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Relation...to...the...Physical and  
Chemical...characteristics of Phosphorus of  
Some Alberta Soils.  
UNIVERSITY...Alberta.....  
DEGREE.....Ph.D.....YEAR GRANTED.....1970.....

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THE UNIVERSITY OF ALBERTA  
AVAILABLE PHOSPHORUS IN RELATION TO  
THE PHYSICAL AND CHEMICAL  
CHARACTERISTICS OF PHOSPHORUS OF  
SOME ALBERTA SOILS

by



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B.Sc.(Agric.), M.Sc.(Agric.)

A THESIS  
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

SPRING, 1970

UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,  
and recommend to the Faculty of Graduate Studies for  
acceptance, a thesis entitled "Available Phosphorus  
in Relation to the Physical and Chemical Characteristics  
of Phosphorus of Some Alberta Soils", submitted by  
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## ABSTRACT

Nine soils of Alberta, with P applied to some, were investigated to assess the available phosphorus status. The experiments involved the growth of the plants, chemical extraction of desired phosphorus forms,  $^{32}\text{P}$  labelling, use of equilibrium techniques and the development of suitable analytical methods for inorganic phosphorus and  $^{32}\text{P}$  determinations.

The new method for inorganic phosphorus determination has increased the sensitivity of the usual ascorbic acid method by a factor of approximately 4. The method for  $^{32}\text{P}$  determination is simple and allows the measurement of  $^{32}\text{P}$  in undigested plant samples.

The results of the experiments on the movement of P to roots clearly showed that P movement by mass flow is the significant process of P transport to roots in soils treated with high rates of P. Diffusion is found to be the major process of P movement to roots in P untreated soils. Root interception is found to be least important in P movement to roots.

The correlation coefficient data from two plant growth room experiments indicated that the soil solution P is very closely related to P supply to the plants. However, since all the variation in the available phosphorus ("A" values) could not be explained by the intensity factor alone (soil solution P,  $I_e$ ), the quantity factor (surface P,  $E_e$ ) was included in the study. A linear multiple regression equation and correlation coefficient relating the "A" value to the intensity and quantity factors were "A" value =  $2.11 + 15.90 \log_{10} I_e + 1.51 E_e$  and 0.972 respectively.

Based on the results of  $^{32}\text{P}$  exchange experiments and other data on the soils, it was concluded that the rates of exchange of soil phosphorus after the 1 hour period are too slow to have any great influence on the immediate supply of phosphorus to the plants.

The comparisons of Ee, Olsen P, Miller and Axley P and Al-P with "A" value indicated that these values are very highly correlated with "A" value and also among themselves. It appears that these chemical extractions remove the exchangeable P and some additional P from the soils.

The data on phosphated soils showed that none of the intensity and quantity factors are very well related to the "A" values. The results indicated that the solution P (Ie) and quantity (Ee, Olsen P, Miller and Axley P) values were increased 24 to 420 and 4 to 20 times the original values respectively by the P treatments.

## ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. J.A. Robertson, Associate Professor of Soils, Department of Soil Science, under whose inspiration this study was undertaken. Deep gratitude is extended to him for the kind guidance, encouragement and assistance in all phases of this study. His help in the preparation of the manuscript is gratefully acknowledged.

Thanks are also extended to the following:

Dr. G.R. Webster, Professor of Soils, for his kind encouragement, constructive criticisms and advice during various stages of the study;

Professors Dr. H.B. Dunford of Chemistry Department, Dr. M. Nyborg of Soil Science Department, and Dr. A.A. Noujaim of Pharmacy Department for their help and also for serving on the committee;

Dr. S. Pawluk, Acting Head of the Department of Soil Science for making staff and facilities available for this study;

Dr. J.A. Toogood, Head of the Soil Science Department,

Dr. F.D. Cook, Professor of Soils and Dr. C.F. Bentley, Professor of soils for their encouragement and help on several occasions during the course of this study;

Messrs. D. Vandrinsky and C. Panter of Soil Science Department and A. Schwarzer of Alberta Research Council for their assistance in carrying out some laboratory and statistical analyses;

Fellow graduate students and friends in the department of Soil Science for their cooperation;

Mrs. V. McGregor for typing the manuscript;

The Canadian Commonwealth Scholarship and Fellowship Committee  
for awarding the Scholarship for this study; and

his wife and parents for their sacrifice and encouragement.

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## CHAPTER I

### INTRODUCTION

Phosphorus occupies an important position in the study of soil fertility. Phosphate deficiency is a factor limiting crop production on a world-wide basis. The causes of low availability of native and applied phosphorus in soils are numerous. The problem is complicated by the lack of suitable methods to isolate and identify the numerous inorganic and organic phosphorus compounds often present in soils. The presence in many soils of negatively charged clays, which may range from an amorphous to crystalline state, make it even more difficult to study the phosphate compounds which may be associated with them. Phosphate compounds may also exist as individual crystals and/or as amorphous particles of varying sizes. It is not surprising then that the field of soil-phosphorus fertility is considered as rather interesting and challenging.

An extensive amount of work has been done on the subject. Most of it deals with the study of the particular phosphate compounds or forms likely to be present in the soils. Generally, the total phosphorus content of a soil is not a good indication of the capacity of soil to supply phosphorus to plants. The availability to plants of soil phosphorus as a whole has not received enough attention and many factors that affect the availability of soil and applied phosphorus are not well understood. To understand these factors a different approach to study the soil phosphorus status is very necessary.

Any system can be defined by intensive and extensive variables of the state. Application of this principle to soil fertility calls for the characterization of both variables. In addition, the study of the rate factors involved in the transport of phosphorus to roots is very important.

With the foregoing approach in mind, a research project was formulated to study:

- the rate factor covering the transport of phosphorus to roots growing in soils.
- the intensity factor reflecting the ease or difficulty of withdrawal of soil phosphorus by roots.
- the quantity factor indicating the amount of available phosphorus in the soils.

The research is described under the following two topics:

- Movement of P to roots growing in soils.
- Intensity and Quantity factors of soil and applied phosphorus.

Each of the above topics is presented as a separate chapter of the thesis, followed by a chapter summarizing the whole investigation. Some of the research work reported here has been published elsewhere. Copies of the publications are presented in the Appendices (D, E, F).

CHAPTER II  
MOVEMENT OF P TO ROOTS  
GROWING IN SOILS

Review of Literature:

The study of ion transport to roots is rather new. It is only very recently that the importance of quantifying the processes at work around the roots has been emphasized. To obtain a realistic estimate of availability of plant nutrients in soils due consideration should be given to the movement of ions to the roots.

In a soil-plant system, ions must move to the roots before they can be absorbed. Barber and coworkers (Barber, 1962; Barber et al., 1963; Oliver and Barber, 1966a; 1966b; Halstead et al., 1968) have shown that three processes involved in the movement of ions to roots are mass flow, diffusion, and root interception. They studied the relative importance of the three processes in supplying Ca, Mg, K, Na, Mn, Fe, B, Cu, Zn, Al, Sr, and Mo to roots growing in soil. They determined the contribution of mass flow by multiplying the amount of water absorbed by the concentration of the ion in this water as measured by analyzing the saturation extract. The contribution of root interception was calculated by assigning all of the exchangeable and soluble ions to the soil pore space. The concentration of ion per cubic centimeter of pore space was multiplied by the volume of the roots to obtain the contribution of root interception for each of the ions measured. Because of the uncertainty involved in the root interception calculation, Halstead



et al. (1968) determined the contribution of root interception by calculating the available ions in a volume of soil equal to the root volume. The contribution of diffusion was always determined by subtracting the contribution of root interception and mass flow from the total ions taken up. Nye (1968) remarked that the definition of the mass flow component as (amount transpired) X (unchanged initial solution concentration) is arbitrary and raised the question, why choose the initial concentration rather than the actual concentration at the root surface?

The research work on the movement of phosphorus to roots is rather limited and contradictory. Some workers (Barber et al., 1963; Olsen et al., 1962; Lewis et al., 1967; Nye, 1968) favoured ion diffusion as the major mechanism for movement of phosphorus to roots. In contrast, Shapiro et al. (1960) thought that the most probable mechanism for the movement of phosphorus to roots is mass flow. They contended that the diffusion coefficients for phosphorus in solution or on the particle as compared to diffusivity of water in the soil are too small for diffusion to have any appreciable part in the movement of P to root surface. Depending on the initial moisture content, the soil water diffusivity is  $5 \times 10^2$  to  $5 \times 10^5$  times greater than the apparent diffusion coefficient of phosphate ion in soil. However, some workers (Bouldin, 1961; Fried, 1967) seemed to take intermediate position. Fried (1967) suggested that the P concentration of soil solution would have to be 20 ppm or greater if all of the P moved to the roots by mass flow. Bouldin (1961), however, speculated that soil solution P needsto be

greater than 2 ppm if all of the P moved to the roots by mass flow.

It is obvious from the above discussion that the relative importance of mass flow and diffusion in phosphorus movement to roots can not be categorically stated. It also seems that the definition of root interception is based on many assumptions and needs further improvements. Therefore, this project was conducted with following objectives:

1. To determine the role of mass flow, root interception and diffusion in phosphorus movement to roots.
2. To make improvements in the procedures used for calculating the contribution of mass flow and root interception in phosphorus movement to roots.
3. To find out the effect of adding phosphorus to soils on the contribution of mass flow and diffusion of phosphorus to the roots.
4. To determine the importance of soil solution phosphorus concentration in mass flow, diffusion and root interception.

#### Materials and Methods:

The Ap of nine soils were collected to the depth of 0-15 cm in September, 1967. The legal locations of the samples are given in Appendix A. The soil material was passed through a screen (diameter of the openings - 0.6 cm) in the field. The soil clods were gently crushed and the stones and crop residues were discarded. The soil was then thoroughly mixed using a large batch mixer. Portions of four soils (Calcareous Dark Brown, Carbonated Dark Brown, Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake)) received treatments of 100 and 300 ppm of phosphorus before storage at 5° C and 75% available moisture. To apply phosphorus, the soil was spread evenly and thinly on a plastic covered bench top and  $\text{KH}_2\text{PO}_4$  was applied in solution form by spraying slowly and uniformly. The soil material was thoroughly mixed during spraying and stored in plastic bags for sufficient time (>6 months) to get "an equilibrium" between soil and applied phosphorus. After this equilibration time, the soils were removed from storage room as and when necessary. For growth room experiments, the stored moist soils were used as they came from the bags while for laboratory determinations, portions of the stored soils were air dried and crushed to pass through a 2 millimeter sieve.

Particle size analysis was done on all soil samples in duplicate by the pipette method as described by Toogood and Peters (1953). The percentages of sand, silt and clay were calculated on the basis of the oven dry weight free of organic matter, calcium carbonate and soluble salts. The methods as described by the U.S.

Salinity Laboratory Staff (Handbook 60, 1954) were used to determine the field capacity (1/3 atm) and the wilting point (15 atm).

pH measurements were made using a Beckman pH meter equipped with glass and calomel electrodes in water and 0.01 M  $\text{CaCl}_2$  solution using a soil to liquid ratio of 1:1 in both cases. A Smolite Calci-meter was used to determine the calcium carbonate equivalent. This method is based on the measurement of the increase in volume of a closed system due to release of carbon dioxide when acid is added to the soil sample. Total carbon was determined by using the Leco carbon analyzer (model 577-100). Organic carbon was estimated by difference between the total and inorganic carbon (as determined in the carbonate determination) contents. For determining free Al and Fe, one gram of soil was extracted with 40 ml of acid ammonium oxalate solution of pH 3.0. Al and Fe in the extracts were determined by aluminon and o-phenanthroline methods respectively. Total phosphorus was determined by the  $\text{HCl-HNO}_3\text{-HF}$  wet digestion method as outlined by Alexander (1968). Soil phosphorus was extracted by the Miller and Axley method ( $0.03 \text{ N NH}_4\text{F} + 0.03 \text{ N H}_2\text{SO}_4$ ) as outlined by Robertson (1962) and also by the Olsen method (1954). Phosphorus in the extracts was determined by the ascorbic acid reduced molybdophosphoric blue color method of Watanabe and Olsen (1965).

Stored moist soils were used for the determination of phosphorus concentration in soil solution at field capacity. This determination was done by extracting with 0.01 M  $\text{CaCl}_2$  solution using four soil to solution ratios (1:1, 1:1.25, 1:2.5 and 1:5-oven dry basis). Phosphorus in the extract was determined by the ascorbic

acid method of Watanabe and Olsen (1965). To determine the extremely low phosphorus concentrations found in some extracts, the modified ascorbic acid method (Omanwar and Robertson, 1969) was used. The method is described in the Appendix E. Phosphorus concentration of the extracts (ppm) was plotted against the grams of soil in 100 ml of solution. A straight line was then drawn and extrapolated to the moisture content at 1/3 atm to obtain an estimate of the soil solution P concentration at field capacity. This method is similar to one proposed by Aslyng (1964) except that 4 soil to solution ratios and a different plotting technique have been used. This method, hereafter, will be called the modified Aslyng's procedure.

Eight months after the collection of soils, a plant growth experiment was conducted in a growth room. Three pots were filled (2000 g oven dry soil) with each of the soils used in this experiment (Table 1). Conquest barley was seeded and after emergence, thinned to six plants per pot in a randomized block design. Fifty ppm of N and S were applied to all the pots and fifty grams of perlite were placed over the pots to reduce evaporation losses. Soil moisture was controlled by weighing and watering the pots to 1/3 atm. A soil temperature of about 15° C was maintained during the growth period and artificial light was supplied daily for 16 hours. To estimate the evaporation losses, pots without barley plants were used. To estimate seed contribution of phosphorus, barley was grown in pots containing only perlite. Three weeks after emergence, the plants were harvested. The roots were separated from the soil and the root volume was measured with a pycnometer. Fresh

Table 1 Soils for Investigation

Order	Great group	Subgroup	Series	P Treat- ment ppm	Soils for investigations reported in Chapter	
					2	3
Chernozemic	Brown	Orthic	Maleb	0	x	x
Chernozemic	Dark Brown	Calcareous	--	0	x	x
Chernozemic	Dark Brown	Calcareous	--	100	-	x
Chernozemic	Dark Brown	Calcareous	--	300	x	x
Chernozemic	Dark Brown	Carbonated	--	0	x	x
Chernozemic	Dark Brown	Carbonated	--	100	-	x
Chernozemic	Dark Brown	Carbonated	--	300	x	x
Chernozemic	Black	Orthic	Peace Hills	0	-	x
Chernozemic	Black	Eluviated	Angus Ridge	0	x	x
Chernozemic	Black	Eluviated	Angus Ridge	100	-	x
Chernozemic	Black	Eluviated	Angus Ridge	300	x	x
Chernozemic	Black	Solodic	--	0	x	x
Luvisolic	Gray Wooded	Orthic	Cooking Lake	0	x	x
Luvisolic	Gray Wooded	Orthic	Cooking Lake	100	-	x
Luvisolic	Gray Wooded	Orthic	Cooking Lake	300	x	x
Luvisolic	Gray Wooded	Orthic	Glory	0	x	x
Luvisolic	Gray Wooded	Orthic	Breton	0	-	x

root weights were determined after blotting with paper towels. The tops and roots were dried at 70° C, weighed, and ground to pass through a 40 mesh sieve. The plant samples were digested with  $\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$  (Goss, 1962) and phosphorus was determined by the ascorbic acid method (Watanabe and Olsen, 1965).

Phosphorus which moved to the roots by mass flow was calculated using a modification of the method of Oliver and Barber (1966a; 1966b). They estimated the soil solution concentration by using a saturation extract and used this concentration for calculating the contribution of mass flow. We thought it more correct to obtain the phosphorus concentration at moisture content (1/3 atm), the upper limit of watering in the plant growth room experiment. The procedure of estimating soil solution phosphorus concentration at field capacity is described above (modified Aslyng's procedure).

To estimate the contribution of root interception in phosphorus supply to the roots, soil solution concentration was multiplied by the total root volume. The basis for the use of this method is the belief of the author that the maximum contribution of root interception to the delivery of ions to the roots is the weight of the ion contained in a volume of solution which the roots displace along their path of development. This approach contrasts with that of Oliver and Barber (1966a; 1966b) who included sorbed ions along the root path in the contribution by root interception.

To estimate the contribution of diffusion of phosphorus to roots, the method (Oliver and Barber, 1966a) of subtracting the

mass flow and root interception contributions from the total uptake of nutrient was followed. The uptake was first corrected by deducting P derived from the seeds as estimated from the plants growing in perlite.

#### Results and Discussion

The soils used in this study had a wide range of Miller and Axley P (6-173 ppm), total P (355-925), solution P (0.02 - 44.65 ppm),  $\text{CaCO}_3$  equivalent (0.08 - 7.12 percent), organic C (1.19 - 5.69 percent) and pH (5.2 - 7.8) (Table 2). Thus the soils provided a wide spectrum of characteristics to study the movement of phosphorus in soils.

The yield data (Table 3) showed that generally the higher the dry matter of the tops, the higher is the dry matter of the roots and the volume of the fresh roots. It can also be noted that the yields on 2 untreated soils (Solodic Black and Orthic Gray Wooded - Glory) approximated that of 4 treated soils. The treatment of 300 ppm of P on four soils resulted in a distinct yield increase of both tops and roots. The total volume occupied by the roots in a pot was very small and varied from 8 to 26 cc. The transpiration ratios ranged from 251 to 400 with an average deviation of 13 percent.

#### Mass Flow

The results (Table 4) showed that the contribution of mass flow to the transport of P to roots is 4 percent or less for untreated soils. For treated soils the range is from 74 to 192 percent.



