)

Shaking - type: hand swirling
- time: 5 min. exactly

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2 g instead of 1 g
2. 20 ml instead of 7 ml
3. open swirling instead of stoppered swirling - common lab methodology
4. filtered instead of allowed to settle

Comments/References

Not all laboratories use the same proportions or shaking time (Olsen and Sommers 1982)

Stirring (analogous to swirling) recommended for operational use in Nigeria by Agboola and Omueti (1980)

Filtering mentioned by Bray and Kurtz (1945)

Whatman #42 called for in Olsen and Sommers (1982)

Inconveniences Noted:

None observed for study soils. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}\left[\frac{20\text{ ml}}{2\text{ g}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

Reagents:

Stock Solutions: 1.0 N NH_4F: Dissolve 37 g NH_4F in distilled water, make to a volume of 1 litre. Store in polyethylene bottle.
0.5 N HCl: Dilute 40.4 ml conc. HCl to a volume of 1 litre.

Extracting Solution: Add 30 ml 1.0 N NH4F and 50 ml 0.5 N HCl to distilled water, make to a volume of 1 litre. This will keep in glass bottle for over 1 year.

P EXTRACTION METHOD NO.7 - Bray P_2: 5 min. shake

ORIGINAL METHOD: Bray and Kurtz (1945)

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 1 minute exactly
4. Filter immediately
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   CM, FF, TS - .5 & 1 ml
   AP, CA, CU, EL, MI - 2 & 4 ml

Extracting Solution: 0.03 N NH_4F + 0.10 N HCl
- pH: 1.5

Soil:Solution Ratio: 2.00 g/20 ml

Container: 50 ml Erlenmeyer flask (pyrex)

Shaking - type: rotational
- time: 5 min. exactly

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2 g instead of 1 g
2. 20 ml instead of 7 ml
3. handswirling instead of stoppered swirling - common lab methodology
4. filtered instead of allowed to settle

Comments/References

Not all laboratories use the same proportions or shaking time (Olsen and Sommers 1982)
Stirring (analogous to swirling) recommended for operational use in Nigeria by Agboola and Omueti (1980)
Filtering mentioned by Bray and Kurtz (1945)
Whatman #42 called for in Olsen and Sommers (1982).

Inconveniences Noted:

None observed for study soils. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}\ \frac{[20\ \text{ml}]}{2\ \text{g}}\left[\frac{2\ \text{ml std}}{x\ \text{ml sample aliquot}}\right]$$

Reagents: (Color development: see page 1-14)

Stock Solutions: 1.0 N NH_4F: Dissolve 37 g NH_4F in distilled water, make to a volume of 1 litre. Store in polyethylene bottle.
0.5 N HCl: Dilute 40.4 ml conc. HCl to a volume of 1 litre.

Extracting Solution: Add 30 ml 1.0 N NH_4F and 50 ml 0.5 N HCl to distilled water, make to a volume of 1 litre. This will keep in glass bottle for over 1 year.

P EXTRACTION METHOD NO.8 - Double-Acid (Nelson *et al.* 1953; North Carolina or "old" Mehlich Method)

ORIGINAL METHOD: Barton (1948)†

Procedure Followed:

1. Weigh 4 g* soil into container
2. Add 20 ml extracting solution
3. Shake for 5 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   CM, FF, TS - 1 ml
   CA, EL, MI - 4 ml
   AP, CU - 2 ml

(* used 2 g for FF)

Extracting Solution: 0.05 N HCl and 0.025 N H_2SO_4
- pH: not determined

Soil:Solution Ratio: 4 g*:20 ml

Container: 60 ml plastic bottle

Shaking - type: reciprocal
- time: 5 minutes

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method†

1. 4 g instead of 5 g
2. extracting solution contains 0.05% polycrylamide, Darco carbon not used.
6. P determination by Ascorbic Acid Method rather than ammonium vanadate reducing agent.

Comments/References

†Differences from Olsen and Sommers (1982)

Inconveniences Noted:

None noted. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank}\left[\frac{20\text{ ml}}{4\text{ g*}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

*2 g FF

Reagents:

Stock Solutions: 2.5 N HCl - add 208 ml conc. HCl to about 600 ml distilled H_2O; make to a volume of 1 litre with distilled water.
1.0 N H_2SO_4 - add 28 ml conc. H_2SO_4 to about 300 ml distilled H_2O; make to a volume of 1 litre with distilled water.

Extracting Solution: Add 20 ml 2.5 N HCl and 25 ml 1.0 N H_2SO_4 to about 300 ml distilled water. Add 5 ml 0.05% aqueous polyacrylamide and make up to a volume of 1 litre.

P EXTRACTION METHOD NO.9 - NH_4OAc at pH 4.8 ("University of Florida" Method) Pritchett and Llewellyn (1966)

ORIGINAL METHOD: Breland (1957)

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 5 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   FF - 4 ml
   AP, CU, CM, EL, MI, CA - 1 ml

Extracting Solution: 1.0 N NH_4OAc adjusted with acetic acid to pH 4.8
- pH: 4.8

Soil:Solution Ratio: 2 g:20 ml

Container: 50 ml erlenmyer

Shaking - type: rotational
- time: 5 minutes

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

1. 2 g instead of 5 g sample
2. 20 ml instead of 25 ml extracting solution
3. Original method calls for reciprocal shaking for 30 min
4. Whatman #5 called for in original method

Comments/References

Inconveniences Noted:

Ae horizon effervesced and was slow in filtering. 11 cm filter paper would be better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{ppm blank} \left[\frac{20\text{ ml}}{2\text{ g}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

Reagents:

Extracting Solution:

1.0 N NH_4OAc adjusted with acetic acid to pH 4.8

P EXTRACTION METHOD NO. 10A - Modified NH_4HCO_3 - DTPA

ORIGINAL METHOD: Soltanpour and Schwab (1977)

Procedure Followed:

1. Weigh 10 g soil into container
2. Add 20 ml extracting solution
3. Shake for 15 minutes, flasks open
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   FF - 1 ml
   AP, EL - 4 ml
   CA, CM, TS - 2 ml
   CU, MI - 8 ml

Extracting Solution: 1.0 M NH_4HCO_3 and 0.005 M DTPA and polyacrylamide - pH: 7.6

Soil:Solution Ratio: 10g:20ml (FF:5g)

Container: 125 ml erlenmyer (FF:250 ml)

Shaking - type: reciprocal
- time: 15 minutes

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

2. polyacrylamide instead of carbon black

Comments/References

Soltanpour and Workman (1979)

Inconveniences Noted:

Major - troublesome because of efferverscence problem, need for color blanks and precipitates. FF reacts quite violently, had to use 250 ml erlenmeyer. FF slow filtering. Post-greenhouse soils could not be read on Gilford due to efferverscence problems.