Table 2 Some Characteristics of Soils Used in this Study (oven dry basis)

Order	Great Group	Subgroup	Series	Texture	P treatment	pH	Organic C %	CaCO <sub>3</sub> equivalent %	Total P ppm	Extractable P (Miller and Axley) ppm	Solution P (modified Aslyng's procedure) ppm
Chernozemic	Brown	Orthic	Maleb	L	untreated	7.1	1.19	0.14	435	12	0.16
Chernozemic	Dark Brown Calcareous		--	L	untreated 300 ppm	7.8 7.5	2.44 --	7.12 --	615 --	9 147	0.09 17.11
Chernozemic	Dark Brown Carbonated		--	SCL	untreated 300 ppm	7.8 7.0	1.36 --	3.03 --	556 --	6 169	0.02 28.09
Chernozemic	Black	Eluviated	Angus Ridge	L	untreated 300 ppm	6.3 6.0	5.69 --	0.12 --	925 --	12 169	0.07 44.65
Chernozemic	Black	Solodic	--	L	untreated	5.2	3.64	0.08	864	62	0.31
Luviosolic	Gray Wooded	Orthic	Cooking Lake	L	untreated 300 ppm	5.8 5.6	1.44 --	0.09 --	355 --	8 173	0.04 35.99
Luviosolic	Gray Wooded	Orthic	Glory	SIL	untreated	6.5	2.23	0.11	880	50	0.19

Table 3 The Dry Matter of Tops and Roots, Volume of Fresh Roots and Transpiration Ratios in the Growth Room Experiment

Soils	Phosphorus Treatment	Dry matter, g/pot Tops	Dry matter, g/pot Roots	Volume of fresh roots cc/pot	Transpiration Ratio g H <sub>2</sub> O/g tops
Orthic Brown (Maleb)	Untreated	1.65	1.59	12	341
Calcareous Dark Brown	Untreated 300 ppm	1.46 3.55	1.45 2.22	12 18	292 354
Carbonated Dark Brown	Untreated 300 ppm	0.75 3.05	0.78 2.89	8 26	310 326
Eluviated Black (Angus Ridge)	Untreated 300 ppm	1.38 2.73	1.23 2.24	11 19	277 453
Solodic Black	Untreated	3.04	2.15	22	400
Orthic Gray Wooded (Cooking Lake)	Untreated 300 ppm	1.44 3.47	2.11 3.00	17 24	251 313
Orthic Gray Wooded (Glory)	Untreated	3.38	1.85	19	367

Table 4 The Uptake of P by Tops and Roots and Estimation of the Contribution of Mass Flow, Root Interception and Diffusion to P Uptake by Conquest Barley Grown on Seven Untreated and Four Treated Soils

Soils	Phosphorus	Uptake of P mg/pot	Mass flow of P		Root interception of P		Diffusion of P	
			mg/pot	% of total P uptake	mg/pot	% of total P uptake	mg/pot	% of total P uptake
Orthic Brown (Maleb)	Untreated	3.19	0.09	3	<0.01	<<1	3.10	97
Calcareous Dark Brown	Untreated 300 ppm	3.60 29.19	<0.04 21.47	1 74	<0.01 0.30	<<1 1	3.56 7.42	99 25
Carbonated Dark Brown	Untreated 300 ppm	0.10 32.57	0.01 27.86	4 86	<0.01 0.73	<<1 2	0.01 3.98	96 12
Eluviated Black (Angus Ridge)	Untreated 300 ppm	3.66 28.67	0.03 55.14	1 192	<0.01 0.83	<<1 3	3.63 --	99 --
Solodic Black	Untreated	13.07	0.40	3	<0.01	<<1	12.66	97
Orthic Gray Wooded (Cooking Lake)	Untreated 300 ppm	4.19 38.88	0.02 39.12	<1 101	<0.01 0.95	<<1 2	4.17 --	100 --
Orthic Gray Wooded (Glory)	Untreated	14.62	0.23	2	<0.01	<<1	14.39	98

More than 100 percent contribution implies the accumulation of P at the root surface since the supply of P by mass flow alone was greater than the total uptake. Under such conditions the concentration gradient is away from the surface of the roots. No diffusion of P to roots can occur but back diffusion of P can be expected. In contrast to treated soils, the untreated soils, no matter whether high or low in available P, could not supply more than 4 percent of P to roots by mass flow movement. The distinct increase in the mass flow contribution in the treated soils clearly showed the greater importance of mass flow of P in soils on which high doses of phosphatic fertilizers are broadcast. Further, it is very likely that mass flow of P to roots may be the major process of P movement in the case of band placement of phosphatic fertilizers where a high concentration of P is expected.

The results (Calcareous Dark Brown treated with 300 ppm; Table 2 and 4) suggested that mass flow is the major process supplying P to the roots when the soil solution P concentration is about 17 ppm or more. However, in the case of soils naturally high in available phosphorus (Solodic Black and Orthic Gray Wooded - Glory), where low rates of phosphatic fertilizers are usually applied, the mass flow of P to the roots seems to be relatively unimportant.

#### Root Interception

The contribution of root interception was no greater than 3 percent (Table 4) and in the case of the untreated soils it was much less than one percent. Thus root interception is not an important process in P transport. This conclusion is perhaps

not surprising in view of the definition of root interception used in this investigation. The author is of the opinion that the maximum contribution of root interception can only be the quantity of ions in the volume of soil solution equal to the fresh root volume. The basis for this opinion is that the roots grow in the soil by displacing part of the soil solid, soil solution and soil air. If it is assumed (as done in this investigation) that the displaced soil solution is equal to the fresh root volume and that all of this solution is absorbed by the roots, it follows that the value so obtained should represent the maximum possible contribution of root interception. This approach is in contrast with Barber's group (Barber et al. 1963; Oliver and Barber, 1966a; 1966b; Halstead et al. 1968) who included sorbed ions in the root interception contribution. It is author's thinking that such inclusion of sorbed ions into root interception is not correct since any ions comprising part of the solid phase, or sorbed into it, must pass into solution before moving by mass flow and/or diffusion toward the absorption sites of the roots. I agree with Low (1962) in doubting that the root absorption sites (Hagen et al., 1957) approach the solid phase closely enough to permit direct contact exchange.

#### Apparent Diffusion

The results (Table 4) indicated that the apparent diffusion of P to the roots was the major process of P movement in soils receiving no P treatment. It is interesting to note that even in soils (Solodic Black and Orthic Gray Wooded - Glory - Table 2 and 3) which gave yields equivalent to that of P treated soils,

the contribution of diffusion to P transport was more than 96 percent.

Since the contribution of diffusion was calculated by difference (total uptake minus mass flow and root interception), the errors in estimating mass flow and root interception affect to a great extent the amount of P calculated as diffusing to roots. However, there are many problems in estimating directly the amounts of P diffusing to the roots. Fried (1967) reported that the published values of the P diffusion coefficient varied by a factor of  $10^7$ . Determination of the effective absorbing surface area of roots and root hairs growing in soils, the magnitude of the concentration gradient and the distance over which the concentration gradient exists are some of the parameters which are difficult to measure with any great degree of accuracy. Since the maximum mass flow and root interception contributions can be estimated more precisely, the indirect estimation of P diffusion appears satisfactory.

The results of the present experiment for P untreated soils generally agreed with the observations of Barber (1963), Lewis et al. (1967) and Olsen et al. (1962) and disagreed with those of Shapiro et al. (1960). The results of the P treated soils are not comparable since work of this type has not been reported in the literature.

#### P Concentration and Movement of P

Since the soil solution P concentration is a component of mass flow, root interception and diffusion, one would expect

it to be an important factor in the delivery of P to the roots no matter which process is involved. An equation of the following type is helpful in understanding the role of soil solution P concentration in P movement to roots.

$$\begin{array}{l} \text{Total.} \quad (\text{contribution}) \quad (\text{contribution}) \quad (\text{contribution}) \\ P = ( \quad \text{of} \quad ) + ( \quad \text{of root} \quad ) + ( \quad \text{of} \quad ) \dots\dots (1) \\ \text{uptake} \quad ( \text{mass flow} \quad ) \quad ( \text{interception} ) \quad ( \text{diffusion} \quad ) \end{array}$$

If the values used for the calculation of the contribution of mass flow, root interception and diffusion are inserted into equation 1, it takes the form:

$$\text{Total P uptake} = (cV_w) + (cV_r) + \left( DA \frac{dc}{dx} \right) \times T \dots\dots\dots (2)$$

Where  $c$  = Soil solution P concentration.

$V_w$  = Volume of water transpired

$V_r$  = Volume of the fresh roots

$D$  = Diffusion coefficient of P

$A$  = Area of diffusion

$\frac{dc}{dx}$  = Concentration gradient

$T$  = Growth period in seconds

The last term in equation 2 is Fick's first law of diffusion which is used here for simplicity of discussion.

It is obvious from the equations that the higher the soil solution P concentration, the higher is the contribution of mass flow, root interception and diffusion. Application of this theoretical approach to the experimental results brings out some interesting points. When the soil solution P concentration was

correlated with the total P uptake, a correlation of 0.82 ( $P = 0.05$ ) was obtained. Using the dry matter yield instead of total P uptake, a correlation (Figure 1) of 0.86 ( $P = 0.02$ ) was obtained between yield and the soil solution P concentration. These experimental findings suggested that about 67 percent of the variation in the P uptake can be explained by soil solution P concentration alone. This relationship between P uptake and soil solution P concentration seems to be less than what may be expected from the equation 2.

However, it may be noted that the soil solution P concentration would change during the plant growth and also that the soils may differ in their abilities to supply P to the solution around the roots. Furthermore, the variations in evapotranspiration; "rhizosphere effect" which may alter the soil solution P concentration and/or nutrient uptake; and thermal gradients which may affect the diffusion and water movement may also influence the relationship between P uptake and soil solution P concentration. Nevertheless, the correlation of 0.82 between P uptake and soil solution P concentration does indicate the importance of soil solution P concentration in supplying P to roots.

#### Conclusions

(1) Mass flow of P to the roots is the most significant process in the transport of P in soils treated with high doses of P and it is likely to be an important process in soils where phosphatic fertilizers are band placed.



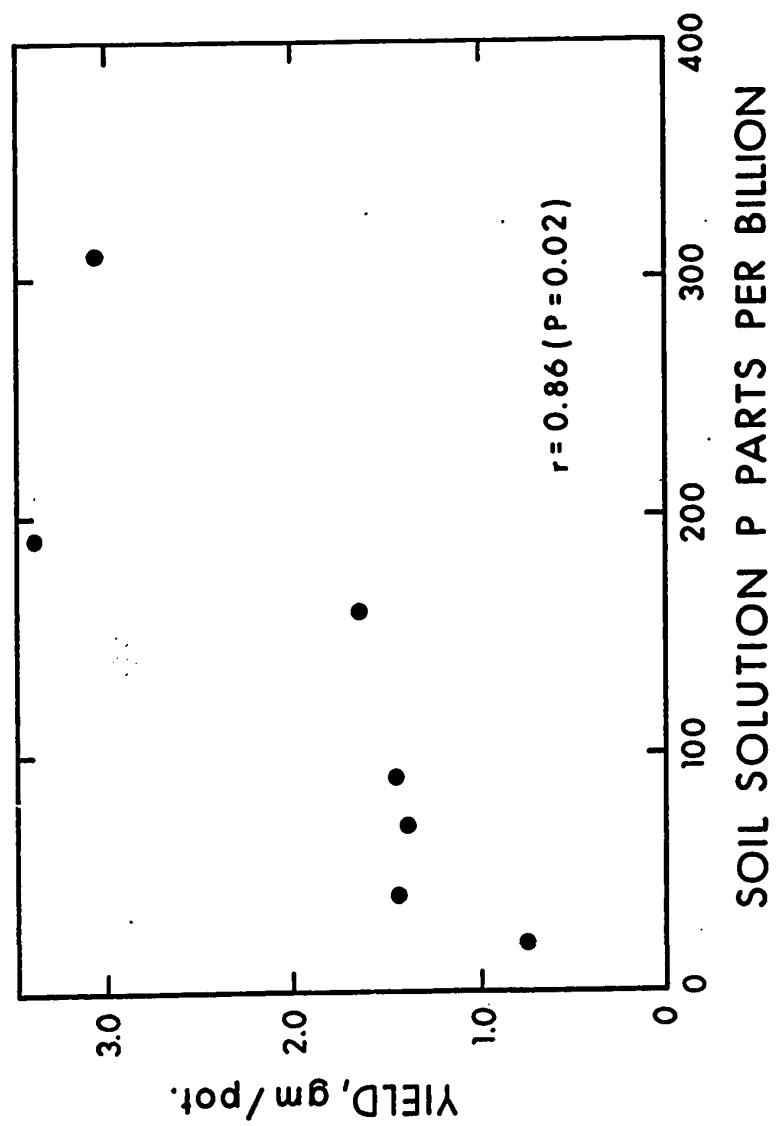


Figure 1 The Relationship between Barley Yields and Soil Solution P

(2) Diffusion of P to the roots is found to be a major process of P transport in untreated soils.

(3) Root interception of P is not important in the overall P transport process.

(4) Since diffusion of P appeared to be the major process supplying P to the roots in untreated soils, a study of P diffusion particularly on P deficient soils is worth considering.

(5) Since the soil solution P concentration affects the amounts of P moving to roots by mass flow, diffusion and root interception, the importance of determining P in the soil solution is emphasized.

CHAPTER III  
INTENSITY AND QUANTITY FACTORS  
OF SOIL AND APPLIED PHOSPHORUS

Review of Literature

In the early stages of agricultural development the general characteristics of different soil types can give valuable information about phosphorus requirements. Intensified crop production, differential effects of cropping and fertilizer applications, and existing natural soil heterogeneity progressively make it very difficult to predict the capacity of soil to supply phosphorus to plants. Recent trends in soil chemistry and fertility increasingly give consideration to more than one factor that may be of value for understanding better the capacity of soil to supply phosphorus to plants. The intensity and quantity factors, in addition to the rate factors discussed in the previous Chapter are of special importance in studying the complex system of soil in relation to plant growth. However the intensity and quantity factors are concepts which are very difficult to define. In the present text, the intensity term is used to indicate the properties of the soil phosphorus that affect the ease or difficulty of phosphorus withdrawal by plants. The quantity factor refers to the total amount of nutrient reserve in the soil that is available to plants. These subjects are reviewed under the following captions.

Intensity factor

Quantity factor

"A" value technique

## Conclusions

### Intensity Factor .

The use of the intensity concept is a fairly recent development in the study of soil phosphorus. Although some early work on solution phosphorus was done by Parker (1927b) and Teakley (1928), Schofield (1955) placed emphasis on the intensity factor. He suggested that availability of soil phosphate is mainly determined by the appropriate chemical potential. He proposed the phosphate potential, defined as  $\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa}$ , to describe soil phosphorus availability and claimed that it is not the amount of available phosphorus in a soil that primarily controls the uptake of phosphate by plants but the work needed to withdraw it from the pool. Following Schofield, his students (Aslyng 1964, Beckett 1964) developed further the concept of phosphate potential. The work is mostly concentrated on the measurement of phosphate potential (Aslyng, 1964; Gough and Beaton, 1963; Beckett and White 1964; Fordham, 1963; Larsen and Court, 1960; Ramamoorthy and Subramaniam, 1960; White and Beckett, 1964). Effects of soil: solution ratio (White, 1966; Larsen and Court, 1960; Larsen and Widdowson, 1964; Aslyng, 1964), temperature (Aslyng, 1964; Beckett and White, 1964), duration of shaking (Fordham, 1963; Beckett and White, 1964; White and Beckett, 1964) and microbial changes (White, 1964) on the phosphate potential are some of the variables encountered in the phosphate potential work. According to the author's thinking, these difficulties are

not serious enough to discard the idea of measuring phosphate potential. More serious objections to the phosphate potential concept were raised by Fried (1967) and Wild (1964). Fried argued that the solid soil-phosphate phase is definitely not monocalcium phosphate and that there is no particular indication that phosphate is taken up by the plant as monocalcium phosphate. On the basis of this argument he claimed that it is very difficult to see how the monocalcium phosphate potential is an improvement over the measurement of phosphate ion concentration in the soil solution. He further remarked that the measurement of phosphate potential may be useful for categorizing soils in a chemical framework but that it neither characterizes the soil in a plant nutrition framework nor helps in understanding the nature of the soil supply of phosphorus to plants. Wild found that phosphorus uptake by plants from solutions of about the same composition as soils is determined by the phosphorus concentration and not by the potential. In addition to the above arguments, the phosphate potential only takes into account the activity of  $\text{H}_2\text{PO}_4^-$  ion while it is known that both  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  ions are taken up by the plants. Several solution culture experiments (Asher and Loneragan, 1967; Loneragan and Asher, 1967; Parker, 1927a; Russell and Martin, 1953; Tidmore, 1930) and excised root studies (Fried et al. 1957; Overstreet and Jacobson, 1946) also seem to support the view that the solution phosphorus concentration is a very important factor affecting the uptake.

It is obvious from the above discussion that the intensity

factor has been estimated by measuring either the phosphate potential or simply the phosphorus concentration. The author is impressed by the findings of the previous experiment (Figure 1), and thinks that the determination of soil solution phosphorus concentration is satisfactory enough to estimate the intensity factor.

#### Quantity Factor

In view of the complex nature of the soil system, it is often difficult to choose the soil factors that can be said to be completely independent or dependent of each other. Intensity and quantity factors are no exceptions. Therefore, it is desirable to study both these factors together. The literature on the quantity factor is very extensive. Comments on the approaches rather than the specific details of the methods used in the measurement of the quantity factor of soil phosphorus are thought to be more appropriate for the present review. On the basis of the approaches, the methods used for measuring the quantity factor are divided into the following groups:

##### Extraction Methods

- Acid extractable phosphorus

- Alkali extractable phosphorus

- Salt extractable phosphorus

- Fractionation of soil phosphorus

- Isotopic tracer techniques

- Equilibrium Technique

Extraction Methods: Many extracting solutions, including CO<sub>2</sub> saturated water, organic and inorganic acids, salts and bases have been tried by various investigators to extract the "available phosphorus" of the soil. The amount of phosphorus extracted by the reagents is compared to the phosphorus uptake or the yield. If a good statistical correlation is obtained, the particular extractant is selected for further use to measure available phosphorus in the soils. In the case of poor correlation, many variations and modifications with respect to the strength of the reagent and the incorporation of the chemical reagents are tried to suit the specific conditions and soils being tested. This approach leads to an endless series of fertilizer trials designed for correlation with an ever increasing number of hit-or-miss extractions (Nye, 1963). Nye (1968) further commented that it is strange that this approach coexisted so long with the clear demonstration by the plant physiologists that the rate of uptake of nutrients in short supply was roughly proportional to their concentration in a nutrient culture solution. Larsen (1967) was of the opinion that methods based on chemical extraction are of little value, since they will cause redistribution of the soil compounds during the extraction procedure and, in any event, do not act specifically on single compounds. Larsen (1967) further expressed a sincere distrust of soil phosphorus studies that have involved the soil under investigation coming into contact with strong chemical reagents because these bring about an extensive and uncontrolled redistribution of the soil phosphorus. No doubt, the approach used in the chemical extraction methods is somewhat

empirical and in any case not the best. Although Bray (1948) and Olsen et al. (1954) tried to show some theoretical basis for their chemical extractants, none has received universal application. Several chemical extractants have been tried and some of them have become much more common than others. A few of the common extractants are: acid extractants of Bray (1948), sodium-bicarbonate of Olsen et al. (1954), sulfuric acid + ammonium fluoride solution of Miller and Axley (1956) and dilute sulfuric acid of Truog (1930).

Since the soil phosphorus fractionation procedure (Chang and Jackson, 1957; Glenn, 1959) is based on the same approach (selective chemical extraction of soil phosphorus) used in the extraction methods described above, it suffers from the disadvantages of disturbing the natural chemical framework of the soil and resulting in possible redistribution of compounds during the extraction. However, some workers have used the procedure in the available soil phosphorus work (Al-Abbas and Barber, 1964; Halstead, 1967; Jenkins, 1966; Kaila, 1965; Alexander, 1967) and also in pedogenesis work (Alexander, 1967; Dahnke, et al., 1964; Hawkins and Kunze, 1965; Westin and Buntly, 1967). A rather detailed review on fractionation of soil phosphorus is given by Alexander (1967).

In general, it would appear from the above discussion that the extraction methods may cause some disturbance to the natural chemical framework of the soil and thus may bring about the redistribution of compounds during the extraction. Therefore, such an approach to measuring available phosphorus is not likely to become universal. Certainly some extraction methods can be found very useful for a



particular group of soils and they may become popular because of their simplicity.