Calculation:

ppm P soil =

$$(\text{ppm solution} - \text{ppm blank} - \text{ppm color blank}) \left[\frac{20\text{ ml}}{10\text{ g}}\right] \left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

Reagents:

Extracting Solution: Add 1.97 g DTPA to 800 ml distilled H_2O, add 2 ml 1:1 NH_4OH solution (aids dissolution and prevents effervescence in next step), stir to dissolve most of the DTPA. Add 79.06 g NH_4HCO_3 and stir gently to dissolve, add 5 ml 0.05% aqueous polyacrylamide. Adjust pH to 7.6 with NH_4OH and make to 1 litre with distilled water. Use solution immediately or store under 3 cm of mineral oil. (Under mineral oil, pH remains fairly stable for 2 weeks).

P EXTRACTION METHOD NO.10 - Modified NH_4HCO_3-DTPA

ORIGINAL METHOD: Soltanpour and Schwab (1977)

Procedure Followed:

1. Weigh 10 g soil into container
2. Add 20 ml extracting solution
3. Shake for 15 minutes, flasks open
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   FF - 1 ml
   AP, EL - 4 ml
   CA, CM, TS - 2 ml
   CU, MI - 8 ml

Extracting Solution: 1.0 M NH_4HCO_3 and 0.005 M DTPA and polyacrylamide - pH: 7.6

Soil:Solution Ratio: 10g:20ml (FF:5g)

Container: 125 ml erlenmyer (FF:250 ml)

Shaking - type: reciprocal
- time: 15 minutes

Filter Paper: Whatman #42
Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Bausch and Lomb
- wavelength: 700 nm

Modifications from Original Method

2. polyacrylamide instead of carbon black

Comments/References

Soltanpour and Workman (1979)

Inconveniences Noted:

Major - troublesome because of efferverscence problem, need for color blanks and precipitates. FF reacts quite violently, had to use 250 ml erlenmeyer. FF slow filtering. Post-greenhouse soils could not be read on Gilford due to efferverscence problems.

Calculation:

ppm P soil = (Linear regression using absorbance readings.)

Reagents:

Extracting Solution: Add 1.97 g DTPA to 800 ml distilled H_2O, add 2 ml 1:1 NH_4OH solution (aids dissolution and prevents effervescence in next step), stir to dissolve most of the DTPA. Add 79.06 g NH_4HCO_3 and stir gently to dissolve, add 5 ml 0.05% aqueous polyacrylamide. Adjust pH to 7.6 with NH_4OH and make to 1 litre with distilled water. Use solution immediately or store under 3 cm of mineral oil. (Under mineral oil, pH remains fairly stable for 2 weeks).

P EXTRACTION METHOD NO.11 - 0.01 N HCl

ORIGINAL METHOD: Not known who first used this, reported by a number of studies.

Procedure Followed:

1. Weigh 2 g soil into container
2. Add 20 ml extracting solution
3. Shake for 5 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   FF - 2 ml
   AP, CM, CU, EL, TS - 10 ml
   CA, MI - 12 ml

Extracting Solution: 0.01 N HCl

- pH: not determined

Soil:Solution Ratio: 2 g:20 ml

Container: 50 ml erlenmyer

Shaking - type: rotational
- time: 5 minutes

Filter Paper: Whatman #42
Size: 92 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

N/A

Comments/References

Inconveniences Noted:

11 cm filter paper would have been better.

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{blank}) \left[\frac{20\text{ ml}}{2\text{ g}}\right]\left[\frac{2\text{ ml std}}{x\text{ ml sample aliquot}}\right]$$

Reagents:

Extracting Solution: 0.01 N HCl.

P EXTRACTION METHOD NO.12(B)* - Mehlich (1978)

ORIGINAL METHOD: Mehlich (1978)

Procedure Followed:

1. Weigh 2.5 g soil into container
2. Add 25 ml extracting solution
3. Shake for 5 minutes
4. Filter
5. Refilter if not clear
6. P determination volumes:

   Std - 2 ml
   FF - 1 ml
   CM, TS - 2 ml
   AP, CA - 4 ml
   CU, EL, MI - 8 ml

Extracting Solution: 0.2 N NH_4CL + 0.2 N HOAc + 0.015 N NH_4F + 0.012 N HCl
- pH: approximately 2.5

Soil:Solution Ratio: 2.5 g:25 ml

Container: 60 ml plastic bottle

Shaking - type: reciprocation (min. of 200/min; 3.5-4.0 cm)
- time: 5 minutes

Filter Paper: Whatman #42
- Size: 9 cm

P determined by: "Ascorbic Acid Method"
- spectrophotometer: Gilford
- wavelength: 700 nm

Modifications from Original Method

Comments/References

Inconveniences Noted:

Calculation:

$$\text{ppm P soil} = (\text{ppm solution} - \text{blank}) \left[\frac{25\ \text{ml}}{2.5\text{g}}\right]\left[\frac{2\ \text{ml std}}{x\ \text{ml sample aliquot}}\right]$$

Reagents:

Extracting Solution:

1. Dissolve 1.12 g NH_4F and 42.8 g NH_4Cl in about 1 litre distilled water.
2. Add 2 ml conc. HCl and 23 ml glacial acetic acid
3. Dilute to 2 litres with distilled water and mix.

*M12B = modification incorporating 50 ml erlenmyers and rotational shaking.