Isotopic tracer techniques: "Isotopically exchangeable soil phosphorus", "Labile soil phosphorus", "Surface soil phosphorus", and E values are common terms used in the soil literature. Basically, all these terms are related in that the measurement of available phosphorus is attempted by use of isotopic tracer techniques. Russell, et al. (1954) preferred to use the term "Labile soil phosphorus". Larsen (1967) defined the labile term for soil phosphorus as that fraction of soil phosphorus which can enter the soil solution by isoionic exchange within an appropriate time span. This term was abbreviated by Russel et al. (1955) to "E" value. In the present text the term E value will be used for isotopically exchangeable phosphorus. McAuliffe et al. (1948) and later Olsen (1953) believed that the initial, more rapid, step of  $^{32}\text{P}$  exchange involved only the phosphorus on the surface of solid particles and consequently named this fraction, "surface phosphorus".

Since isotopic exchange of phosphorus between soil and the solution in which it is suspended occurs continuously, the kinetics of  $^{32}\text{P}$  exchange can be studied by analyzing the relationship between time and the loss of  $^{32}\text{P}$  from the solution phase. This led Talibudeen (1958) and Arambarri and Talibudeen (1959a) to subdivide isotopically exchangeable soil phosphorus according to the number of reaction steps, fast or slow. This principle has recently been used by Tondon et al. (1969) to study the exchange characteristics of Fe and Al bound phosphorus fractions of soils.

Since the soil phosphorus that takes part in the fast exchange reaction step was thought to be more important in determining the available phosphorus, an appreciable effort was made to find out a suitable time period to cover the initial more rapid reaction step. Some of the exchange reaction periods suggested are half hour (Amer, 1962; 1969), one hour (Rennie and McKercher, 1959; Beckett and White, 1964), 24 hours (Chu and Chang, 1966), 48 hours (Russell et al., 1954), 60 hours (Dunbar, 1965), 96 hours (Al-Abbas et al., 1967) and 168 hours (Russell et al., 1955). It is, of course, not very surprising that widely different suggestions with respect to the time period have been made since the time of reaction to cover the initial fast reaction step depended on the experimental conditions and soils being tested. Other factors also seemed to affect the exchange reaction such as the presence of organic anions (Arambarri and Talibudeen, 1959a), exchangeable base status (Arambarri and Talibudeen, 1959b; Russell et al., 1954) and temperature (Arambarri and Talibudeen, 1959c). In general, it seems more desirable for a complex system such as soil to use shorter exchange time periods since longer periods may cause microbial interference (White, 1964) and side reactions such as crystal growth and tracer occlusion (Amer, 1962).

Although there are some difficulties involved in measuring the  $E$  value, the approach used seems to be less arbitrary than that of chemical extraction methods. Loosely bound and surface soil phosphorus is likely to participate in the initial fast exchange reactions and also likely to be a source of available phosphorus to

the plants. Moreover, the method of E value measurement causes less disturbance of the soil system than the chemical extraction methods discussed earlier. Therefore, the determination of E value seems to have a special place in soil phosphorus work. It seems desirable to measure it in any study of the quantity factor.

**Equilibrium Technique:** A rather unique approach for estimating the quantity factor has recently been proposed by Beckett and White (1964) and White and Beckett (1964). The approach also allows concurrent estimation of the equilibrium phosphorus concentration and the phosphorus buffering capacity of the soil. The basis of the approach is that when a soil is equilibrated with solutions of known varying phosphorus concentration, the amounts of phosphorus ( $\Delta P$ ) gained or lost by the soil in coming to equilibrium with each solution can be calculated from the loss or gain of phosphorus by the solution. From a graph of  $\Delta P$  values plotted against the respective concentrations of the solution in equilibrium with the soil,  $\Delta P$  can be extrapolated to the zero solution concentration (Figure 3). The P value at zero solution concentration is called  $Q_0$  or "net exchange sites" (White and Beckett, 1964; Beckett and White, 1964).  $Q_0$  (net exchange sites) measures the amount of phosphorus which must be removed if the solution concentration is to be reduced to zero. According to Beckett and White (1964), phosphorus held at net exchange sites is capable of isotopic exchange with  $H_2^{32}PO_4$  ions in the solution. From the same graph (Figure 3) it is also possible to interpolate  $I_e$ , the solution concentration at  $\Delta P$  value of zero. The slope of the line,  $\frac{Q_0}{I_e}$ , is the phosphorus

buffering capacity (Figure 3) of the soil.

It is obvious from the above discussion that the approach attempts to relate the quantity factor ( $Q_0$ ) with the intensity factor ( $I_e$ ) for a soil. Since the slope of the line  $\frac{Q_0}{I_e}$  could differ from soil to soil, different  $Q_0$  values could be obtained for the same value of  $I_e$ . This would, of course, make it difficult to compare the soils without considering the slope of the line. In general, the proposed approach seems to be excellent for studying a complex system such as the soil since it is based on equilibrium principles. More work is needed to test the importance of this approach in studying the capacity of soil to supply phosphorus to plants.

#### "A" Value Technique

The significance to plants of the intensity and quantity factors reviewed earlier can only be assessed by plant growth experiments. Some of the routine methods involving the growth of plants under controlled conditions are Neubauer and Mitscherlich techniques. A rather unique technique ("A value") to study the soil-plant system in relation to nutrient availability has been proposed by Fried and Dean (1952). This method has an advantage over the Neubauer and Mitscherlich procedures in that the plants do not have to be grown under abnormal conditions of severe nutrient stress. In short, this technique for measuring the amount of available nutrient in soils involves the introduction of a known quantity of a standard source of the nutrient under consideration into a soil. The desired crop is grown and the proportion of the total nutrient absorbed

that was derived from the standard source is determined. The amount of available nutrient in the soil, "A" value is calculated by use of the equation:

$$A = \frac{B(1-y)}{y} \quad \text{..... (3)}$$

where, A = amount of available nutrient in soil, B = amount of available nutrient in applied standard and y = proportion of the nutrient in the plant derived from the applied standard. The determination of y can best be accomplished by use of radioactive or stable isotopes.

The derivation of this equation is based on the assumption that a plant when presented with two sources of a given nutrient (soil and applied standard), will absorb nutrient from each of these sources in proportion to the respective quantities available in them. However, the concept for measuring soil nutrient by this method is similar in principle to the well known technique for analysis by isotope dilution method where the addition of an isotopically labelled compound to an unknown mixture is followed by isolation of the same compound from the system. The specific activity of the original compound is then compared with the isolated sample and the amount of compound in the unknown mixture is then calculated. If soil is considered as the unknown mixture, the fertilizer standard as the labelled compound, and the plant as the isolation method, the similarities between the isotope dilution method and "A" value method for measuring the available soil nutrient become obvious.

"A" value technique has been used extensively for phosphorus work (Lathwell et al., 1958; Hunter, et al., 1961; Mistry, 1962; Rennie and Spratt, 1960; Shapiro, 1958; Armiger and Fried, 1958; Beaton et al., 1962; Kalra and Soper, 1968; Ozbek, 1966) and to some extent for work on Zn (Shaw et al., 1954), Ca (Fried and Dean, 1952), N (Legg and Allison, 1959) and S (Harward et al., 1962).

Although, the "A" value technique has been used very extensively, some problems do arise because of the tendency of reaction between soil and applied phosphorus (Russell, et al. 1954). To minimize this reaction either a band placement of fertilizer standard or a relatively insoluble resin phosphorus can be used (Rennie, 1960). The use of large particle size of the fertilizer standard and coating the fertilizer standard are also suggested to reduce the interaction between soil and applied phosphorus (Fried, 1964; 1967). Ideally, there should not be any interaction between soil and applied phosphorus and both the sources should be equally accessible to the plants. Fried (1964) has outlined the idealized conditions for the measurement of "A" value (Table 5).

It appears from the review on "A" value technique that if due care is taken to satisfy the conditions outlined by Fried (Table 5), "A" values for soil should give very valuable information on the soils. Every attempt was made to satisfy the conditions outlined by Fried (Table 5) in the present research project.

### Conclusions

It becomes apparent from the literature review that numerous approaches have been made to assess the phosphorus status of the soil.

Table 5 Idealized Conditions for "A" Value Measurement

Subject	Required conditions
Nutrient referred to	Any nutrient
Type of measurement	Greenhouse or growth chamber
Solubility of added salt	Arbitrary
Medium measured	Any source of nutrient (soil or fertilizers)
Sampling device	Plant
Extent of interaction with soil	None
Chemical entity measured	Not defined
Duration of experiment	As short as necessary to make an accurate measurement

Not surprisingly, there is no agreement on any one approach. The basic reasons for having numerous approaches seem to be the complex and widely different chemical framework of soils, the disturbance caused to the soils during measurement, the experimental difficulties encountered in the measurement such as microbial, temperature, and soil solution ratio effects and above all the complex nature of plant growth effects. There seems to be a great fundamental need to study and understand the intensity and quantity factors as measured under the conditions causing least disturbance to the soil. The soil solution phosphorus concentration and the E value need to be included when studying the quantity and intensity factors. Since the chemical extraction methods are presently used for soil testing purposes all over the world, the comparison of some of these methods with E value is very necessary.

In addition to the fundamental need of studying more about the intensity and quantity factors and testing the approach suggested by Beckett (1964) and White and Beckett (1964), there is a great need to initiate such research work on soils of Alberta. No attempt has been made on these soils to study the soil phosphorus system by the methods that cause least disturbance to the soils during the measurement. No information is available on the fate of applied phosphorus to these soils. Since every soil is an entity formed under unique environmental conditions and has unique physical and chemical features, a study of the phosphorus status of these soils itself should form an independent and fundamental research project.

In view of the discussions given in the review of literature



and the comments presented above, it was thought desirable to study the intensity and quantity factors of soil and applied phosphorus on some soils of Alberta.

#### Materials and Methods

Some physical and chemical properties of the soils under study are given in Appendix B. The methods used for determining the physical and chemical properties of the soils have been described in the previous chapter.

#### Intensity and Quantity Factors of Soil Phosphorus

**Equilibration and Extraction:** To determine the equilibrium phosphorus concentration ( $I_e$ ), the net exchange sites ( $Q_o$ ), the phosphorus buffering capacity (PBC) and isotopically exchangeable phosphorus at equilibrium phosphorus concentration ( $E_e$ ), 5 g samples of soil were transferred to each of four polypropylene tubes. To the tubes were added 50 ml of 0.01 M  $\text{CaCl}_2$  solution containing one of four phosphorus concentrations. The phosphorus in the  $\text{CaCl}_2$  solutions was labelled with  $^{32}\text{P}^*$  in the form of  $\text{H}_3\text{PO}_4$ . For each soil, 4 standard phosphorus concentrations in duplicate were used giving a total of 8 soil suspensions for each soil. These were then shaken for one hour on a wrist action shaker. The suspensions were filtered through a Whatman No. 42 paper and the clear filtrates were analysed for inorganic phosphorus and  $^{32}\text{P}$ .

**Phosphorus Determination:** The inorganic phosphorus content of the filtrates was determined by the ascorbic acid method (Watanabe

\*  $^{32}\text{P}$  was obtained from the Atomic Energy of Canada Ltd., Ottawa.

and Olsen, 1965). The phosphorus contents of the 0.01 M  $\text{CaCl}_2$  solutions added to soils were already known and will be called standard phosphorus solutions. The  $^{32}\text{P}$  contents of the standard phosphorus solutions and the filtrates were determined by using the Gas Flow Counter. The solutions were transferred to cup shaped stainless steel planchets and then evaporated to dryness before counting. The Gas Flow Counter was adjusted to record 10,000 counts for each sample to give a standard error of counting near one percent.

Calculations and Plotting: The amount of phosphorus gained ( $+\Delta P$ ) or lost ( $-\Delta P$ ) by the soil in coming to equilibrium with each standard phosphorus solution was calculated from the difference between the phosphorus concentration of the standard phosphorus solution and the filtrate after equilibration. The gain or loss ( $\Delta P$ ) of phosphorus was then plotted against the respective phosphorus concentration (ppm) of the filtrate as shown in Figure 2. A good linear relation was observed and hence a straight line was drawn. The phosphorus concentration at the zero loss or gain of phosphorus was interpolated. This is the phosphorus concentration ( $I_e$ ) with which the original soil undergoes no net exchange of phosphorus during the equilibration time (Figure 2).

The intercept ( $Q_0$  or net exchange sites) on the  $\Delta P$  axis of Figure 2 measures the amount of phosphorus which must be removed if the concentration is to be reduced to zero. The phosphorus buffering capacity (PBC) was calculated by dividing the  $Q_0$  by the  $I_e$ ,  $\frac{Q_0}{I_e}$ .  $\frac{Q_0}{I_e}$  is obviously the slope of the line (Figure 2).

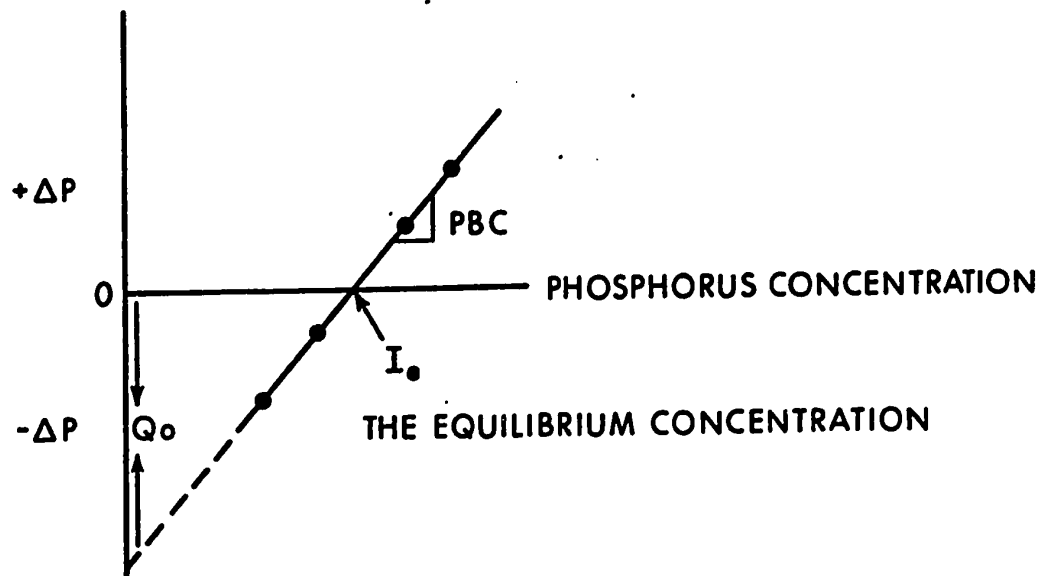


Figure 2 A Typical Plot Showing the Relationship between Intensity, Quantity and Phosphorus Buffering Capacity

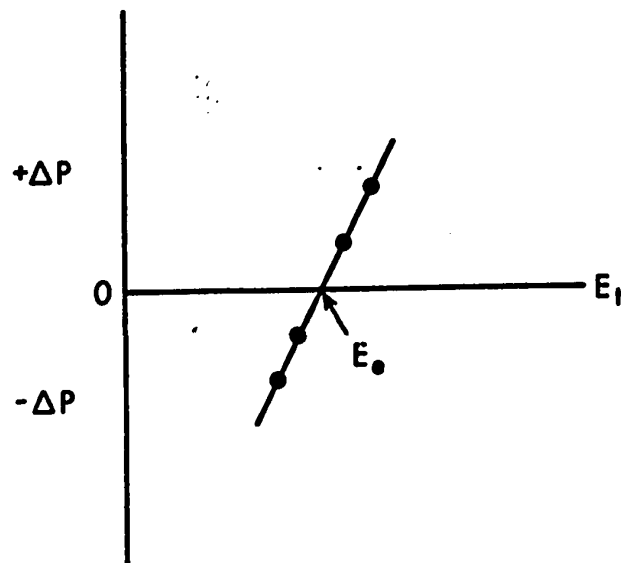


Figure 3 A Typical Plot Showing the Relationship between Isotopically Exchangeable Phosphorus and  $\Delta P$  Values

The first step in the calculation of the isotopically exchangeable phosphorus was to obtain  $E_t$  from the following equation:

$$E_t = \frac{(Y - Y_t)}{Y_t} X_t \quad \text{..... (4)}$$

where  $Y$  = initial radioactivity of the standard solution,

$Y_t$  = radioactivity of the filtrate,

$X_t$  = quantity of phosphorus in the filtrate

and  $E_t$  = the quantity of phosphorus in the soil after an equilibration time of one hour that had undergone isotopic exchange. The value of  $E_t$  was calculated for each standard solution and then the values of  $\Delta P$  for each soil were plotted against the respective values of  $E_t$  as shown in Figure 3. Since the plotting of the data showed a good linear relationship, a straight line was drawn. From this line, the value of  $E_t$  at  $\Delta P = 0$  ( $E_e$ ) was interpolated. This is the quantity of isotopically exchangeable phosphorus at the equilibrium phosphorus concentration.

Reliability of the Techniques Used: The approach for obtaining the various parameters described above is the same as the one proposed by Beckett and White (1964) and White and Beckett (1964).

The characteristics of the equilibrating solution, the time of equilibration and the method of calculating the parameters are the most important factors that affect the reliability of the techniques used. The 0.01 M  $\text{CaCl}_2$  solution was used to keep the soil flocculated and thus obtain clear filtrates. Any colloidal material in the filtrate would affect the  $^{32}\text{P}$  determination

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Reliability of the Techniques Used: The approach for obtaining the various parameters described above is the same as the one proposed by Beckett and White (1964) and White and Beckett (1964).

The characteristics of the equilibrating solution, the time of equilibration and the method of calculating the parameters are the most important factors that affect the reliability of the techniques used. The 0.01 M  $\text{CaCl}_2$  solution was used to keep the soil flocculated and thus obtain clear filtrates. Any colloidal material in the filtrate would affect the  $^{32}\text{P}$  determination

(Fergus, 1967) and possibly the determination of the inorganic phosphorus in the extracts. The  $\text{CaCl}_2$  concentration of 0.01 M is not high enough to cause any appreciable changes in the various parameters being measured. First, Ca is the dominating exchangeable cation in many soils, and secondly Larsen (1967) found no effect of calcium chloride concentration on the phosphate potential of acid soils. He calculated the maximum error of the phosphate potential to be 0.27 units in a calcareous soil equilibrated with 0.01 M  $\text{CaCl}_2$  solution. William (1967) indicated that the water and  $\text{CaCl}_2$  extracts could serve as convenient alternatives to measure the intensity factor of the soil phosphorus. Schofield, as quoted by Larsen (1967), suggested that the effects of soil to solution ratio and ionic strength on phosphorus concentration can be reduced by standardizing the soil to solution ratio at 1:10 and using 0.01 M  $\text{CaCl}_2$  as extractant. Many workers have used the 0.01 M  $\text{CaCl}_2$  solution in phosphorus work (Aslyng, 1964; Beckett and White, 1964; White and Beckett, 1964; Williams, 1967; Mattingly, 1965; White, 1965; Talibudeen, 1957; Gunary and Sutton, 1967; Barrow, 1967b). Therefore, it was thought that 0.01 M  $\text{CaCl}_2$  solution would be suitable in the equilibration work.