APPENDIX 2: PHOSPHORUS TEST VALUE AND FRACTION CORRELATIONS FOR PODZOLIC SOILS ALONE

CORRELATION MATRIX CORRELATIONS BETWEEN EXTRACTABLE P AND P FRACTIONS

N= 5 DF= 3 R@ .0100= .9587 R@ .0500= .8783 R@ .1000= .8054

VARIABLE												
16.ALP	-.5568	.4735	.4685	.6148	.4082	.3879	.4269	.3710	.2981	.4865	.4148	-.0041
17.FEP	.6355	.1737	.1365	.1222	.3295	.3328	.2642	.3125	.3929	.0097	.2051	.8326
18.REDP	.7484	-.0712	-.1212	-.1863	.0664	.0811	-.0033	.0675	.1803	-.2393	-.0123	.6997
19.CAP	.8221	.0457	.0760	-.1046	.1691	.1878	.1485	.2069	.2725	.0298	.1000	.4609
	2. M1P	3. M2P	4. M3P	5. M3AP	6. M4P	7. M5P	8. M6P	9. M7P	10. M8P	11. M9P	12. M10P	14. M11P

	15. M12P
16.ALP	.4435
17.FEP	.1968
18.REDP	-.0481
19.CAP	.0984

APPENDIX 3: PHOSPHORUS EXTRACTION DATA FOR GREENHOUSE STUDY

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Appendix 3-1. Initial Analysis Data (3 soils)[1]

Treatment	H_2O-sol P	Truog	Mod. Olsen (880 nm)	Mod. Olsen (700 nm)	Bray P_1 - 1 min	Bray P_1 - 5 min	Bray P_2 - 1 min	Bray P_2 - 5 min	North Carolina	Univ. of Florida	Mod. NH_4HCO_3 -DTPA(880 nm)	0.01N HCl	New Mehlich	Foliar P
	ppm P in Soil													%P
111	138.0	139.0	90.4	99.4	130.0	146.0	134.0	150.0	114.0	59.3	61.6	77.0	143.0	.2093
112	64.0	44.0	32.2	50.0	32.0	39.0	36.0	40.0	30.0	19.3	19.7	21.5	38.5	.1220
121	98.0	92.0	71.2	90.0	108.0	128.0	116.0	122.0	72.0	36.5	46.6	40.0	104.0	.2318
122	62.0	54.0	45.2	56.8	42.0	50.0	42.0	48.0	34.0	22.5	23.3	24.0	47.0	.0923
131	68.0	60.0	47.8	63.6	56.0	66.0	64.0	66.0	40.0	22.0	22.0	25.0	65.0	.3548
132	96.0	48.0	34.0	50.8	28.0	44.0	34.0	38.0	26.0	16.5	N.V.[3]	19.0	39.0	.1118
211	6.2	18.0	18.5	18.9	29.0	39.0	37.5	35.5	23.0	5.9	11.6	8.0	40.5	.1580
212	.6	2.0	2.7	2.6	1.5	2.5	2.5	2.0	1.6	.5	1.0	.8	2.7	.0918
221	6.6	18.0	19.4	19.8	30.0	53.0	43.0	34.0	24.0	6.0	13.1	10.0	42.0	.2459
222	.8	6.0	4.6	6.0	4.5	6.0	6.5	6.0	4.3	1.0	1.6	1.8	7.0	.1226
231	5.3	16.0	17.8	18.4	31.0	39.0	40.0	31.0	22.5	4.5	11.2	8.2	45.0	.2850
232	.5	2.0	2.8	3.8	2.0	2.0	3.0	3.0	1.9	.8	1.3	1.0	3.8	.0963
311	0.0	15.0	15.2	13.9	50.0	52.0	108.0	49.0	32.3	2.9	6.6	.5	28.0	.1020
312	0.0	10.0	14.2	13.3	46.0	50.0	100.0	45.0	33.0	2.3	5.7	.2	20.5	.1195
321	0.0	16.0	15.4	14.2	56.0	60.0	124.0	54.0	39.0	3.3	7.3	.6	27.0	.0866
322	0.0	12.0	13.8	12.8	48.0	56.0	100.0	52.0	31.0	2.0	5.7	.2	25.0	.0811
331	0.0	16.0	17.0	15.6	52.0	52.0	120.0	52.0	36.0	3.5	7.0	.4	28.0	.1150
332	0.0	10.0	13.4	12.4	48.0	44.0	104.0	48.0	33.0	1.8	5.6	.2	21.0	.1050

[1]Soil data from treatment composite samples; foliar data represents means of individual replicate analyses.

[2]Treatment Codes are: 1 1 1

Soil	Species	Treatment
1 = FF	1 = LODGEPOLE PINE	1 = PADDED
2 = PA	2 = WESTERN HEMLOCK	2 = CONTROL
3 = TS	3 = DOUGLAS-FIR	

[3]N.V. = no value obtained due laboratory complications with FF.

Appendix 3-2. Final Analysis Data (5 Soils)[1]

Treatment[2]	Bray P_1 - 1 min	0.01 N HCl	New-Mehlich	Foliar P
	ppm Soil P			%P
411	83.0	1.5	39.0	.1858
412	74.5	1.2	35.5	.1640
421	90.0	1.4	40.0	.2040
422	74.0	0.6	35.0	.1480
431	90.0	1.2	40.0	.3200
432	76.0	0.8	38.0	.3053
511	39.5	0.6	15.0	.1503
512	31.0	0.3	13.3	.1243
521	37.0	0.2	15.5	.0858
522	33.0	0.4	13.5	.0553
531	36.0	0.4	15.5	.2178
532	34.0	0.2	12.5	.1023
611	3.8	0.2	2.3	.1008
612	3.5	0.1	1.8	.0438
621	5.0	0.2	2.3	.0553
622	4.5	0.2	1.8	.0646
631	5.5	0.2	2.5	.0565
632	4.0	0.0	1.8	.0395
711	25.0	0.3	13.8	.0820
712	18.0	0.1	7.5	.0710
722	17.5	0.2	9.5	.0991
731	24.5	0.2	12.5	.0720
732	17.5	0.0	6.0	.0560
821	0.7	3.6	29.0	.2540
822	0.3	3.0	24.0	.2010
831	1.0	2.8	28.0	.2707
832	0.3	2.0	21.0	.2123

[1]Soil data from treatment composite samples; foliar data represents means of individual replicate analyses.