The equilibration time of one hour was selected since some preliminary work showed that most of the  $^{32}\text{P}$  in the equilibrating solution exchanged with the soil phosphorus in the first hour. Subsequent experiments on the kinetics of  $^{32}\text{P}$  exchange (reported later on) showed that more than 90 percent of the  $^{32}\text{P}$  of the equilibrium solution exchanged in the first one hour. This indicated

that satisfactory equilibrium conditions are obtained in one hour. The work of Khan (1967) on some soils of Alberta established that one hour is sufficient to obtain equilibrium conditions between soil and solution phases. A longer time of equilibration (> 4-8 hrs) may cause microbial interference in the determination (White, 1964).

The use of equation 4 to calculate the  $E_e$ , involves the assumption that all phosphate held in the soil that has undergone isotopic exchange is in isotopic equilibrium with the solution analysed. Following Beckett and White (1964), the author used the equation with this assumption in the  $E_e$  determination.

#### Kinetics of $^{32}\text{P}$ Exchange

Three Orthic Gray Wooded soils (Cooking Lake, Breton and Glory) from the Luvisolic Order and one Orthic Brown soil (Maleb) from the Chernozemic Order were selected for this study. The soil samples (5 g) were transferred to polypropylene tubes to which were then added 50 ml of 0.01 M  $\text{CaCl}_2$  solutions with phosphorus concentrations equal to the respective  $I_e$  concentrations of soils.  $I_e$  concentrations for all these soils were known from the previous experiment. The phosphorus in the solutions was labelled with  $^{32}\text{P}$ . The soil suspensions were shaken on a wrist action shaker for various time periods ranging from zero to 16 days. The tubes were occasionally opened to aerate the suspensions. The same procedures as described in the previous section were used for the filtration and  $^{32}\text{P}$  determination. The calculation of isotopically exchangeable phosphorus for various time periods was done using equation 4.

The value of  $X_t$  was a constant since  $^{32}\text{P}$  exchange took place under equilibrium conditions.

#### Fractionation of Soil Phosphorus

Inorganic phosphorus fractionation of the soil, in duplicate, was carried out according to the procedure outlined by Alexander (1967). The procedure is essentially the same as that proposed by Chang and Jackson (1957) and modified by Glenn et al. (1959). The determination of inorganic phosphorus in the various extracts was done by the ascorbic acid method instead of stannous chloride method. The forms of inorganic phosphorus along with the extractants used are given in Table 6.

#### "A" Value Experiment

The reaction of the applied phosphorus with the soil and the accessibility of soil and applied phosphorus to the roots were important considerations for the "A" value experiment. In order to have equal accessibility of soil and applied phosphorus, the phosphorus source was thoroughly mixed with the soil. To reduce the reaction of applied phosphorus with the soil, a relatively insoluble  $^{32}\text{P}$  labelled anion exchange resin was used as a phosphorus source and the duration of the plant growth experiment was kept as short as possible.

Amberlite IR-4B, weakly basic anion exchange resin was equilibrated following the procedure of Rennie (1960) with tagged phosphorus solution ( $\text{KH}_2\text{PO}_4$ ). In short, the reagent grade  $\text{KH}_2\text{PO}_4$  was dissolved in distilled and demineralised water and sufficient



Table 6 Forms of Inorganic Phosphorus and the Extractants Used in the Modified Chang and Jackson Procedure

Forms of inorganic phosphorus	Abbreviation	Extractant
*Water soluble plus loosely bound		1.0N $\text{NH}_4\text{Cl}$
Aluminum-bound	Al-P	0.5N $\text{NH}_4\text{F}$ , pH 8.2
Iron-bound	Fe-P	0.1N NaOH
*Reductant soluble iron-bound		0.3M Sodium Citrate, Sodium dithionite, and 1 M $\text{NaHCO}_3$
*Occluded aluminum-iron-bound		0.1N NaOH
Calcium-bound	Ca-P	0.5N $\text{H}_2\text{SO}_4$

\* Not determined

$^{32}\text{P}^*$  (approximately 2000  $\mu\text{C/g}$   $^{31}\text{P}$ ) in the form of  $\text{H}_3\text{PO}_4$  was then added to the phosphorus solution. A subsample of this solution was stored for measuring specific activity at the time when plant samples were to be analysed for  $^{32}\text{P}$  and  $^{31}\text{P}$ . For determining the phosphorus content of the resin, the air dry resin was wet ashed (Goss, 1962) and phosphorus in the extracts was determined by the ascorbic acid method. The appropriate quantity of air dry resin was then weighed to apply 14 ppm of P to the soils for the growth room experiment.

A plant growth experiment was conducted in a growth room. Four pots were filled (800 g oven dry soil) with each of the soil-resin mixtures. The soils used in this study are given in the Table 1. Conquest barley was seeded in a randomized block design and after emergence thinned to 4 plants per pot. Fifty ppm of N and S and 122 ppm K were applied in the solution form to all pots. Twenty g of perlite were placed over the pots to reduce evaporation and formation of a crust on the surface. Soil moisture was controlled by weighing and watering the pots to the 1/3 atm. A soil temperature of about  $15^\circ\text{C}$  was maintained during the growth period and artificial light was supplied daily for 16 hours. One hundred ppm of N ( $\text{NH}_4\text{NO}_3$ ) in the solution form was supplied in two equal doses during the growth period. Three weeks after emergence, the plant tops were harvested. They were dried at  $70^\circ\text{C}$ , weighed, and ground to pass through a 40 mesh sieve. The plant samples were digested with  $\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$  (Goss, 1962) and phosphorus was determined

\* Obtained from the Atomic Energy of Canada Limited, Ottawa.

by the ascorbic acid method. For  $^{32}\text{P}$  determination of the plant samples, 0.05 g ground plant material was transferred to a cup shaped stainless steel planchet. About one ml. of distilled water was added to the planchet, mixed with the plant material and evaporated slowly on a hot plate. This resulted in a fine cake of plant material adhering to the bottom of the planchet. Similarly, unlabelled plant material (0.05g) was transferred to a planchet and the appropriate quantity of the original labelled phosphorus solution, which was used in preparing the resin phosphorus source, was transferred with about one ml. of distilled water to the planchet. The planchet was then prepared as described above in preparation for  $^{32}\text{P}$  measurement. All samples were counted with the Gas Flow Counter which was adjusted to give a total of 10,000 counts per planchet. The detailed procedures for determining  $^{31}\text{P}$  and  $^{32}\text{P}$  (Omanwar and Robertson, 1970b) of the plant samples are outlined in Appendix C and D respectively.

Equation No. 3, proposed by Fried and Dean (1952), was used to calculate "A" values. Since the dose of applied resin P was expressed in terms of parts per million of soil (14 ppm), the units obtained for "A" values were in terms of ppm of soil.

## Results and Discussion

### Characterization of Soils

The results of the analyses (Table 2, Appendix B) showed that the soils covered a wide range of physical and chemical characteristics. This was to be expected since soils were collected from widely different locations and included several great groups. For the present

study the soil phosphorus characteristics were the most important.

The total phosphorus content of the Chernozemic soils ranged from 435 to 925 ppm. The range for the remaining soils (Orthic Gray Wooded) was 355 to 880 ppm. A rather wide range for the soils within same subgroup (Orthic Gray Wooded) appears to be the result of the differences in parent material. This statement is based on the findings of Alexander (1967) that the sample from the C horizon of the Orthic Gray Wooded -Glory soil (pitted deltaic parent material) contained much more total phosphorus than the sample from the C horizon of another Orthic Gray Wooded - Breton (till parent material) soil. Al-P + Fe-P contents of the soils (Table 7) ranged from 22 to 297 ppm. The range for Ca-P was 28 to 224 ppm. The relative abundance of a particular phosphorus form seems to be related to the pH value. Generally, the lower is the pH (<7) the higher is the Al-P + Fe-P forms. Isotopically exchangeable phosphorus (Ee), Olsen P and Miller and Axley P of the soils ranged from 7 to 43, 5 to 36 and 6 to 62 ppm respectively (Table 7).

The soil solution phosphorus concentration (Modified Aslyng's procedure) ranged from 0.02 to 0.31 ppm of solution (Table 7). Using a different technique (White, 1964 and White and Beckett, 1964), the equilibrium concentration (Ie) was found to range from 0.01 to 0.26 ppm of solution. Although the range of values is similar, the Ie value for each soil is lower than the value for soil solution phosphorus concentration estimated by modified Aslyng's procedure. The differences in the phosphorus concentrations are attributed to both the differences in the methods used and the fact that air dried

**Table 7 "A" Values and the Phosphorus Characteristics of P Untreated Soils**

Soils	"A" values ppm of soil	Mod.. Aslyng		Ie		PBC $\frac{Q_0}{I_e}$
		P conc. pp 100 million of soln.	$\log_{10}$ of P conc.	P conc. pp 100 million of soln.	$\log_{10}$ of P conc.	
Orthic Brown (Maleb)	22	16	1.20	3	0.48	166
Calcareous Dark Brown	17	9	0.95	1	0.00	200
Carbonated Dark Brown	11	2	0.30	2	0.30	300
Orthic Black (Peace Hills)	43	20	1.30	25	1.40	28
Eluviated Black (Angus Ridge)	31	7	0.85	4	0.60	75
Solodic Black	80	31	1.49	26	1.42	58
Orthic Gray Wooded (Cooking Lake)	19	4	0.60	2	0.30	150
Orthic Gray Wooded (Glory)	83	19	1.28	11	1.04	109
Orthic Gray Wooded (Breton)	46	24	1.38	12	1.08	33

Table 7 Continued .....

Qo	Phosphorus in ppm of soil						Total P
	Ee	Miller and Axley P	Olsen P	Al-P	Fe-P	Ca-P	
5	13	12	7	30	31	136	435
2	7	9	8	19	3	216	615
6	9	6	5	16	7	224	556
7	17	23	18	75	56	78	833
3	9	12	13	31	46	75	925
15	34	62	36	130	97	35	864
3	5	8	5	10	32	28	355
12	43	50	22	108	189	107	880
4	14	31	18	44	90	63	537

soil samples were used for the Ie method while the moist stored samples were used for the modified Aslyng's procedure.

A wide range of total P, inorganic phosphorus forms, Olsen P, Miller and Axley P, Ee and soil solution P provided desirable phosphorus characteristics for the present study.

### Plant Growth Experiments

Since the importance of the physicochemical properties of a soil nutrient is evaluated by the plant growth experiments, the use of a suitable plant growth technique for measuring the available nutrients is essential. Since a routine method of growing the plants under controlled conditions (described in the Chapter II) and a rather specialised technique ("A" value technique, described in this chapter) have been used to determine the available phosphorus status of these soils, a comparison of the two methods is desirable.

The data obtained from the plant growth experiments using the two methods are presented in Table 8. In order to compare the "A" value data with that of P uptake, a linear correlation coefficient was calculated. A correlation coefficient of 0.94 ( $P = 0.001$ ) was obtained when P treated and untreated soils were included in the comparison. When the P treated soils were excluded from the comparison, a correlation coefficient of 0.98 ( $P = 0.001$ ) was obtained. This suggests that both methods provide similar information on the nutrient status of the soils. However, (Fried, 1967) suggested that the "A" value technique has the advantage that the plant is not grown under nutrient stress. This may be a consideration in the plant growth studies.

Table 8 The Relationship between the Routine Plant Growth Method and the "A" Value Technique

Soils	P treatment ppm	Experiment, 1967 total P uptake mg/pot	Experiment, 1969 "A" value ppm of soil
Orthic Brown (Maleb)	0	3.19	22
Calcareous	0	3.60	17
Dark Brown	300	29.19	282
Carbonated	0	0.10	11
Dark Brown	300	32.57	263
Eluviated Black	0	3.66	31
(Angus Ridge)	300	28.67	244
Solodic Black	0	13.07	80
Orthic Gray Wooded	0	4.19	19
(Cooking Lake)	300	38.88	206
Orthic Gray Wooded (Glory)	0	14.62	83



### Kinetics of $^{32}\text{P}$ Exchange

Since the determination of available phosphorus by the isotopic tracer technique is based on the kinetics of  $^{32}\text{P}$  exchange, a study of the  $^{32}\text{P}$  exchange in some soils was thought essential. The results of the phosphorus fractionation studies (Table 7) on the soils used in this study revealed that Al-P + Fe-P forms are more dominant than the Ca-P in the Gray Wooded soils (Cooking Lake, Breton, Glory). In the Chernozemic soil (Maleb), Ca-P is the dominant form of phosphorus. Because of low organic carbon contents and wide differences in the inorganic phosphorus forms and levels of extractable phosphorus (Miller and Axley P), these soils were selected for the kinetic study.

The percentages of  $^{32}\text{P}$  remaining in the solution and the amounts of soil phosphorus that took part in the exchange reaction at various time periods are reported in Table 9. Percentages of the  $^{32}\text{P}$  remaining in the solution after the first hour of exchange ranged from 1.5 to 7.1 for the soils. Comparatively the  $^{32}\text{P}$  loss to soil after the first hour was very small. These observations suggested that the initial reaction was extremely fast. Since the soils were equilibrated with  $^{32}\text{P}$  labelled solutions having phosphorus concentrations equal to the respective  $I_e$  values of the soils, no "fixation" of phosphorus by the soil or release of phosphorus to solution would take place. Under these conditions, it is believed that the only mechanism for the disappearance of  $^{32}\text{P}$  from the solution is the exchange of  $^{32}\text{P}$  for  $^{31}\text{P}$  of the soil. As far as the author is aware, there are no reports in the literature

**Table 9 Percent of  $^{32}\text{P}$  Remaining in the Solution and Isotopically Exchangeable Phosphorus for Some Soils after Increasing Periods of Exchange**

Time (hours)	SOILS							
	Orthic Brown (Maleb)		Orthic Gray Wooded (Cooking Lake)		Orthic Gray Wooded (Breton)		Orthic Gray Wooded (Glory)	
	% 32P in the solution	Exchange- able P ug/g soil	% 32P in the solution	Exchange- able P ug/g soil	% 32P in the solution	Exchange- able P ug/g soil	% 32P in the solution	Exchange- able P ug/g soil
0	100	--	100	--	100	--	100	--
0.25	2.8	11	6.4	2	10.6	10	4.8	21
1	2.5	13	1.5	10	7.1	16	2.3	45
2	2.5	13	1.5	10	6.0	19	2.2	47
4	1.9	16	1.3	11	4.8	24	1.8	58
8	1.8	17	1.2	12	3.8	30	1.5	71
24	1.5	21	0.4	44	2.4	49	1.3	80
48	1.4	23	0.4	43	1.7	68	1.1	97
96	1.1	28	0.4	41	1.6	75	1.1	96
192	0.5	68	--	--	0.7	170	0.8	126
384	0.3	111	0.2	85	0.4	276	0.6	165

of studies where  $^{32}\text{P}$  exchange in the soil has been measured when the added solution phosphorus concentration is equal to the  $I_e$  concentration for the soil. Very recently, Tondon et al. (1969) equilibrated soils with solutions of fixed phosphorus concentration (0.2 ppm of solution) in their exchange kinetics study. My argument is that the selection of a fixed concentration for the equilibration solution would usually result, depending on the soils used, in either loss or gain of phosphorus by the solution. The exchange of  $^{32}\text{P}$  under such conditions would then be affected by the phosphate "fixation" or release reactions. The effect is likely to be more serious for initial short exchange periods. This effect is avoided by the use of a phosphorus concentration equal to the  $I_e$  value for the soil in the present experiment. However the effect of microbial interference on the  $^{32}\text{P}$  exchange during longer exchange periods (>4-8 hrs) was not studied. The main object of the investigation was to concentrate on the initial fast exchange reaction. While the study of the exchange over longer periods is faced with microbial problems, the selection of very short time periods is limited by the time (3-4 minutes) required to obtain a clear filtrate from the soil suspensions. An additional factor is the initial time required to get an uniform suspension in which optimum exchange can occur. Therefore, choice of the first one hour time period to study the initial fast exchange reaction appears to be satisfactory. The data (Table 9) suggested, however, that a considerable exchange reaction took place in the first 15 minutes.

Some workers (McAuliffe, et al. 1948; Olsen, 1953) suggested that the soil phosphorus that takes part in the initial fast exchange reaction is "surface phosphorus". Obviously, such phosphorus should include the clay bound surface phosphorus and the surface phosphorus of the amorphous and crystalline phosphorus compounds that may be present in the soils studied. Whatever may be the nature and distribution of surface phosphorus in the soils, it seems reasonable to conclude that the phosphorus which can exchange so rapidly with  $^{32}\text{P}$  in the solution has to be very reactive and hence likely to be more important in supplying phosphorus to plants.

To compare the rates of the exchange reactions, the amounts of soil phosphorus that took part (Table 9) during the various time periods can be grouped (Table 10). The data (Table 10) show clearly that the rate ( $\mu\text{gP/g soil/hr}$ ) of exchange during the first hour is 10 to 225 times higher than the rate of exchange during the 1 to 16 day interval. The rate of exchange for the 1 to 24 hour interval was also very low. It is hypothesized that the rates of exchange of soil phosphorus after the first one hour period are too slow to have any great influence on the immediate supply of phosphorus to the plants. This hypothesis is based on the observations that the rate of the initial exchange reaction (the first one hour period) was 10  $\mu\text{gP/g soil/hr}$  (Table 9) for the Orthic Gray Wooded - Cooking Lake soil and yet this soil can not supply enough phosphorus to the plants (P uptake, Table 3; "A" value, Table 7; Productivity Economic Field Trials, unpublished data). This hypothesis is further supported

Table 10 Rates of Isotopically Exchangeable Phosphorus in Some Selected Time Periods

Time periods	ugP/g soil exchanged per hour			
	Orthic Brown Maleb	Cooking Lake	Orthic Gray Wooded Breton	Glory
0-1 hour	12	10	16	45
1-24 hours	0.4	1.5	1.5	1.5
1-16 days	0.3	0.1	0.6	0.2

by the observations that the exchange rates in the Orthic Gray Wooded soils for the first one hour interval are 10, 16 and 45 ugP/g soil/hr for the Cooking Lake, Breton and Glory soils respectively and their abilities to supply available phosphorus are in the same order ("A" values, Table 7).

It appears from the above discussion that exchange periods of longer durations not only meet with the problems of microbial interference but are of less value in determining the immediate reserve of phosphorus supply to the plants. However, the information obtained from longer exchange periods is indicative of the slowly available phosphorus supply of the soils.

The data (Table 11) indicated that only a small fraction (2.8 to 5.1 percent) of the total phosphorus has exchanged during the first one hour. This seems to suggest that a very large fraction of the total phosphorus is not immediately available to the plants. The percentage of total phosphorus that exchanged during 0-16 days varied from 18.8 to 51.4. If the percentages obtained for 0-1 hr period are subtracted from those of 0-16 days, it becomes obvious that a large portion of the soil phosphorus is only slowly available. It can be noted that the Orthic Gray Wooded (Breton) soil, in spite of the lower content of total phosphorus, has more slowly exchangeable phosphorus than the other Orthic Gray Wooded (Glory) soil. These differential exchange characteristics seem to be due to differences in the phosphorus characteristics of the parent material and the effects of pedogenesis on the phosphorus characteristics.