[2]Treatment Codes are:

411

Soil	Species	Treatment
4 = CM	1 = LODGEPOLE PINE	1 = P ADDED
5 = AP	2 = WESTERN HEMLOCK	2 = CONTROL
6 = MI	3 = DOUGLAS-FIR	
7 = CU		
8 = AE		

APPENDIX 4: ADDITIONAL STATISTICAL TESTS FOR EXPERIMENTAL DATA

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APPENDIX 4-1 Spearman Rank Correlation Coefficients for the Relationships Among Soil Phosphorus Test Values Obtained from 12 Extraction Methods

N= 8

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
2.M1P						
	3.M2P	.1200	.1132	.2982	.9049	.1636
	4.M3P	.2593	.2546	.2917	.5484	.2994
	5.M3AP	.2593	.2546	.2917	.5484	.3593
	6.M4P	.1111	.1091	.2917	.9049	.1557
	7.M5P	.1111	.1091	.2917	.9049	.1557
	8.M6P	.0370	.0364	.2917	.9049	.1078
	9.M7P	.0370	.0364	.2917	.9049	.1078
	10.M8P	.1111	.1091	.2917	.9049	.1916
	11.M9P	.1111	.1091	.2917	.9049	.1317
	12.M10P	.2593	.2546	.2917	.5484	.4072
	14.M11P	.6296	.6183	.2917	.0610	.7425
	15.M12P	.1852	.1818	.2917	.7195	.2755
3.M2P						
	4.M3P	.8462	.8154	.2950	.0055	.8916
	5.M3AP	.6923	.6671	.2950	.0312	.8555
	6.M4P	.5385	.5189	.2950	.1087	.4097
	7.M5P	.5385	.5189	.2950	.1087	.4097
	8.M6P	.4615	.4447	.2950	.1789	.3856
	9.M7P	.4615	.4447	.2950	.1789	.3856
	10.M8P	.5385	.5189	.2950	.1087	.5302
	11.M9P	.8462	.8154	.2950	.0055	.9278
	12.M10P	.6923	.6671	.2950	.0312	.8434
	14.M11P	.5385	.5189	.2950	.1087	.6988
	15.M12P	.9231	.8895	.2950	.0017	.9519
4.M3P						
	5.M3AP	.7143	.7143	.2887	.0141	.8810
	6.M4P	.7143	.7143	.2887	.0141	.7619
	7.M5P	.7143	.7143	.2887	.0141	.7619
	8.M6P	.6429	.6429	.2887	.0312	.7381
	9.M7P	.6429	.6429	.2887	.0312	.7381
	10.M8P	.7143	.7143	.2887	.0141	.8333
	11.M9P	.5714	.5714	.2887	.0610	.7619
	12.M10P	.7143	.7143	.2887	.0141	.8810
	14.M11P	.6429	.6429	.2887	.0312	.7857
	15.M12P	.9286	.9286	.2887	.0004	.9762
5.M3AP						
	6.M4P	.4286	.4286	.2887	.1789	.5714
	7.M5P	.4286	.4286	.2887	.1789	.5714
	8.M6P	.3571	.3571	.2887	.2751	.4762
	9.M7P	.3571	.3571	.2887	.2751	.4762
	10.M8P	.4286	.4286	.2887	.1789	.5952
	11.M9P	.7143	.7143	.2887	.0141	.8571
	12.M10P	.8571	.8571	.2887	.0017	.9524
	14.M11P	.6429	.6429	.2887	.0312	.7857
	15.M12P	.7857	.7857	.2887	.0055	.9286
6.M4P						
	7.M5P	1.0000	1.0000	.2887	.0000	1.0000
	8.M6P	.9286	.9286	.2887	.0004	.9762
	9.M7P	.9286	.9286	.2887	.0004	.9762
	10.M8P	.8571	.8571	.2887	.0017	.9524
	11.M9P	.2857	.2857	.2887	.3988	.2619
	12.M10P	.4286	.4286	.2887	.1789	.5476
	14.M11P	.3571	.3571	.2887	.2751	.4524
	15.M12P	.6429	.6429	.2887	.0312	.6429
7.M5P						
	8.M6P	.9286	.9286	.2887	.0004	.9762
	9.M7P	.9286	.9286	.2887	.0004	.9762
	10.M8P	.8571	.8571	.2887	.0017	.9524
	11.M9P	.2857	.2857	.2887	.3988	.2619
	12.M10P	.4286	.4286	.2887	.1789	.5476
	14.M11P	.3571	.3571	.2887	.2751	.4524
	15.M12P	.6429	.6429	.2887	.0312	.6429
8.M6P						
	9.M7P	1.0000	1.0000	.2887	.0000	1.0000
	10.M8P	.9286	.9286	.2887	.0004	.9762
	11.M9P	.2143	.2143	.2887	.5484	.1905
	12.M10P	.3571	.3571	.2887	.2751	.4762
	14.M11P	.2857	.2857	.2887	.3988	.4286
	15.M12P	.5714	.5714	.2887	.0610	.5952
9.M7P						
	10.M8P	.9286	.9286	.2887	.0004	.9762
	11.M9P	.2143	.2143	.2887	.5484	.1905
	12.M10P	.3571	.3571	.2887	.2751	.4762
	14.M11P	.2857	.2857	.2887	.3988	.4286
	15.M12P	.5714	.5714	.2887	.0610	.5952
10.M8P						
	11.M9P	.2857	.2857	.2887	.3988	.3333
	12.M10P	.4286	.4286	.2887	.1789	.5714
	14.M11P	.3571	.3571	.2887	.2751	.5476
	15.M12P	.6429	.6429	.2887	.0312	.7143
11.M9P						
	12.M10P	.5714	.5714	.2887	.0610	.8095
	14.M11P	.5000	.5000	.2887	.1087	.6429
	15.M12P	.6429	.6429	.2887	.0312	.8571
12.M10P						
	14.M11P	.6429	.6429	.2887	.0312	.8571
	15.M12P	.7857	.7857	.2887	.0055	.9048
14.M11P						
	15.M12P	.5714	.5714	.2887	.0610	.7619