Table 11 Percentages of Soil Phosphorus Exchangeable During Some Selected Time Periods

Soils	Total P ppm	Time periods	Percent of total P exchanged
Orthic Brown (Maleb)	435	0-1 hr	2.8
		0-24 hrs	4.8
		0-16 days	25.5
Orthic Gray Wooded (Cooking Lake)	355	0-1 hr	2.8
		0-24 hrs	12.4
		0-16 days	23.9
Orthic Gray Wooded (Breton)	537	0-1 hr	3.0
		0-24 hrs	9.1
		0-16 days	51.4
Orthic Gray Wooded (Glory)	880	0-1 hr	5.1
		0-24 hrs	9.1
		0-16 days	18.8

### Intensity Factor

On the basis of the review of literature and the findings of the experiments reported in the second chapter, it seems that solution phase phosphorus is very important. Therefore, a study of soil solution phosphorus should form an essential part of any investigation of soil phosphorus availability. Some work on the soil solution phosphorus was reported in Chapter II. Further work is presented here.

The intensity factor was estimated by the modified Aslyng's procedure described in Chapter II and also by the  $I_e$  method described in this chapter. To find out the relationship between the results of the two methods, a linear correlation coefficient was calculated. When the results of the P untreated soils only were used for calculating the correlation coefficient, a significant correlation ( $r = 0.83$ ,  $P = 0.01$ ) was obtained. Inclusion of the results of P treated soils in the comparison increased the correlation coefficient to 0.95 ( $P = 0.001$ ). It is rather interesting to note the close relationship between the results of the two methods. Since most of the phosphorus determinations including  $I_e$ , but not Aslyng's method, were done on air dry soils and since the  $Q_0$  and  $E_e$  determinations were done concurrently with  $I_e$ , only  $I_e$  values will be used hereafter to describe the intensity factor.

A high correlation (Table 12, Figure 4) between the "A" values and the  $\log I_e$  values supported the findings of the previous experiments that the soil solution phosphorus is a very important factor in supplying phosphorus to the plants. However correlation



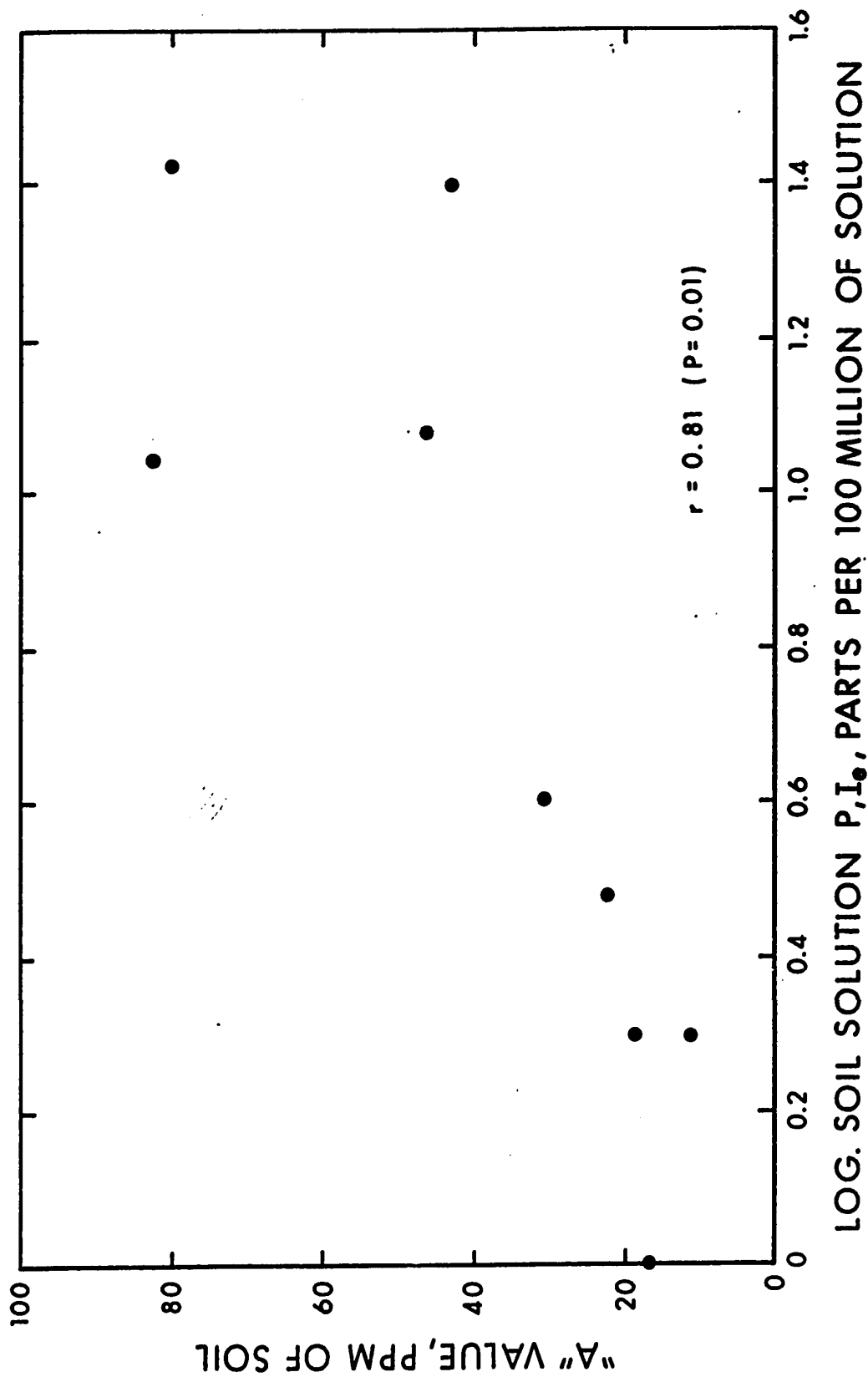


Figure 4 The Relationship between "A" Value and Soil Solution P

Table 12 Relationship between the "A" Value and the Intensity Factor

Intensity Factor	No. of soils	linear correlation coefficient	Probability level, P
Ie P concentration	9*	0.72	0.05
	17**	0.71	0.01
$\log_{10}$ of Ie P concentration	9*	0.81	0.01
	17**	0.85	0.001

\* P untreated soils

\*\* Nine P untreated + eight P treated soils

coefficients (Table 12, Figure 4) in the range of 0.81 to 0.85 explain only about 2/3 of the variation between the variables. This leads one to look for other factors influencing the relationship. Some of these factors (ability of the soil to supply P to the solution, "rhizosphere effects", effects of evapotranspiration and thermal gradients on soil solution phosphorus) were noted in the previous Chapter. In this study, emphasis is placed on the quantity factor assuming that soils have different levels of phosphorus reserves from which the soil solution phosphorus is replenished in the event of P uptake by plants.

#### Quantity Factor

In the literature review the quantity factor was defined as the total amount of nutrient reserve in the soil that is "available" to the plants. It is a conceptual entity and can only be approximated from plant growth experiments. The use of the term available in the definition requires that some time limit be specified since all soil phosphorus could be mobilized and made available to plants over an infinite time period. To specify the levels of immediately available phosphorus, one crop growth period seems appropriate. Such a definition of the quantity factor implies that before a crop is grown, the soil has a particular level of nutrient reserve which could be made available to the plants during the growth time. Any slow reactions contributing nutrient to this reserve are of very little value since they are likely to make very little contribution during one crop growth period. The laboratory methods for estimating

the quantity factor were discussed under the literature review. According to the principles of physical chemistry (Maron and Prutton, 1965), the properties of a system may be divided into two types, namely, extensive and intensive. Intensive properties are those whose values are independent of the total amounts, but are dependent instead on the concentration of the substance or substances in the system. An extensive property of a system is any property whose magnitude depends on the amount of substance present. Since the quantity factors tend to measure the total amount of available phosphorus in the soil system, they are related to the extensive property of the system. Since, ideally, the intensive and extensive properties should be independent of each other, it is desirable to learn more about the relationship between the intensity ( $I_e$ ) and quantity factors ( $E_e$  and  $Q_o$ ) for the soils studied in the present investigation.

The linear correlation (Table 13) between  $I_e$  and  $E_e$  values was not significant at 5 percent level. Poor relationships between solution phosphorus and isotopically exchangeable phosphorus were also noted by Weir and Soper (1962) and Rennie and McKercher (1959). Beckett and White (1964) proposed that the  $E_e$  is composed of at least two kinds of sites namely the "net exchange sites" ( $Q_o$ ) and "the isotopic exchange sites" ( $E_e - Q_o$ ). According to them the latter may attain isotopic equilibrium with the solution but can make no contribution to the values of  $Q_o$ . For Greensand soil, they found that  $Q_o$  was one fifth of the  $E_e$ . Based on their observations, it seems possible that a fraction ( $Q_o$ ) of the  $E_e$  may be directly related to the soil solution phosphorus concentration. In order to verify

Table 13 Relationships between the Intensity Factor (Ie) and Ee, Qo and PBC for P Untreated Soils

Factors	Linear Correlation Coefficients	Probability level, P
Ie and Ee	0.60	0.10
Ie and Qo	0.71	0.05
$\log_{10}$ Ie and PBC	-0.80	0.01

if this was the reason for the poor relationship between Ee and Ie, Qo values were compared with the Ie values. The increase (Table 13) in the correlation coefficient from 0.60 to 0.71 suggests that the poor linear relationship between Ee and Ie is partly due to the kinds of exchange sites taking part in the isotopic exchange reaction. In addition, the organic matter contents and ionic composition of the equilibrium solution may also affect the relationship between them. However, the use of 0.01 M  $\text{CaCl}_2$  solution for all soils in the present investigation minimized the variation in the ionic composition of the equilibrium solution. Therefore, the organic matter contents and the kinds of exchange sites appear to be the reasons for poor relationship between Ie and Ee. Since, the kind of exchange sites and organic matter contents are likely to vary from soil to soil, it is reasonable to expect a rather poor relationship between Ie and Ee. In the present study the Orthic Gray Wooded (Glory and Breton) soils had similar Ie values (11 and 12 pp 100 million of solution respectively) and yet their Ee values (Table 7) differed by a factor of approximately 3. In the author's opinion, for a given Ie value, the Ee values for the fine textured soils will be higher than those for the coarse textured soils. Based on this reasoning, the Ie and Ee values were considered independent of each other for multiple regression and correlation analyses with available phosphorus ("A" value) as the dependent variable and Ie and Ee as the independent variables. The following data from Table 7 also illustrated the necessity for multiple regression and correlation analyses since "A" values increased with Ee at a given Ie concentration.

Soils	Ie pp 100 million of solution	Ee ppm of soil	"A" ppm of soil
Orthic Gray Wooded (Breton)	12	14	46
Orthic Gray Wooded (Glory)	11	43	83

Because of these observations, a multiple linear regression analysis was done using the function,  $A = f(\log_{10} Ie, Ee)$ . The linear multiple regression equation and the correlation coefficient were

$$"A" = 2.11 + 15.90 \log_{10} Ie + 1.51 Ee \text{ and } 0.972 \text{ respectively.}$$

Since this equation enables one to predict the "A" if the data on the intensity (Ie) and quantity (Ee) factors are known, some information on the P fertilizer response on the soils can be obtained for practical purposes. Field fertilizer trials (unpublished data, University of Alberta) on some of the soils used in this investigation and the yield data on P treated soils of the present investigation (Chapter II, Table 3) tend to indicate that distinct, moderate, and little or no response to applied P fertilizer may be obtained on soils having "A" values <30, 40 to 50 and >80 ppm of soil respectively.

It is obvious from the multiple regression and correlation data that both the factors (Ie, Ee) are important in the supply of P to the plants. There is, of course, a big step between showing a correlation and showing cause and effect. The basis for the relationship between available phosphorus ("A" value) and solution

phosphorus was explained in the previous Chapter (equations 1 and 2). An attempt is made here to explain the relationship between Ee and available phosphorus ("A" value). For this, it is necessary to note the earlier statement that Qo was better related to Ie than was Ee and also the fact that Ee is better related to "A" value than was Qo (Table 14). The phosphates held at Qo and/or Ee-Qo sites have to pass into solution if they are important in P supply to the plants. Since  $Ee (Qo + (Ee-Qo))$  is better related to available phosphorus than is Qo, it implies that phosphates (Ee-Qo) in addition to the Qo phosphates are important in supplying P to the plants. These observations are interpreted to mean that in addition to the intensity factor (Ie) and the solid phase phosphates held at Qo sites (which are directly and closely related to the Ie), the solid phase phosphates held at Ee-Qo sites (which are not directly related to the Ie concentration) are important in the available phosphorus. Suggested mechanisms to explain the supply of phosphorus held at Qo and Ee-Qo sites to the plants are as follows: When growing roots absorb phosphorus from the soil solution, the parameter directly related to the solution phosphorus (Qo) tries to renew the soil solution phosphorus concentration by releasing phosphate ions to the solution. The soil solution phosphorus has to be renewed several times a day to supply sufficient phosphorus to the plants. Once the phosphorus held at Qo sites is reduced, the phosphorus held at Ee-Qo sites will readjust in an attempt to equilibrate with phosphorus held at Qo sites by releasing some phosphorus to the Qo sites for its further entry into the solution. Another possibility is that the phosphorus



held at  $E_e$ - $Q_o$ , being easily accessible (surface phosphorus), may be attacked by root exudates and thereby released to the solution and/or  $Q_o$  sites. Based on these observations, it is suggested that  $E_e$  (includes  $Q_o$ ) is a better measure of quantity factor than is  $Q_o$ .

#### Buffering Capacity for Phosphate (PBC)

The buffering capacity for phosphate has been defined by Beckett and White (1964) as the slope of the "quantity-intensity" relationship  $\left(\frac{\Delta P}{\Delta I}\right)$ , that is the relationship between change in sorbed phosphorus ( $\Delta P$ ) and the change in solution phosphorus. According to them the PBC value is indicative of the ability of the soil to maintain the soil solution phosphorus activity on the addition of phosphate to or its removal from the soil. PBC values have been studied for phosphorus (Beckett and White, 1964; White and Beckett, 1964; Barrow, 1967a; Barrow, 1967b) and potassium (Zandstra and MacKenzie, 1968).

The results (Table 7) of the present study indicated that the buffering capacity for phosphate is related to the  $I_e$  concentration. A negative linear correlation (Table 13) of 0.80 ( $P = 0.01$ ) was obtained between the PBC and the log of  $I_e$ . A negative correlation of 0.7 ( $P = 0.05$ ) was obtained when PBC was compared with  $I_e$  concentration rather than its log. term. This clearly indicates that the higher the PBC the lower is the  $I_e$  concentration. Similar observations have been made by Barrow (1967a; 1967b) for phosphorus and by Zandstra and MacKenzie (1968) for potassium. It was noted earlier that the log  $I_e$  is highly correlated with available phosphorus

("A" value). Hence, the PBC is negatively correlated ( $r = -0.62$ ) to the available phosphorus ("A" value) mainly because it is associated with the lower values of  $I_e$  in the group of soils used in this investigation. Zandstra and MacKenzie (1968) also found a negative correlation ( $r = -0.31$ ) between PBC and available potassium ( $0.1 \text{ N NH}_4\text{Ac} + 0.5 \text{ N H}_2\text{SO}_4$  extractable).

The significant correlation at 1 percent level between the PBC and the  $\log I_e$  led us to conclude that these are not independent variables to be considered in the supply of P to the plants.

#### Comparison of Chemically Extractable P with the Quantity ( $E_e$ ) Factor

Chemical extraction procedures are by far the most commonly used methods to determine the "available phosphorus" of the soils. The soil testing laboratory of Alberta and, the author believes most soil testing laboratories elsewhere, use chemical extraction procedures to determine the "available phosphorus" in the soils. Recently, attempts have also been made to fractionate the soil phosphorus by selective chemical extractions into active and inactive phosphorus forms, the former being more available to the plants. Supposedly, in all of these methods, the attempt is to measure the amount of available phosphorus in the soils. Since  $E_e$  determination was done using a very different approach ( $^{32}\text{P}$  exchange at equilibrium P concentration) and also that it was found to be very important in supplying phosphorus to the plants ("A" values), it was thought desirable to compare it with the results obtained with chemical extraction procedures.

The comparisons of Miller and Axley P, Olsen P and Al-P (chemical extraction methods) and Ee (isotopically exchangeable P) with "A" values gave linear correlation coefficients (Table 14, Figures 5 to 8) in the range of 0.92 to 0.97. This very clearly indicates that similar information is obtained on the quantity factor of available phosphorus using chemical extraction procedures and  $^{32}\text{P}$  exchange technique (Ee). Although the Miller and Axley P, Olsen P, Al-P and Ee values were highly correlated among themselves and with "A" values, they differed considerably in the absolute values. Olsen P values (Table 7) for the P untreated soils on the average were slightly less than the Ee values. The amounts of Al-P (Table 7) in the soils are about 2 to 5 times higher than those of Olsen P or Ee and about 1.5 to 3 times larger than those of Miller and Axley P. It is of interest to note a close relationship between them when the values are very different. This leads one to attempt to find out the nature of phosphorus measured by these methods. Ee is a measure of "surface phosphorus" of the soils. This phosphorus may be associated with the clays, aluminum phosphates, iron phosphates and/or calcium phosphates. The relative contribution of these phosphates to the surface phosphorus (Ee) depends on the relative abundance and size of the crystals and/or amorphous particles of each of the phosphate complexes. However, it is certain that Ee phosphorus is held at easily and quickly accessible sites (exchanged with  $^{32}\text{P}$  in one hour). It is rather uncertain as to what extent the chemical reagents (Miller and Axley -  $0.03\text{ N NH}_4\text{F} + 0.03\text{ N H}_2\text{SO}_4$ ; Olsen  $0.5\text{ M NaHCO}_3$  adjusted to pH of 8.5; Al-P -  $0.5\text{ N NH}_4\text{F}$  adjusted to pH of 8.2) extract "the surface phosphorus" in addition to the other forms. Olsen's reagent contains bicarbonate anions which can desorb

Table 14 Relationships between the "A" Value and Quantity Factors for P Untreated Soils

Factors	Linear Correlation Coefficient	Probability level, P
"A" and Ee	0.95	0.001
"A" and Qo	0.86	0.01
"A" and Miller and Axley P	0.97	0.001
"A" and Olsen P	0.92	0.001
"A" and Al-P	0.96	0.001