APPENDIX 4-2 Spearman Rank Correlation Coefficients for the Relationships Between Extractable Phosphorus and Phosphorus Fractions

N= 8

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
2.M1P						
	16.ALP	-.6296	-.6183	.2917	.0610	-.7904
	17.FEP	-.5000	-.4619	.3001	.1789	-.5400
	18.REDP	-.4815	-.4728	.2917	.1789	-.5389
	19.CAP	-.0370	-.0364	.2917	.9049	-.2275
3.M2P						
	16.ALP	0.	0.	.2950	.9049	.0723
	17.FEP	-.0435	-.0392	.3035	.9049	-.1111
	18.REDP	-.0769	-.0741	.2950	.9049	-.0964
	19.CAP	.3077	.2965	.2950	.3988	.4338
4.M3P						
	16.ALP	.1429	.1429	.2887	.7195	.1667
	17.FEP	.0400	.0378	.2968	.9049	.0244
	18.REDP	-.0714	-.0714	.2887	.9049	-.0476
	19.CAP	.0714	.0714	.2887	.9049	.1667
5.M3AP						
	16.ALP	0.	0.	.2887	.9049	0.
	17.FEP	-.2800	-.2646	.2968	.5484	-.3416
	18.REDP	-.3571	-.3571	.2887	.2751	-.4524
	19.CAP	-.0714	-.0714	.2887	.9049	-.0714
6.M4P						
	16.ALP	.2857	.2857	.2887	.3988	.4286
	17.FEP	.2800	.2646	.2968	.5484	.2684
	18.REDP	.0714	.0714	.2887	.9049	.0952
	19.CAP	-.2143	-.2143	.2887	.5484	-.2381
7.M5P						
	16.ALP	.2857	.2857	.2887	.3988	.4286
	17.FEP	.2800	.2646	.2968	.5484	.2684
	18.REDP	.0714	.0714	.2887	.9049	.0952
	19.CAP	-.2143	-.2143	.2887	.5484	-.2381
8.M6P						
	16.ALP	.3571	.3571	.2887	.2751	.4762
	17.FEP	.3600	.3402	.2968	.3988	.4148
	18.REDP	.1429	.1429	.2887	.7195	.2619
	19.CAP	-.1429	-.1429	.2887	.7195	-.1429
9.M7P						
	16.ALP	.3571	.3571	.2887	.2751	.4762
	17.FEP	.3600	.3402	.2968	.3988	.4148
	18.REDP	.1429	.1429	.2887	.7195	.2619
	19.CAP	-.1429	-.1429	.2887	.7195	-.1429
10.M8P						
	16.ALP	.2857	.2857	.2887	.3988	.3810
	17.FEP	.2800	.2646	.2968	.5484	.2928
	18.REDP	.0714	.0714	.2887	.9049	.1667
	19.CAP	-.0714	-.0714	.2887	.9049	-.0476
11.M9P						
	16.ALP	0.	0.	.2887	.9049	.0476
	17.FEP	-.2000	-.1890	.2968	.7195	-.2684
	18.REDP	-.2143	-.2143	.2887	.5484	-.2857
	19.CAP	.2143	.2143	.2887	.5484	.3571
12.M10P						
	16.ALP	0.	0.	.2887	.9049	-.0238
	17.FEP	-.1200	-.1134	.2968	.9049	-.1952
	18.REDP	-.2143	-.2143	.2887	.5484	-.3095
	19.CAP	-.0714	-.0714	.2887	.9049	-.0714
14.M11P						
	16.ALP	-.2143	-.2143	.2887	.5484	-.3333
	17.FEP	-.2000	-.1890	.2968	.7195	-.2440
	18.REDP	-.2857	-.2857	.2887	.3988	-.3095
	19.CAP	0.	0.	.2887	.9049	0.
15.M12P						
	16.ALP	.0714	.0714	.2887	.9049	.0952
	17.FEP	-.0400	-.0378	.2968	.9049	-.1220
	18.REDP	-.1429	-.1429	.2887	.7195	-.1667
	19.CAP	.1429	.1429	.2887	.7195	.2143

APPENDIX 4-3 Spearman Rank Correlation Coefficients for the Relationships Among Phosphorus Fractions

N= 8 CORRELATIONS ACROSS ALL 8 SOILS

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
16.ALP						
	17.FEP	.5200	.4914	.2968	.1789	.7319
	18.REDP	.3571	.3571	.2887	.2751	.5952
	19.CAP	-.0714	-.0714	.2887	.9049	.0476
17.FEP						
	18.REDP	.9200	.8693	.2968	.0055	.9515
	19.CAP	.2000	.1890	.2968	.7195	.2196
18.REDP						
	19.CAP	.2857	.2857	.2887	.3988	.4524

N= 5 CORRELATIONS ACROSS PODZOLIC HORIZONS

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
16.ALP						
	17.FEP	-.2000	-.2000	.4082	.8167	0.
	18.REDP	-.4000	-.4000	.4082	.4833	-.4000
	19.CAP	-.8000	-.8000	.4082	.0833	-.9000
17.FEP						
	18.REDP	.8000	.8000	.4082	.0833	.9000
	19.CAP	0.	0.	.4082	.8167	-.1000
18.REDP						
	19.CAP	.2000	.2000	.4082	.8167	.3000

APPENDIX 4-4 Spearman Rank Correlation Coefficients for the Relationship Between Soil Extractable Phosphorus and Foliar Phosphorus for 12 Methods and 3 Soils

N= 11 ALL SPECIES

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
4.M1P	17.FOLIARP	.3091	.3091	.2335	.2190	.4545
5.M2P	17.FOLIARP	.2830	.2778	.2365	.2805	.4338
6.M3P	17.FOLIARP	.3091	.3091	.2335	.2190	.4545
7.M3AP	17.FOLIARP	.3091	.3091	.2335	.2190	.4545
8.M4P	17.FOLIARP	.3818	.3818	.2335	.1216	.5000
9.M5P	17.FOLIARP	.4231	.4114	.2375	.0992	.6055
10.M6P	17.FOLIARP	.4909	.4909	.2335	.0408	.6727
11.M7P	17.FOLIARP	.2727	.2727	.2335	.2835	.4273
12.M8P	17.FOLIARP	.3091	.3091	.2335	.2190	.4545
13.M9P	17.FOLIARP	.2727	.2727	.2335	.2835	.3727
15.M11P	17.FOLIARP	.3455	.3455	.2335	.1652	.4909
16.M12P	17.FOLIARP	.4909	.4909	.2335	.0408	.6182

RANK-ORDER CORRELATION <1> SPECIES:LPINE INITIAL ANALYSIS CORRELATION BY SPECIES

N= 6

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
4.M1P	17.FOLIARP	.5714	.5521	.3608	.2722	.7537
5.M2P	17.FOLIARP	.7333	.7333	.3549	.0556	.8857
6.M3P	17.FOLIARP	.7333	.7333	.3549	.0556	.8857
7.M3AP	17.FOLIARP	.7333	.7333	.3549	.0556	.8857
8.M4P	17.FOLIARP	.2000	.2000	.3549	.7194	.4286
9.M5P	17.FOLIARP	.2857	.2760	.3608	.7194	.4638
10.M6P	17.FOLIARP	.3333	.3333	.3549	.4694	.4857
11.M7P	17.FOLIARP	.2000	.2000	.3549	.7194	.4286
12.M8P	17.FOLIARP	.3333	.3333	.3549	.4694	.4857
13.M9P	17.FOLIARP	.7333	.7333	.3549	.0556	.8857
15.M11P	17.FOLIARP	.4667	.4667	.3549	.2722	.7143
16.M12P	17.FOLIARP	.8667	.8667	.3549	.0167	.9429
18.M6BP	17.FOLIARP	.3333	.3333	.3549	.4694	.4857

Continued...

APPENDIX 4-4, continued

RANK-ORDER CORRELATION <2> SPECIES:WHEM INITIAL ANALYSIS CORRELATION BY SPECIES

N= 6

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
4.M1P	17.FOLIARP	.5714	.5521	.3608	.2722	.6957
5.M2P	17.FOLIARP	.3333	.3333	.3549	.4694	.4286
6.M3P	17.FOLIARP	.3333	.3333	.3549	.4694	.4286
7.M3AP	17.FOLIARP	.3333	.3333	.3549	.4694	.4286
8.M4P	17.FOLIARP	-.2000	-.2000	.3549	.7194	-.2571
9.M5P	17.FOLIARP	-.0667	-.0667	.3549	1.0000	-.0857
10.M6P	17.FOLIARP	-.2000	-.2000	.3549	.7194	-.2571
11.M7P	17.FOLIARP	-.2000	-.2000	.3549	.7194	-.2571
12.M8P	17.FOLIARP	-.0667	-.0667	.3549	1.0000	-.1429
13.M9P	17.FOLIARP	.3333	.3333	.3549	.4694	.4286
15.M11P	17.FOLIARP	.6000	.6000	.3549	.1361	.7143
16.M12P	17.FOLIARP	.3333	.3333	.3549	.4694	.4286
18.M6BP	17.FOLIARP	-.1429	-.1380	.3608	1.0000	-.1739

RANK-ORDER CORRELATION <3> SPECIES:DFIR INITIAL ANALYSIS CORRELATION BY SPECIES

N= 6

VARIABLE	VARIABLE	G-K GAMMA	TAU-B	SE	SIGNIF	SPEARMAN'S RHO
4.M1P	17.FOLIARP	.2857	.2760	.3608	.7194	.3769
5.M2P	17.FOLIARP	.7143	.6901	.3608	.1361	.8117
6.M3P	17.FOLIARP	.7333	.7333	.3549	.0556	.8286
7.M3AP	17.FOLIARP	.7333	.7333	.3549	.0556	.8286
8.M4P	17.FOLIARP	.6000	.6000	.3549	.1361	.7143
9.M5P	17.FOLIARP	.5714	.5521	.3608	.2722	.6377
10.M6P	17.FOLIARP	.3333	.3333	.3549	.4694	.3714
11.M7P	17.FOLIARP	.4667	.4667	.3549	.2722	.6000
12.M8P	17.FOLIARP	.4667	.4667	.3549	.2722	.6000
13.M9P	17.FOLIARP	.7333	.7333	.3549	.0556	.8286
15.M11P	17.FOLIARP	.4667	.4667	.3549	.2722	.6000
16.M12P	17.FOLIARP	.8667	.8667	.3549	.0167	.9429
18.M6BP	17.FOLIARP	.3333	.3333	.3549	.4694	.3714

APPENDIX 4-5 Mann-Whitney U Test of Significance Between Two Bray P_2 - 1 Minute Extractions and Correlation Coefficients for Their Relationship with Foliar Phosphorus.

```
<TWOSAMPLE OPTIONS=PERCENTILE,QUANTILE,DIFFERENCE VAR=M6 STRAT=M6TYPE LEVELS=.9,.95,.99>
TWO-SAMPLE COMPARISON

TEST OF 2.M6                SIGNIF      LOCATION DIFFERENCES
                                        0.9000      0.9500      0.9900
MANN-WHITNEY U=  102.50     .0596  L    3.0000     -2.5000    -17.000
```

CORRELATION MATRIX . INITIAL ANALYSIS CORREALTION (NO STRATA)

N= 11 DF= 9 R0 .0100= .7348 R0 .0500= .6021 R0 .1000= .5214

VARIABLE	4. M1P	5. M2P	6. M3P	7. M3AP	8. M4P	9. M5P	10. M6P	11. M7P	12. M8P	13. M9P	15. M11P	16. M12P
17.FOLIARP	.2668	.3278	.3852	.3738	.4421	.4815	.5051	.4290	.3776	.2725	.2901	.4934
17.FOLIARP	.5725											
	18. M6BP											

CORRELATION MATRIX <1> SPECIES:LPINE . INITIAL ANALYSIS CORRELATION BY SPECIES

N= 4 DF= 2 R0 .0100= .9900 R0 .0500= .9500 R0 .1000= .9000

VARIABLE	4. M1P	5. M2P	6. M3P	7. M3AP	8. M4P	9. M5P	10. M6P	11. M7P	12. M8P	13. M9P	15. M11P	16. M12P
17.FOLIARP	.7621	.8601	.8845	.8210	.9219	.9361	.9407	.9242	.9089	.8430	.8573	.9419
17.FOLIARP	.9717											
	18. M6BP											