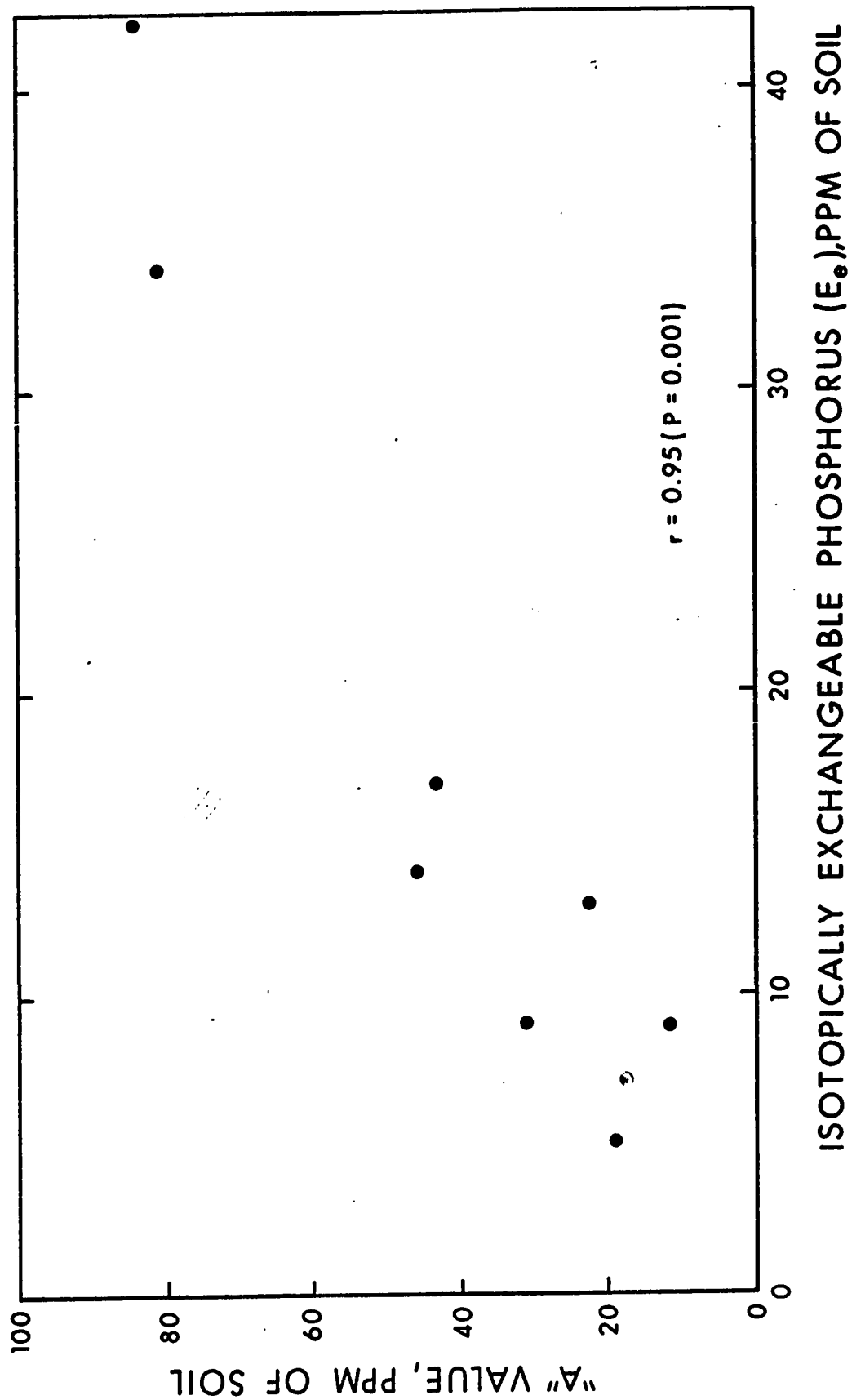


Figure 5 The Relationship between "A" Value and "E<sub>e</sub>"

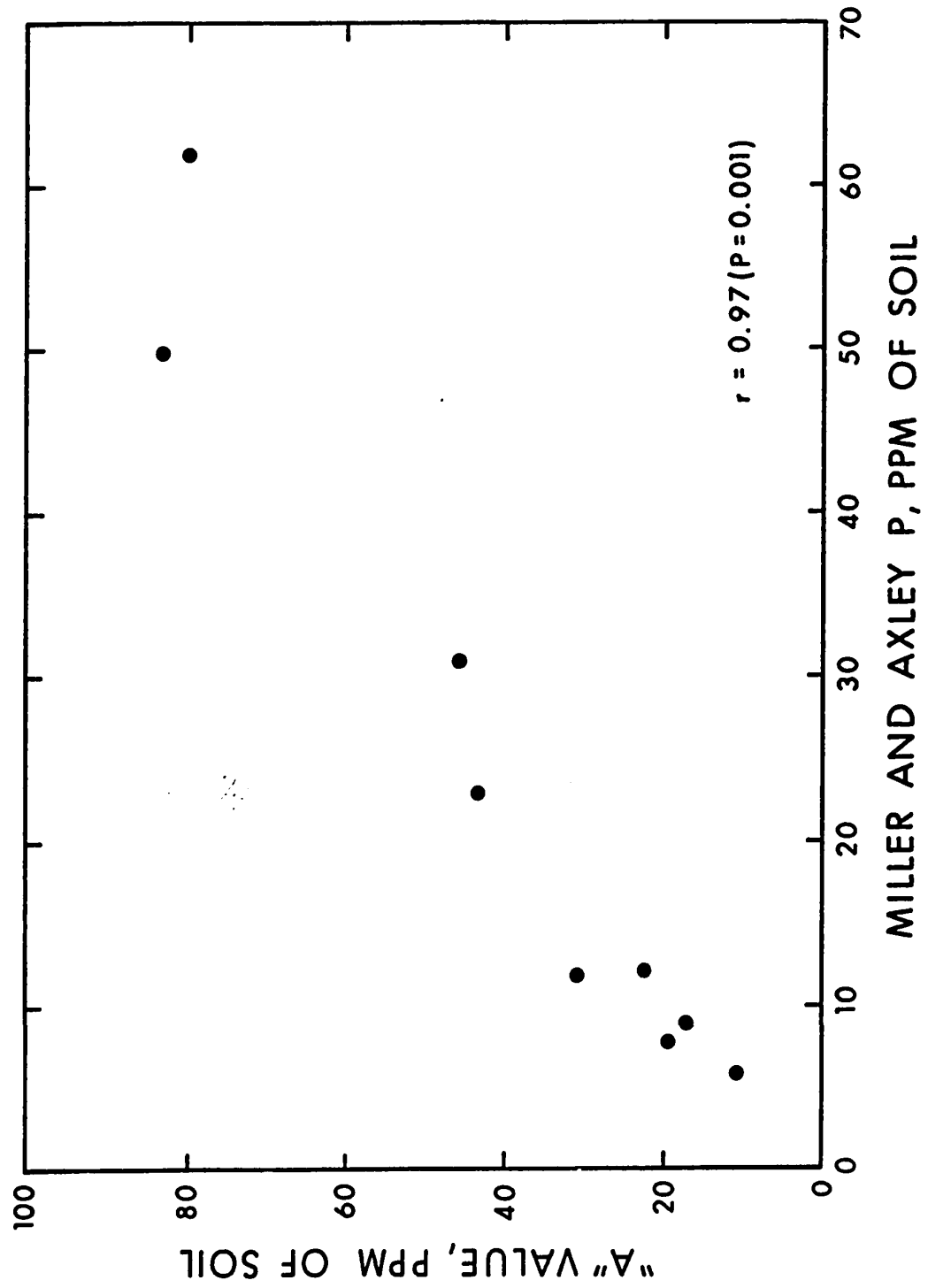


Figure 6 The Relationship between "A" Value and Miller and Axley P

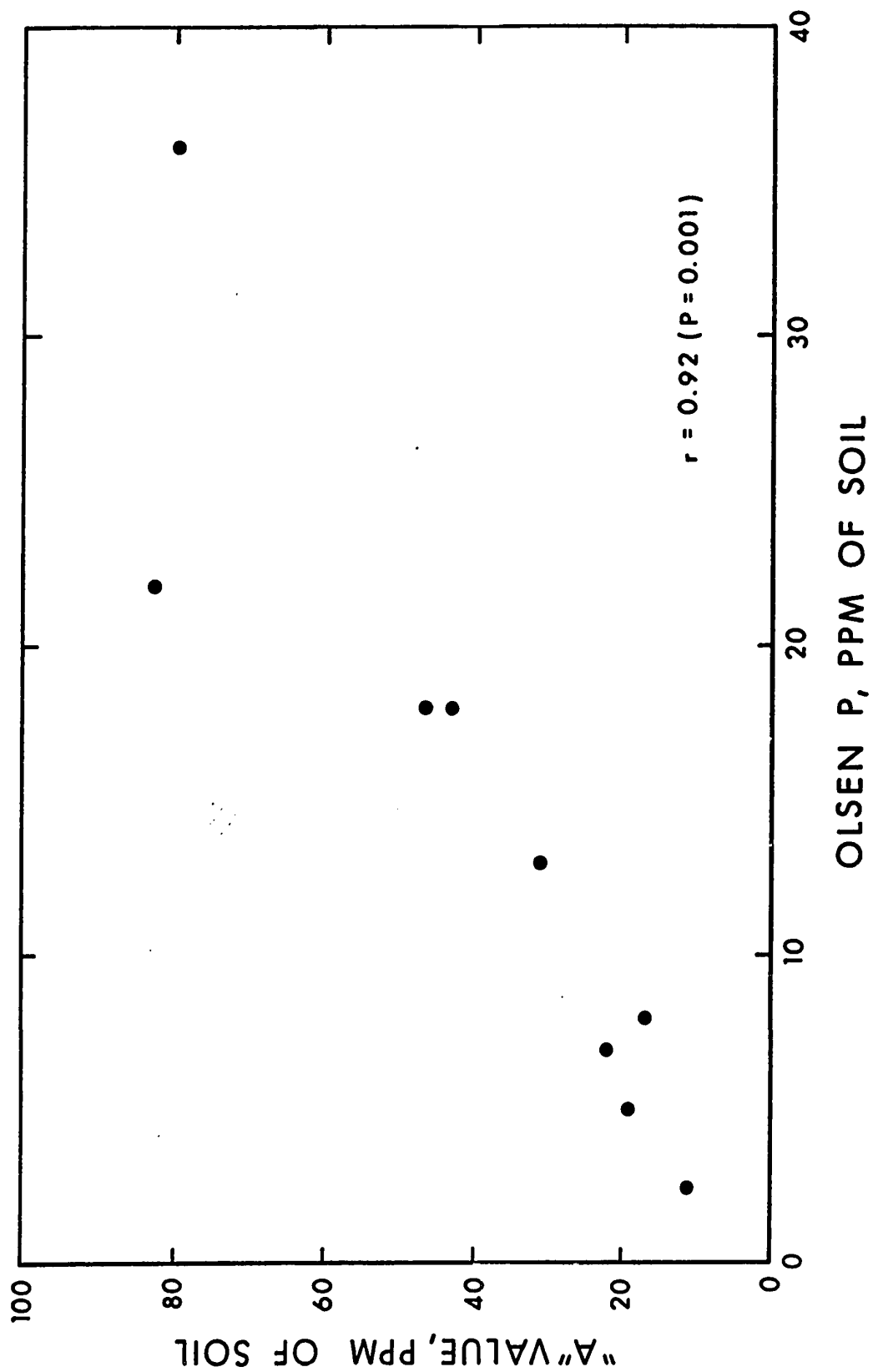


Figure 7 The Relationship between "A" Value and Olsen P

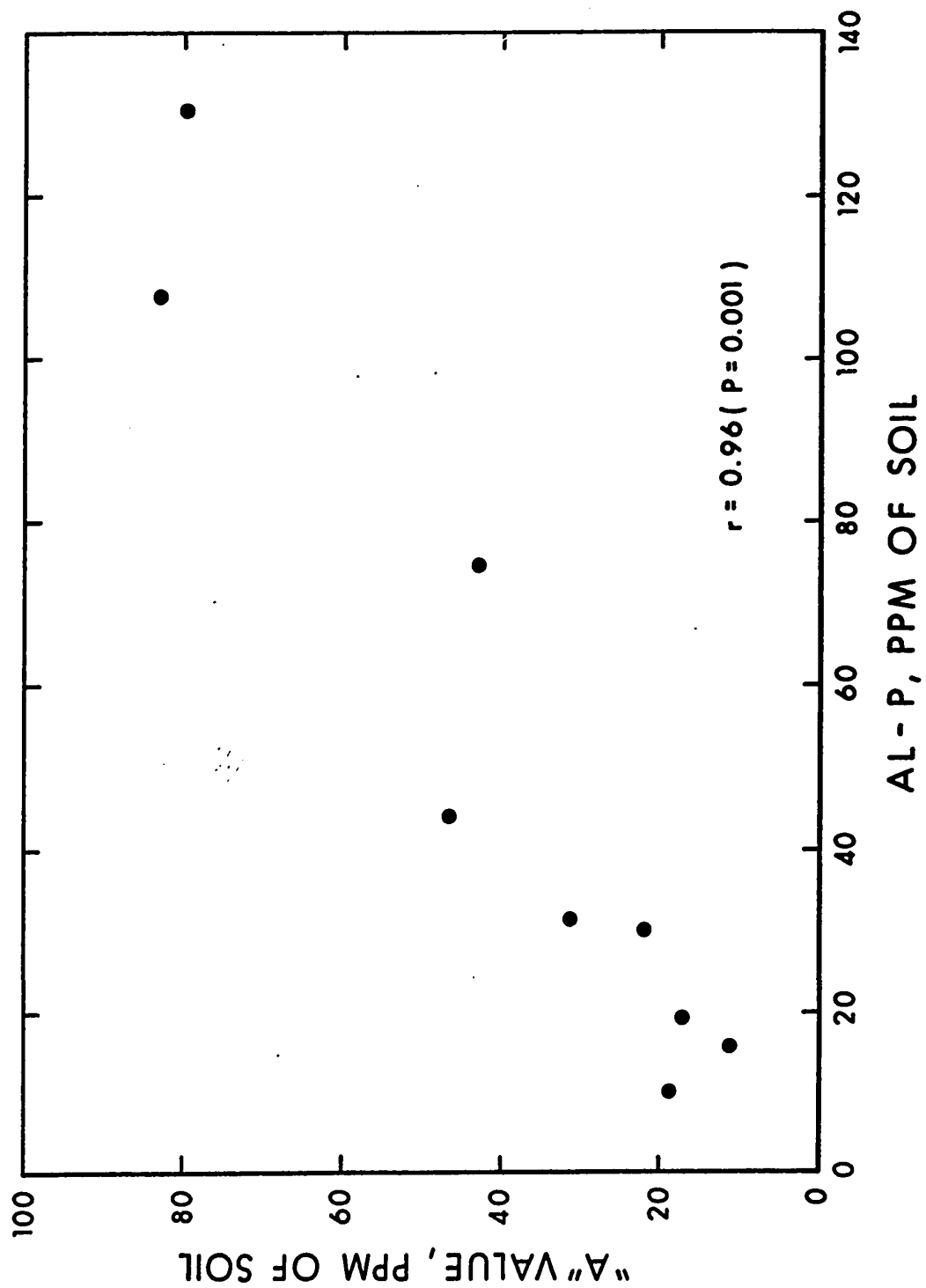


Figure 8 The Relationship between "A" Value and Al-P



the phosphate anion from the soil much like an anion exchange although a stoichiometric exchange of phosphate ions by bicarbonate ions may not occur (Nagarajah, et al., 1968). The  $\text{OH}^-$  ion activity (alkaline pH) of the reagent may also release some phosphorus from the aluminum and iron phosphates. Excess of bicarbonate anions suppresses the activity of  $\text{Ca}^{++}$  and minimizes the reprecipitation of calcium phosphates during extraction (Olsen, 1954) in the calcareous soils. Since similar values are obtained for Ee and Olsen P for these soils (regression equation  $\text{Ee} = 1.69 + 1.03 \text{ Olsen P}$ ) it seems that most of the phosphorus extracted by Olsen's reagent was surface phosphorus (Ee). The Miller and Axley reagent ( $0.03 \text{ N H}_2\text{SO}_4 + 0.03 \text{ N NH}_4\text{F}$ ) depending on the soils, may take out some of the phosphorus from Ca-P, Al-P, and Fe-P.  $\text{F}^-$  ions contained in the reagent may complex Al and/or Fe to release phosphates to the solution. Phosphate adsorbed onto the clay may be replaced and released by the  $\text{F}^-$  ions. Similarly the acid pH of the reagent can dissolve some phosphorus from the Ca, Al and Fe phosphates. Since surface phosphorus (Ee) is most likely to be first attacked by the chemical reagent, it is claimed that Miller and Axley reagent extracts the surface phosphorus (Ee) from the soil. Since the Ee values are about 60 percent of Miller and Axley P values, (regression equation,  $\text{Ee} = 2.8 + 0.59 \text{ Miller and Axley P}$ ) some of the difficultly available phosphorus (non surface phosphorus) must be extracted by the Miller and Axley reagent as well. Thus, the Miller and Axley method will overestimate the immediately available phosphorus status of the soil. The  $\text{NH}_4\text{F}$  reagent ( $0.5 \text{ N NH}_4\text{F}$ , pH-8.2) of the modified Chang and

Jackson procedure, being first in the sequence ( $\text{NH}_4\text{Cl}$  extracts very little P), appears to extract surface P (Ee) in addition to the Al-P from the soils. Nonselectivity of  $\text{NH}_4\text{F}$  reagent for Al-P was also noted by Weir and Soper (1962), Murrman and Peech (1969) and MacKenzie (1962).

If the chemical reagents cause considerable disturbance to the chemical framework of the soil and to the solid-liquid interface of the soil system, the redistribution of phosphorus compounds may take place during the extraction as claimed by Larsen (1967). My opinion is that the Miller and Axley reagent and Olsen's reagent are not sufficiently reactive to change the soil system to a great extent during the extraction. However, the  $\text{NH}_4\text{F}$  reagent of the Chang and Jackson procedure is very reactive and may extract some non available phosphorus of the soil (insoluble crystalline Al-P).

#### General Comments

It was found that the P uptake by plants was closely related to the Ie phosphorus concentration. It was also observed that soil's buffering capacity for phosphate (PBC) was a function of Ie concentration. The author thinks that the Ie concentration is an unique property of the soil. It is measured under conditions that cause little disturbance to the natural soil system. Since the Ie concentration represents the equilibrium phosphorus concentration of a soil system, in the event of P uptake by plants, the soil system will readjust in an attempt to maintain the Ie concentration. If the limited amount of soil around the roots is not sufficient to maintain the Ie concentration, the phosphorus concentration around the roots will be lowered. A

concentration gradient will be created and diffusion of P to the soil around the roots will take place. This means that the  $I_e$  concentration of the soil further away from the roots is lowered in the same manner as the soil around the roots. The results of the experiments on the movement of P to the roots (2nd Chapter) have clearly indicated that the movement of P to roots is mostly by way of diffusion in the P untreated soils. The amount of P diffusing to the roots depends on the concentration gradient. The upper limit for the concentration gradient is likely to be set by the  $I_e$  concentration of the soil. If the "rhizosphere effect" is prominent in the soil-plant system, phosphorus may be released to soil solution, and the net effect may be an increase in the soil solution concentration beyond the  $I_e$  value. Even under such conditions, the soil system will quickly readjust by adsorbing the phosphorus again in an attempt to maintain the concentration near to  $I_e$  value. In any event, the  $I_e$  concentration of the soil seems to be a very important factor affecting the P uptake in the soil plant system.

The quantity factor (as defined in this text) seems to also affect the P uptake by plants. The multiple correlation coefficient for the available phosphorus and  $I_e$  and  $E_e$  showed that both  $I_e$  and  $E_e$  are important factors in determining the available P status of the soils. It is suggested that the effect of the quantity factor ( $E_e$ ) on P supply to the plants is indirect. The phosphorus of the quantity factor is believed to be composed of two types. The one type is directly related to the solution phosphorus ( $Q_o$ ) and the second type ( $E_e - Q_o$ ) although not as closely related to  $I_e$  may contribute

phosphorus to the soil solution during the plant growth. Mechanisms (Rhizosphere influence and readjustment between (E-Qo) and Qo) for the release of phosphorus from quantity factor (Ee) to the solution during the plant growth are suggested.

Is it correct that the solid phase phosphorus is released to the solution by the proposed mechanisms? There is ample evidence that solid phase phosphorus contributes to a great extent the P supply to the plants. In order to account for the total P uptake by the plants from the soil solution, it is necessary to postulate complete renewal of soil solution phosphate on the average of ten times each day (Stout and Overstreet, 1950). This renewal of soil solution phosphorus each day has to be from the solid phase phosphorus. It is reasonable to suppose that the phosphorus (Qo) held at net exchange sites will pass into solution first to renew the phosphorus concentration in the solution. Even if root exudates release some phosphorus from Ee-Qo sites, the readjustment of the system will still occur.

#### Intensity and Quantity Factors for the Phosphated Soils

Phosphorus fertilization is a common practice in agriculture. Many cultivated soils are phosphated regularly. Although the primary object of the present investigation was to study the intensity and quantity factors in P untreated soils, it seemed desirable to prepare some phosphated soils in the laboratory to study the effect of applied P on the intensity and quantity factors of the soils. Since for the determination of the intensity and quantity factors,

it is necessary to obtain a uniform and well equilibrated phosphated soil system, the usual band application used in the field could not be simulated. However, it was reasoned that the 100 and 300 ppm of P treatments could simulate to some extent the application of low levels of P in the bands. Whatever may be the mode of fertilizer application, the applied phosphorus is mixed into the soil when land is prepared for the next crop. Therefore, the study of well mixed and equilibrated phosphated soil system seems to be appropriate for the present project.

"A" Values for the Phosphated Soils: It can be noted from Figure 9 that there is a fairly good linear relationship between the levels of applied P and the "A" values of the soils after equilibration. However, the relationship for Calcareous and Carbonated Dark Brown soils is not as good as that for Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake) soils. This suggests that at the higher levels of applied P, a greater proportion of the applied P is available in Calcareous and Carbonated Dark Brown soils as compared to the Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake) soils. At lower doses of applied P (100 ppm or less) the differences in the increase of "A" values (Figure 9) for the soils are relatively small indicating that the applied phosphorus is equally available irrespective of the chemical characteristics of the soils used. The linear relationship between "A" values and the levels of applied P for the Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake) soils suggests that the same proportion of applied P is available at 100 and

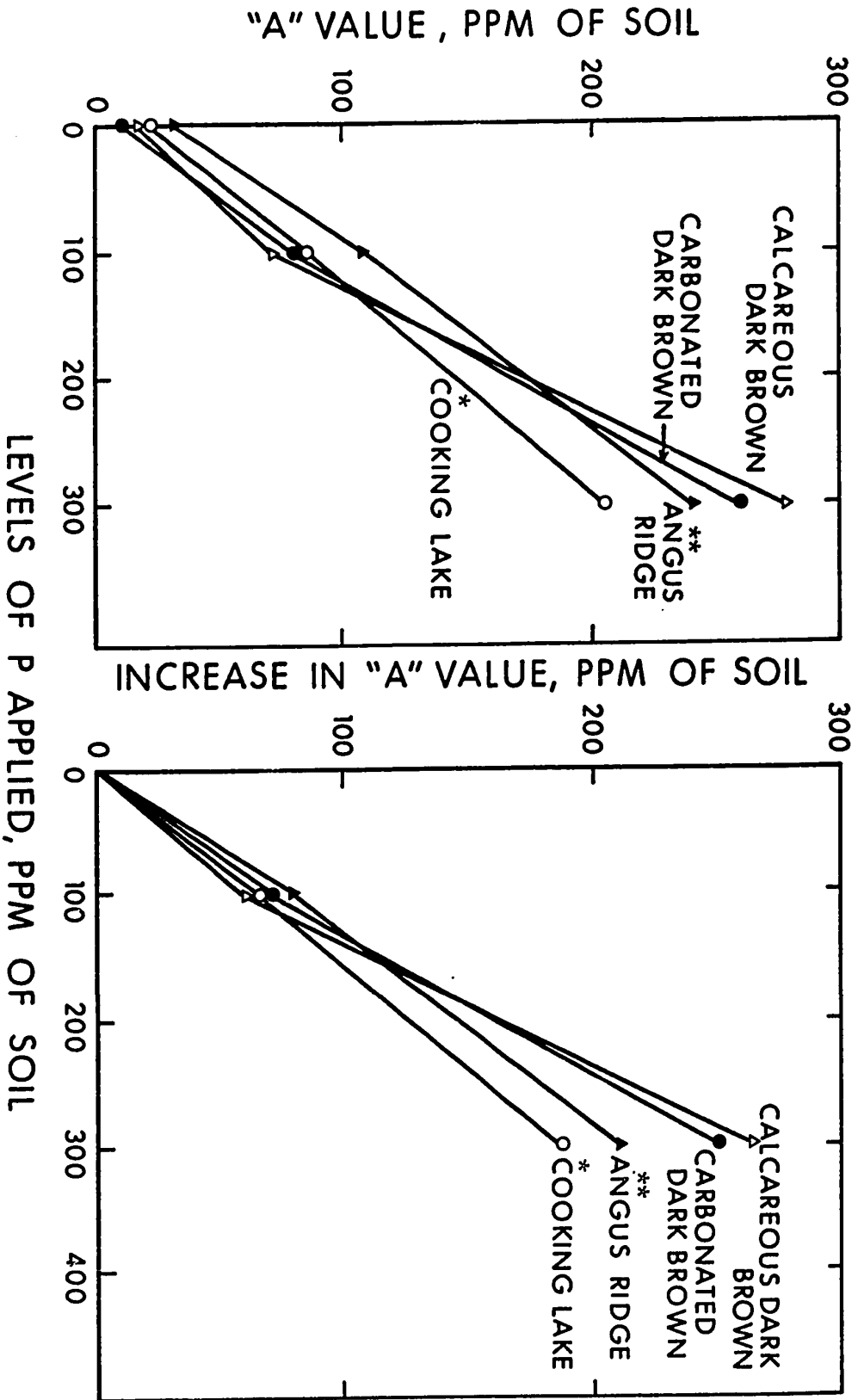


Figure 9 The Effect of Applied P on the "A" Values

\* Orthic Gray Wooded    \*\* Eluviated Black

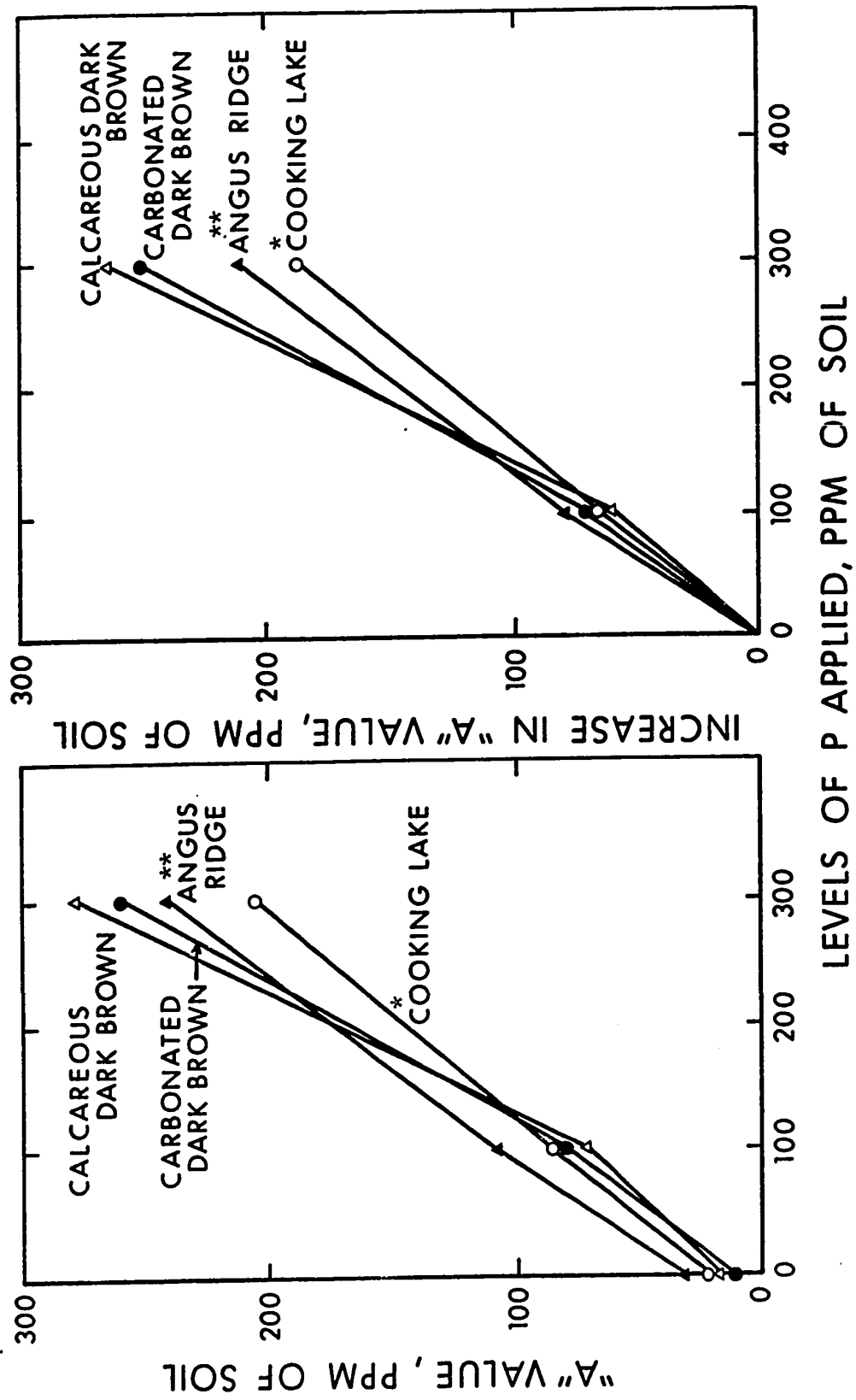


Figure 9 The Effect of Applied P on the "A" Values

\* Orthic Gray Wooded \*\* Eluviated Black

300 ppm of P treatments. The curves (Figure 9) are not extrapolated beyond 300 ppm of P treatments because it is uncertain that a linear relationship exists beyond the 300 ppm of P treatments. Most likely, the Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake) soils would follow the trend already shown by the Calcareous and Carbonated Dark Brown soils.

Intensity Factor for the Phosphated Soils: The data (Table 15) show that the "Ie" concentrations of the soils are increased 24 to 420 times the original values by the P treatments. It is of interest to note (Figure 10) that the Ie concentrations of the Calcareous and Carbonated Dark Brown soils are lower than those of the Orthic Gray Wooded (Cooking Lake) and Eluviated Black (Angus Ridge) soils at both the 100 and 300 ppm of P treatments. This implies that a greater amount of applied phosphorus is adsorbed and/or precipitated by the Calcareous and Carbonated Dark Brown soils, although, from the "A" values it apparently remains available. The data (Appendix B) indicate that the Orthic Gray Wooded (Cooking Lake) and Eluviated Black (Angus Ridge) soils have higher Al + Fe (acid ammonium oxalate soluble) contents, lower pH's and very low calcium carbonate equivalents as compared to the Calcareous and Carbonated Dark Brown soils. These factors, in addition to the type of clays seem to be responsible for the differences in adsorption and/or precipitation of added phosphates. The amount of adsorbed and/or surface phosphorus in phosphated soils is measured by the quantity factors discussed below. The nature of adsorbed and/or precipitated phosphorus in the phosphated soils is being studied further in this laboratory.



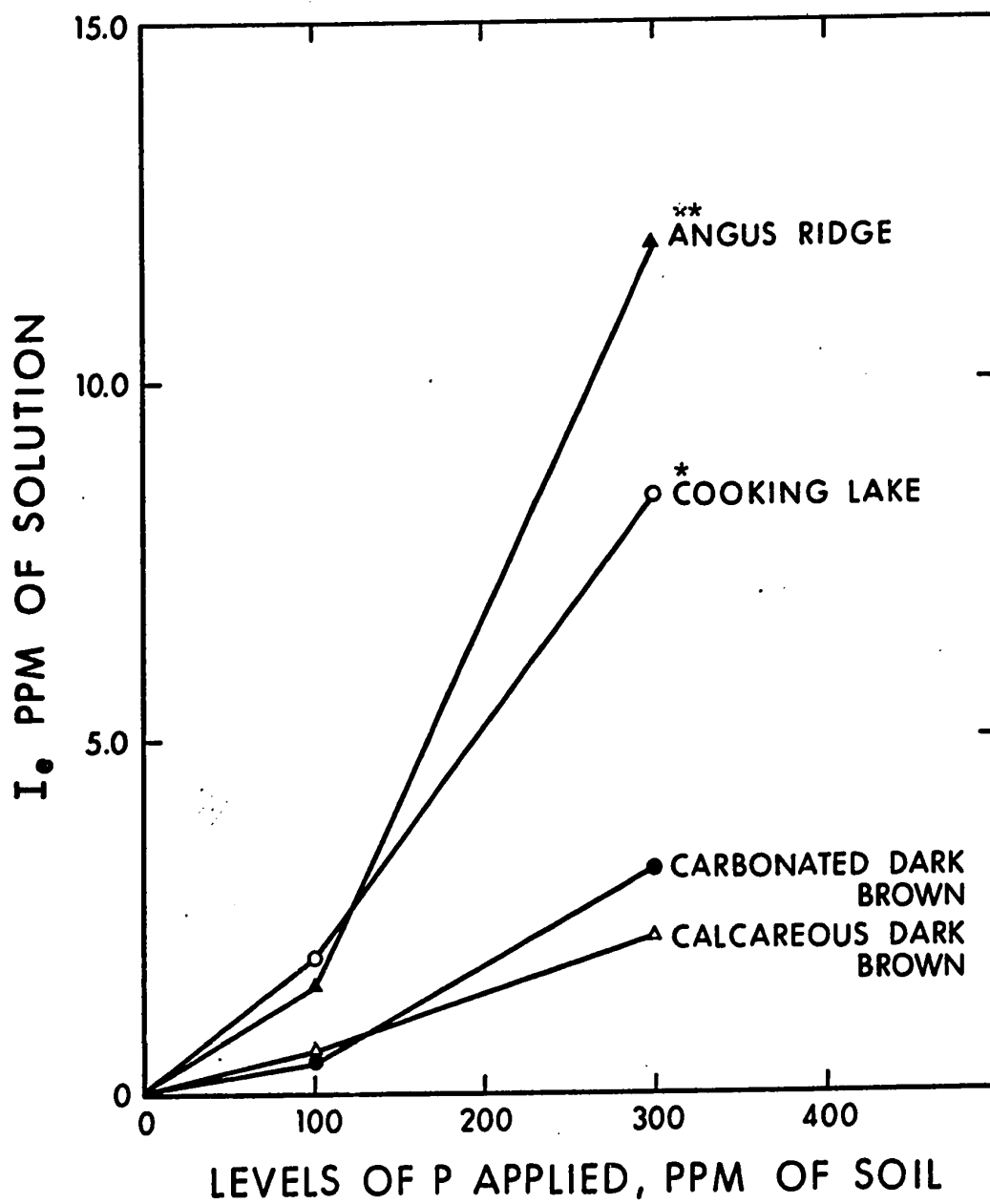


Figure 10 Effect of Applied P on the "Ie" Values

\* Orthic Grey Wooded    \*\* Eluviated Black

Table 15 Intensity and Quantity Factors for the Phosphated Soils

Soils	P treatment ppm	Ie ppm of solution	Ee ppm of soil	"A" values ppm	Miller and Axley P ppm	Olsen P ppm
Calcareous	0	0.01	7	17	9	8
Dark Brown	100	0.53	50	74	53	48
	300	2.10	104	282	147	160
Carbonated	0	0.02	9	11	6	5
Dark Brown	100	0.48	41	79	57	39
	300	3.20	120	263	169	155
Eluviated Black	0	0.04	9	31	12	13
(Angus Ridge)	100	1.50	54	109	61	48
	300	12.00	147	244	169	161
Orthic Gray	0	0.02	5	19	8	5
Wooded	100	1.89	64	85	67	50
(Cooking Lake)	300	8.40	75	206	173	84

Quantity Factors for the Phosphated Soils: The data in Table 15 and Figure 11 show the effect of addition of P to the soils on the Ee values. It can be noted from Figure 11 that Carbonated Dark Brown and Eluviated Black (Angus Ridge) soils tend to show a fairly good linear relationship between applied P and the Ee values much like the relationship between applied P and the "A" values. The relationship between applied P and Ee values is not linear for the Calcareous Dark Brown and Orthic Gray Wooded (Cooking Lake) soils. It appears that at higher rates of applied P, a greater proportion of the applied P becomes non exchangeable (Ee) in Orthic Gray Wooded (Cooking Lake) and Calcareous Dark Brown soils. While the Calcareous Dark Brown soil has a higher calcium carbonate equivalent than the carbonated Dark Brown soil, the Orthic Gray Wooded (Cooking Lake) soil is higher in amorphous Al and Fe oxides (acid ammonium oxalate soluble) than the Eluviated Black (Angus Ridge) soil. These chemical characteristics seem to be responsible for keeping a relatively smaller proportion of P applied at higher rates in the labile form (Ee) in Calcareous Dark Brown and Orthic Gray Wooded (Cooking Lake) soils. It can be also noted (Table 16) that Eluviated Black (Angus Ridge) soil had a fairly high Ee value at 300 ppm of P treatment. It was noted earlier that Eluviated Black (Angus Ridge) soil also had a higher Ie value. The lower percentage of  $\text{CaCO}_3$  equivalent and higher contents of organic matter in the Eluviated Black (Angus Ridge) soil seem to be the factors responsible for keeping a larger proportion of added P in Ie and Ee. An additional factor appears to be the lower contents of Al + Fe