CORRELATION MATRIX <2> SPECIES:WHEM INITIAL ANALYSIS CORRELATION BY SPECIES

N= 4 DF= 2 R0 .0100= .9900 R0 .0500= .9500 R0 .1000= .9000

VARIABLE	4. M1P	5. M2P	6. M3P	7. M3AP	8. M4P	9. M5P	10. M6P	11. M7P	12. M8P	13. M9P	15. M11P	16. M12P
17.FOLIARP	.1092	.2270	.2506	.2081	.4797	.5995	.5836	.4755	.4567	.1890	.2689	.5386
17.FOLIARP	.7348											
	18. M6BP											

CORRELATION MATRIX <3> SPECIES:DFIR . INITIAL ANALYSIS CORRELATION BY SPECIES

N= 3 DF= 1 R0 .0100= .9999 R0 .0500= .9969 R0 .1000= .9877

VARIABLE	4. M1P	5. M2P	6. M3P	7. M3AP	8. M4P	9. M5P	10. M6P	11. M7P	12. M8P	13. M9P	15. M11P	16. M12P
17.FOLIARP	.7522	.8526	.9006	.8542	.9766	.9857	.9906	.9481	.9775	.8156	.8840	.9981
17.FOLIARP	.9969											
	18. M6BP											

APPENDIX 4-6 Spearman Rank Correlation Coefficients for the Relationship Between Soil Extractable Phosphorus and Foliar Phosphorus for 3 Candidate Methods and all 8 Soils.

Soils	Species	n	Bray P_1	0.01 N HCl	New-Mehlich
All	All	45	.3413**	.7362***	.7399***
All	Lodgepole pine	14	.8110**	.7850**	.8330***
All	Western hemlock	15	.0447	.7560**	.6595*
All	Douglas-fir	16	.5559*	.7819***	.8961***
All but CA	Lodgepole pine	14	.8110**	.7850**	.8330***
"	Western hemlock	13	.4215	.7283*	.6850*
"	Douglas-fir	14	.8549***	.8130***	.9131***
All but CU, CA	Lodgepole pine	12	.7692**	.7215*	.8322**
"	Western hemlock	12	.4667+	.8055**	.7776**
"	Douglas-fir	12	.8252**	.7231**	.9021***
All but FF	Lodgepole pine	12	.7902**	.7874**	.8182**
"	Western hemlock	13	-.0826	.8332**	.7235*
"	Douglas-fir	14	.4637+	.8108***	.9217***
All but FF, CA	Lodgepole pine	12	.7902**	.7874**	.8182**
"	Western hemlock	11	.3470	.7473*	.7062*
"	Douglas-fir	12	.8322**	.8288**	.9177***
All but FF, AP	Lodgepole pine	10	.8182**	.7927*	.8424**
"	Western hemlock	11	-.0364	.8861**	.7545*
"	Douglas-fir	12	.4336	.8148**	.9263***
All but FF, AP, CA	Lodgepole pine	10	.8182**	.7927*	.8424**
"	Western hemlock	9	.4854	.8394*	.8333*
"	Douglas-fir	10	.8303**	.8493**	.9030***

Continued . . .

Appendix 4-6 continued

Soils	Species	n	Bray P_1	0.01 N HCl	New-Mehlich
All but EL	Lodgepole pine	12	.8601***	.8506***	.8112**
"	Western hemlock	13	.2036	.7425**	.7043*
"	Douglas-fir	14	.5516*	.8419***	.8820***
All but EL, CA	Lodgepole pine	12	.8601***	.8506***	.8112**
"	Western hemlock	11	.7745**	.6802*	.7654**
"	Douglas-fir	12	.9231***	.9074***	.9212***
All but FF, EL, AP	Lodgepole pine	8	.9048**	.8555*	.9048**
"	Western hemlock	9	.0167	.8831**	.7333*
"	Douglas-fir	10	.4061	.8863**	.9573***
All but FF, EL, AP, CA	Lodgepole pine	8	.9048**	.8555*	.9048**
"	Western hemlock	7	.8571*	.7769	.8571*
"	Douglas-fir	8	.9762***	.9698**	.9762***
All but CM	Lodgepole pine	12	.6993*	.7417**	.7832**
"	Western hemlock	13	.1846	.7329**	.6080*
"	Douglas-fir	14	.3495	.8464***	.8842***
All but CM, CA	Lodgepole pine	12	.6993*	.7417**	.7832**
"	Western hemlock	11	.1781	.6737*	.5604
"	Douglas-fir	12	.7902**	.8359**	.9107***

+, *, **, *** significance at 10, 5, 1 and 0.1% levels, respectively.

APPENDIX 4-7 Mann-Whitney U Test of Significance Between Two New-Mehlich Extractions Differing in Extraction Procedure and Correlation Coefficients for Their Relationship with Foliar Phosphorus

```
<TWOSAMPLE OPTIONS=PERCENTILE,QUANTILE,DIFFERENCE VAR=M12 STRAT=M12TYPE LEVELS=.9,.95,.99>
TWO-SAMPLE COMPARISON

TEST OF 2.M12                  SIGNIF      LOCATION DIFFERENCES
                                           @.9000      @.9500      @.9900
MANN-WHITNEY U=  281.50         .1509  L  -14.750     -15.750     -18.750


CORRELATION MATRIX              FIANL ANALYSES CORRELATION

N= 27  DF= 25  R@ .0100= .4869  R@ .0500= .3809  R@ .1000= .3233

    VARIABLE

  8.FOLIARP      .4499      .7117      .8244      .8009

                 4.         5.         6.  1      7.   2
                 M4P        M11P       M12P       M12BP


CORRELATION MATRIX  <1> SPECIES:LPINE          FINAL ANALYSES CORRELATION

N= 8  DF= 6  R@ .0100= .8343  R@ .0500= .7067  R@ .1000= .6215

    VARIABLE

  8.FOLIARP      .8929      .8911      .8599      .8587

                 4.         5.         6.         7.
                 M4P        M11P       M12P       M12BP


CORRELATION MATRIX  <2> SPECIES:WHEM           FINAL ANALYSES CORRELATION

N= 9  DF= 7  R@ .0100= .7977  R@ .0500= .6664  R@ .1000= .5822

    VARIABLE

  8.FOLIARP      .1455      .8936      .8077      .7452

                 4.         5.         6.         7.
                 M4P        M11P       M12P       M12BP


CORRELATION MATRIX  <3> SPECIES:DFIR           FINAL ANALYSES CORRELATION

N= 10  DF= 8  R@ .0100= .7646  R@ .0500= .6319  R@ .1000= .5494

    VARIABLE

  8.FOLIARP      .6055      .6876      .9527      .9525

                 4.         5.         6.         7.
                 M4P        M11P       M12P       M12BP
```

[1] M12P = NEW-MEHLICH WITH RECIPROCAL SHAKING (NORMAL PROCEDURE)

[2] M12BP = NEW-MEHLICH WITH ROTATIONAL SHAKING (MODIFIED PROCEDURE)

Appendix 4-8 Spearman Rank Correlation Coefficients for the Relationship Between Soil Extracted by the Mehlich Method and Foliar Phosphorus for all Treatment Replicates.

Soil	Species	n	rho
All	All	176	.6736***
All but CA	All	162	.7194***
All but FF	All	152	.6812***
All but EL, CA	All	145	.6849***
All	Lodgepole pine	56	.7741***
All	Western hemlock	56	.5687***
All	Douglas-fir	64	.7938***
FF	Lodgepole pine	8	.6747
FF	Western hemlock	8	.8743*
FF	Douglas-fir	8	.6429
AP	Lodgepole pine	8	.4762
AP	Western hemlock	8	.3234
AP	Douglas-fir	8	.9701*
MI	Lodgepole pine	8	.8729+
MI	Western hemlock	8	-.3751
MI	Douglas-fir	8	.7260
CM	Lodgepole pine	8	.3516
CM	Western hemlock	6	.5218
CM	Douglas-fir	8	.2771
EL	Lodgepole pine	8	.6205
EL	Western hemlock	15	.6925*
EL	Douglas-fir	8	.7306
TS	Lodgepole pine	8	.0549
TS	Western hemlock	4	.2000
TS	Douglas-fir	8	.4880
CU	Lodgepole pine	8	.6747
CU	Western hemlock (too few cases for analysis)		
CU	Douglas-fir	8	.1437
CA	Lodgepole pine	0	N/A
CA	Western hemlock	6	.6088
CA	Douglas-fir	8	.4157

+,*,**,***significant at the 10, 5, 1 and 0.1% levels respectively.

APPENDIX 4-9 Analysis of Variance for Foliar Phosphorus on all Treatment Replicates

ANALYSIS OF VARIANCE FOR FOLIAR P (L=SOIL&BLOCK T=TREE SPECIES P=P LEVEL: L IS RANDOM, T & P ARE FIXED FACTORS)

Analysis for FOLP

Analysis of variance table

Source	Sum of squares	DF	Mean square	F-ratio	Probability	Test term
L	0.62202	7.	0.88860E-01	70.906	0.00000	RESIDUAL
T	0.56469E-01	2.	0.28234E-01	2.8223	0.09595	L*T
P	0.18198	1.	0.18198	10.024	0.01580	L*P
L*T	0.13005	13.	0.10004E-01	7.9827	0.00000	RESIDUAL
T*P	0.16635E-01	2.	0.83174E-02	2.5000	0.12371	L*T*P
L*P	0.12709	7.	0.18155E-01	14.487	0.00000	RESIDUAL
L*T*P	0.39924E-01	12.	0.33270E-02	2.6547	0.00323	RESIDUAL
Residual	0.16417	131.	0.12532E-02			
Total	1.3532	175.				

APPENDIX 4-10 Analysis of Covariance for Foliar Phosphorus with New-Mehlich Phosphorus Values as the Covariate, on all Treatment Replicates

ANALYSIS OF COVARIANCE FOR MEHLICHP (L=SOIL&BLOCK T=TREE SPECIES P=P LEVEL: L IS RANDOM, T & P ARE FIXED FACTORS)

Analysis for FOLP

Analysis of variance table

Source	Sum of squares	DF	Mean square	F-ratio	Probability	Test term
L	0.37603	7.	0.53719E-01	42.668	0.00000	RESIDUAL
T	0.35726E-01	2.	0.17863E-01	1.9247	0.18528	L*T
P	0.47609E-01	1.	0.47609E-01	4.6960	0.06691	L*P
MEHLICHP	0.50344E-03	1.	0.50344E-03	0.39987	0.52826	RESIDUAL
L*T	0.12065	13.	0.92810E-02	7.3718	0.00000	RESIDUAL
T*P	0.94692E-02	2.	0.47346E-02	1.6697	0.22921	L*T*P
L*P	0.70967E-01	7.	0.10138E-01	8.0527	0.00000	RESIDUAL
L*T*P	0.34028E-01	12.	0.28356E-02	2.2523	0.01272	RESIDUAL
Residual	0.16367	130.	0.12590E-02			
Total	1.3532	175.				

APPENDIX 5

This study has provided useful information on soil testing for P in British Columbia forest soils. However, a few considerations regarding experimental design and procedures may be useful for similar studies in the future. This experiment involved a large factorial design (8 soils x 3 species x 2 P levels x 4 replications x 12 P methods) which required simplification during analysis. This design provided some insight into the various soils and methods, but perhaps a different design might be preferable, considering that some of the soils were similar, and that an additional P level might have allowed better evaluation of methods. Growth of some tree species on some soils in the greenouse was poor; perhaps more fertilization (without P) would have been useful.

In order to be consistent, a number of laboratory procedures (Appendix 1) were kept the same throughout. In another study on British Columbia forest soils, the use of swirling in some methods might best be replaced by reciprocal shaking to reduce variability caused by hydrophobic samples. Filter paper size should be matched to solution volumes and faster paper would be preferred for some methods. It is recommended that future soil P methods employ the ascorbic acid method for P determination in extract solutions, following the method of John (1970) rather than Watanabe and Olsen (1965).