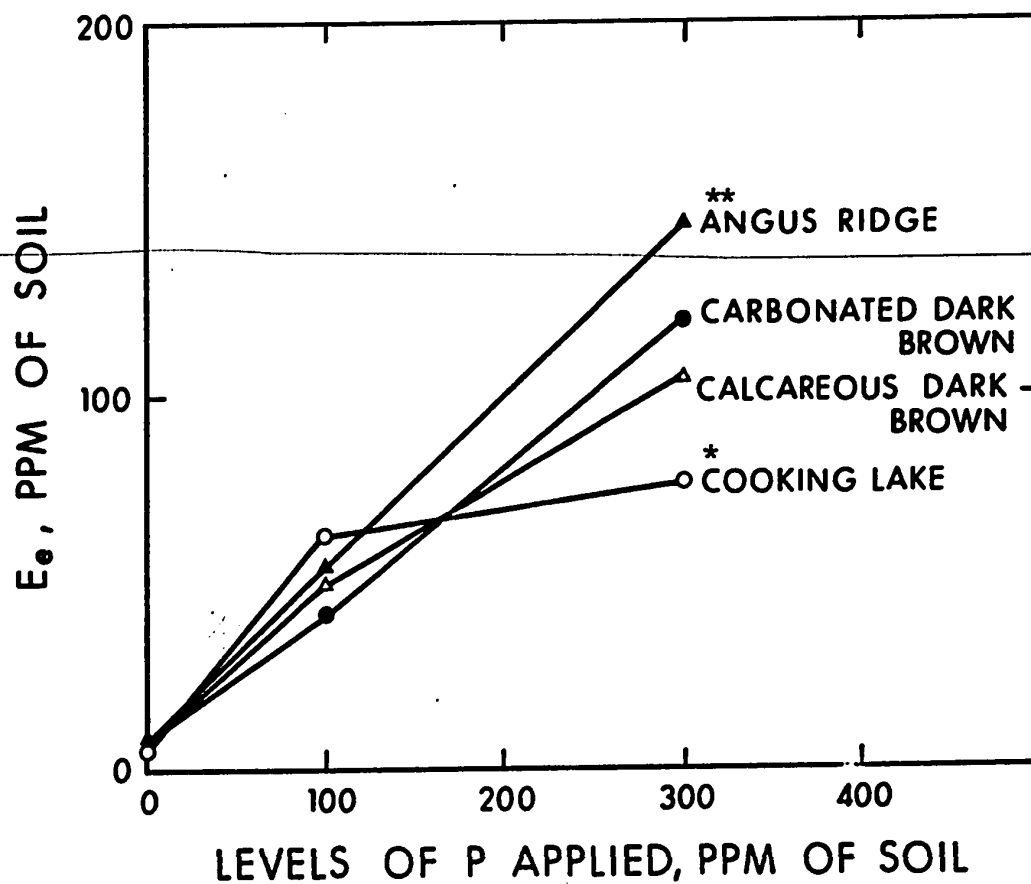


Figure 11 Effect of Applied P on the Quantity Factor ( $E_e$ )

\* Orthic Gray Wooded    \*\* Eluviated Black

Table 16 Percent Recovery of the Applied Phosphorus in the Various Phosphorus Forms

Soils	Percent of the applied P in			
	Al-P	Fe-P	Al-P+Fe-P	Ca-P
Calcareous Dark Brown 100 ppm P treatment	24	6	30	62
Calcareous Dark Brown 300 ppm P treatment	21	3	24	36
Carbonated Dark Brown 100 ppm P treatment	33	5	38	22
Carbonated Dark Brown 300 ppm P treatment	30	7	37	4
Eluviated Black (Angus Ridge) 100 ppm P treatment	60	33	93	-
Eluviated Black (Angus Ridge) 300 ppm P treatment	48	19	67	3
Orthic Gray Wooded (Cooking Lake) 100 ppm P treatment	44	47	91	-
Orthic Gray Wooded (Cooking Lake) 300 ppm P treatment	48	28	76	-

oxides than the Orthic Gray Wooded (Cooking Lake) soil.

The curves (Figure 12) clearly show that there is a good linear relationship between the Miller and Axley P and levels of P applied. This means that up to 300 ppm of P treatment, a definite proportion of applied P (44 to 59%) in these soils can be recovered by the Miller and Axley extracting solution. The data (Table 15) ( $0.03\text{ N NH}_4\text{F} + 0.03\text{ N H}_2\text{SO}_4$ ) show that the Miller and Axley P values for the phosphated Calcareous Dark Brown soils are lower than those of Eluviated Black (Angus Ridge) and Orthic Gray Wooded (Cooking Lake) soils. This seems to suggest that Miller and Axley reagent is comparatively less effective in removing P from phosphated Calcareous soils.

The curves (Figure 12) and the data show that there are only very small differences between the Olsen P values for phosphated Eluviated Black (Angus Ridge), Calcareous and Carbonated Dark Brown soils. This indicates that sodium bicarbonate reagent is equally effective in removing P from the Calcareous and acidic soils (Angus Ridge being a slightly acidic soil). The effect of 300 ppm of applied P on the Olsen P value for the Orthic Gray Wooded (Cooking Lake) soil is different from what is noted for the other three soils. It is suggested that some of the applied P in the 300 ppm treatment of the Orthic Gray Wooded (Cooking Lake) soil is bonded to phosphate sites so that the bicarbonate reagent (Olsen P) is not effective in removing it. It is also suggested that the phosphorus from these sites is extracted by the Miller and Axley reagent ( $0.03\text{ N H}_2\text{SO}_4 + 0.03\text{ N NH}_4\text{F}$ ). Such a situation could occur

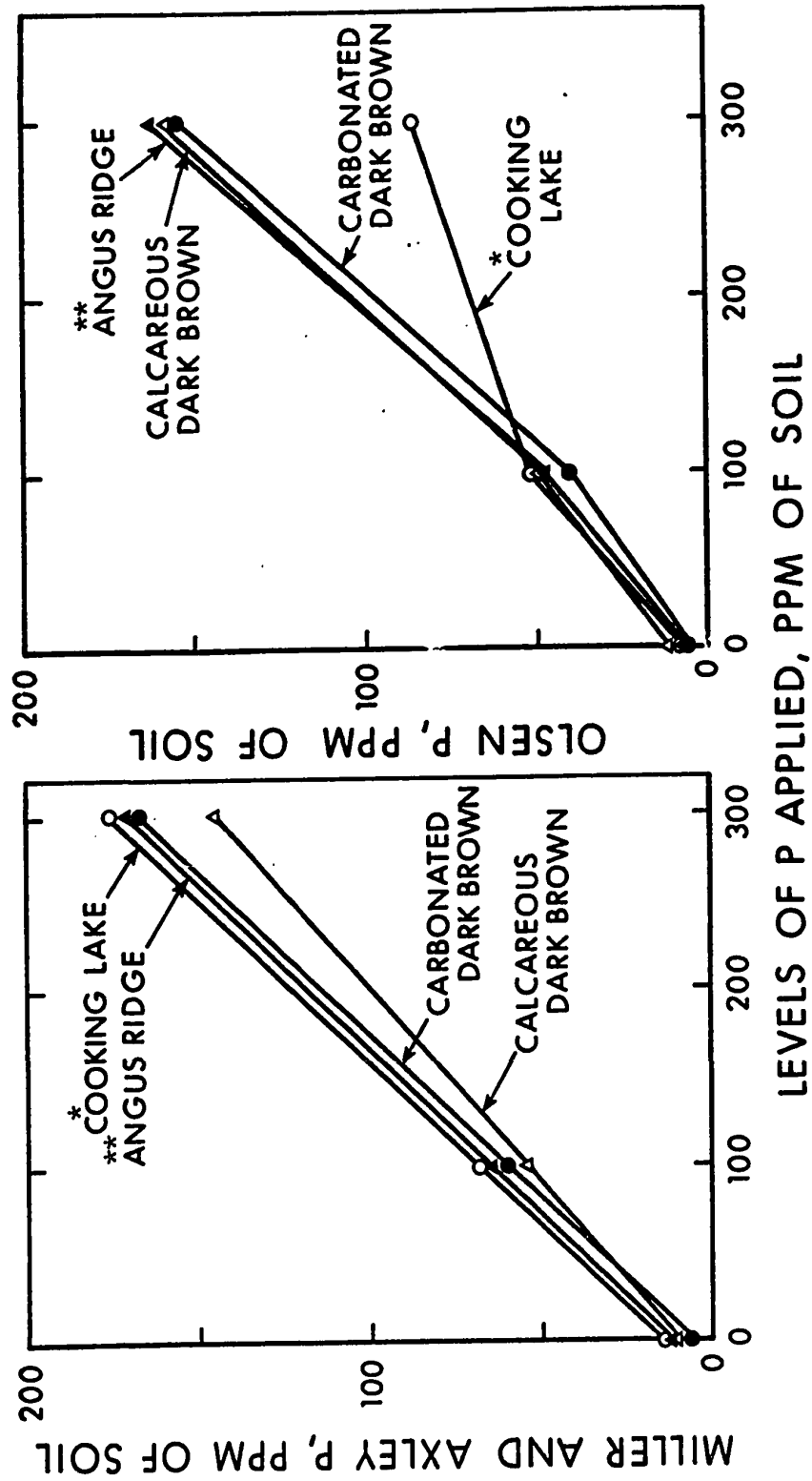


Figure 12 Effect of Applied P on the Miller and Axley P and Olsen P

\* Orthic Gray Wooded \*\* Eluviated Black

if the applied phosphorus reacted with aluminum and/or iron (pH 5.5 of the Cooking Lake soil is low enough to expect some Al and Fe ion activities) to form precipitates and/or amorphous particles of iron and aluminum phosphates which would be fresh and active enough to allow  $F^-$  complexing of some Al or Fe thereby releasing phosphates to the solution. The data (Table 16) on the phosphorus fractionation of the phosphated soils seem to support the above view. The percent recovery of added P in Al + Fe - P in the Orthic Gray Wooded (Cooking Lake) soil at 300 ppm of P treatment is higher than for any of the other soils.

The data (Table 17) indicate that none of the quantity or intensity factors for the phosphated soils is very well related to the "A" values. All the three methods of measuring the quantity factor seem to give similar information on the available phosphorus of the phosphated soils. More research work is needed to find out the nature of phosphorus measured by these methods in phosphated soils. It was remarked earlier that the nature of phosphorus extracted by the Miller and Axley reagent and Olsen's extractant from the P untreated soils is not satisfactorily known although some information can be drawn from the knowledge of the chemical composition of the reagents used and soils being tested.



Table 17 Ordering of the Phosphated Soils According to the Values for "A", Ee, Miller and Axley P, Olsen P and Ie

P treatment		Soils numbered from 1 to 8 in order of increasing values				
ppm of soil	"A" values	Ee +	Miller & Axley	Olsen P	Ie	
Calcareous Dark Brown 100	1	2	1	2	2	
Carbonated Dark Brown 100	2	1	2	1	1	
Orthic Gray Wooded (Cooking Lake) 100	3	4	4	4	4	
Eluviated Black 100 (Angus Ridge)	4	3	3	3	3	
Orthic Gray Wooded (Cooking Lake) 300	5	5	8	5	7	
Eluviated Black 300 (Angus Ridge)	6	8	6	8	8	
Carbonated Dark Brown 300	7	7	7	6	6	
Calcareous Dark Brown 300	8	6	5	7	5	

## CHAPTER IV

### SUMMARY

Several soils of Alberta with P treatments on some were investigated for assessing the intensity and quantity parameters of phosphorus. The experiments involved the growth of plants, chemical extraction of desired phosphorus forms,  $^{32}\text{P}$  labelling, the use of equilibrium techniques, and the development of suitable analytical methods for inorganic phosphorus and  $^{32}\text{P}$  determinations. First, satisfactory analytical procedures for inorganic phosphorus determination in dilute solutions and  $^{32}\text{P}$  determination in the plant samples were developed and the methods have been published (see Appendix). The new method for inorganic phosphorus determination has increased the sensitivity of the usual ascorbic acid method by a factor of approximately 4. The method for  $^{32}\text{P}$  determination is very simple and allows the measurement of  $^{32}\text{P}$  in the undigested plant samples without any loss of  $^{32}\text{P}$  by self absorption.

To study the movement of P to roots growing in the soils, a plant growth room experiment was conducted using seven P untreated and four P treated (300 ppm of P treatment) soils. The procedures of Barber and coworkers for calculating the contribution to P delivery of mass flow, diffusion and root interception were modified. It was found that the diffusion of P to the roots is a major process of P transport in P untreated soils. Mass flow of P to the roots was found to be the most significant process in the transport of P in soils treated with high doses of P and it is likely to be an

important process in soils where phosphatic fertilizers are band placed. Root interception of P was found to be unimportant process in P transport to the roots. The dependence of mass flow, root interception and diffusion of P on the soil solution phosphorus concentration was discussed. A correlation coefficient of 0.82 ( $P = 0.05$ ) was obtained between P uptake and soil solution P concentration. The research work done on the movement of P to the roots has also been published (Appendix F).

The routine method of growing the plants under controlled conditions was compared with a more specialised technique ("A" value). A correlation coefficient of 0.94 ( $P = 0.001$ ) was obtained between the results of the methods when P treated and P untreated soils were included in the comparison. When P treated soils were excluded from the comparison, a correlation coefficient of 0.98 ( $P = 0.001$ ) was obtained. Both the methods seem to give similar information on the nutrient status of the soils.

$^{32}\text{P}$  exchange experiments were conducted on four selected soils. It was found that the initial exchange reaction was extremely fast. The rate of exchange ( $\mu\text{gP/g soil/hr}$ ) during the first hour was 10 to 225 times higher than the rate of exchange observed after 24 hrs. Based on the knowledge of phosphorus characteristics, available phosphorus status ("A" values), root extension and the exchange rates for these soils, it was concluded that the rates of exchange of soil phosphorus after the 1 hour period are too slow to have any great influence on the immediate supply of phosphorus to the plants.

The soil solution phosphorus concentration (intensity factor) was found to be a very important factor in determining the available phosphorus status of the soils. A correlation coefficient of 0.81 ( $P = 0.01$ ) was found between  $\log I_e$  (intensity factor) and the "A" value (available phosphorus). This supported the earlier finding that soil solution phosphorus is closely related to P supply to the plants. It was also found that the phosphorus buffering capacity is closely related to the  $I_e$  concentration. The processes that are likely to take place during the active uptake of P by plants were discussed in relation to the  $I_e$  values. It was concluded that  $I_e$  value is a unique property of the soil system. Its measurement has the advantage that the natural framework of the soil and the nature of the solid-liquid interface are least disturbed during the measurement.

Since all the variation in the available phosphorus ("A" value) could not be explained by the intensity ( $I_e$ ) factor alone, the quantity factor ( $E_e$ ) was considered as an additional factor. The direct comparison of  $E_e$  and  $Q_o$  with "A" value indicated that  $E_e$  is better correlated with "A" than is the  $Q_o$ . This was the basis for the conclusion that  $E_e$  is a better measure of quantity factor than the  $Q_o$ . However, it was argued that the phosphorus measured as  $E_e$ , to be important in phosphorus supply to the plants, must pass into the solution before being absorbed by the plants. Mechanisms (action of root exudates, readjustment of  $E_e$ - $Q_o$  with  $Q_o$ ) for the release of  $E_e$  phosphorus to  $I_e$  phosphorus were suggested. Since the correlation between  $E_e$  and  $I_e$  was not significant at the

5 percent level, Ee and Ie were considered essentially independent of each other. Moreover, it was found that at a given Ie value, the "A" values increased with Ee values. Because of these observations, a multiple linear regression and correlation coefficient were calculated using available phosphorus ("A" value) as a function of log Ie and Ee. The regression equation and correlation coefficient were 
$$A = 2.11 + 15.90 \log_{10} Ie + 1.51 Ee$$
 and 0.972 respectively. It is claimed that this equation should be of great practical value to predict the available phosphorus of the soils.

Since chemical extraction procedures are by far the most commonly used methods to determine the "available phosphorus" of the soils, it was thought desirable to compare the results obtained by using these methods with the quantity factor (Ee). The comparisons between Miller and Axley P, Olsen P, Al-P and Ee revealed that all of these factors were highly correlated among themselves but they differed considerably in the absolute values. Olsen P values on the average were slightly less than Ee values for the P untreated soils. The amounts of Al-P in the soils were about 2 to 5 times higher than those of Olsen P or Ee and about 1.5 to 3 times larger than those of Miller and Axley P. It was claimed that Olsen P, Miller and Axley P and Al-P includes most, if not all, of the surface P (Ee).

The data on "A" values for the phosphated soils suggested that at higher levels of applied P, a greater proportion of applied P is available in Calcareous and Carbonated Dark Brown soils. It was found that the Ie concentration of the soils were increased 24 to 420 times the original values by the P treatments. Ee, Miller and

Axley P and Olsen P values were increased approximately 4 to 20 times the original values by the P treatments. The comparison of all these values with "A" values suggested that none of the factors are very well related to the "A" values. The complete fractionation of phosphorus of the phosphated soil is being further investigated in this laboratory.

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# APPENDIX A

## Classification and Legal Locations of the Soils

Soil No.	Order	Great Group	Subgroup	Series	Legal location
1	Chernozemic	Brown	Orthic	Maleb	SE 1-12-17-W4
2	Chernozemic	Dark Brown	Calcareous	--	NW 22-7-25-W4
3	Chernozemic	Dark Brown	Carbonated	--	Lethbridge Research* station, Lethbridge (irrigated rotational trial)
4	Chernozemic	Black	Orthic	Peace Hills	NE 24-40-24-W4
5	Chernozemic	Black	Eluviated	Angus Ridge	SE 11-54-22-W4
**6	Chernozemic	Black	Solodic	--	NE 28-42-14-W4
7	Luvisollic	Gray Wooded	Orthic	Cooking Lake	SE 28-52-21-W4
8	Luvisollic	Gray Wooded	Orthic	Glory	NW 22-51-2-W5
9	Luvisollic	Gray Wooded	Orthic	Breton	NW 29-41-23-W4

\* The soil was collected from the check plot where no P is applied

\*\* Although this soil has been classified in the Chernozemic order, the field observations of the profile indicated that it had marginal characteristics of Solodic Black and Black Solod.



APPENDIX B

Some Physical and Chemical Characteristics of Soils  
(oven dry basis)

Soil No.	Soil	Particle size analysis			class	Soil Moisture		pH in	
		sand %	silt %	clay %		1/3 Atm. %	15 Atm. %	water	0.01M CaCl <sub>2</sub>
1	Orthic Brown (Maleb)	42	38	20	L	21	10	7.1	7.1
2	Calcareous Dark Brown	37	38	25	L	26	12	7.8	7.4
3	Carbonated Dark Brown	57	20	23	SCL	23	10	7.8	7.3
4	Orthic Black (Peace Hills)	56	23	21	SL	28	15	5.6	5.5
5	Eluviated Black (Angus Ridge)	38	36	26	L	33	16	6.3	6.2
6	Solodic Black	42	37	21	L	27	12	5.2	4.9
7	Orthic Gray Wooded (Cooking Lake)	40	45	15	L	23	7	5.8	5.5
8	Orthic Gray Wooded (Glory)	4	73	23	SiL	34	11	6.5	6.2
9	Orthic Gray Wooded (Breton)	45	44	11	SL	23	7	5.9	5.6

APPENDIX B Continued .....

Organic C %	CaCO <sub>3</sub> equiv. %	Acid ammonium oxalate soluble		Total P ppm	Extractable P ppm	
		Fe %	Al %		Miller and Axley	Olsen
1.19	0.14	0.15	0.05	435	12	7
2.44	7.12	0.17	0.04	615	9	8
1.36	3.03	0.16	0.03	556	6	5
4.80	trace	0.31	0.09	833	23	18
5.69	0.12	0.39	0.12	925	12	13
3.64	trace	0.34	0.14	864	62	36
1.44	trace	0.67	0.21	355	8	5
2.23	0.11	0.49	0.08	880	50	22
2.05	trace	0.26	0.08	537	31	18

APPENDIX C

MICRO METHOD FOR TOTAL P DETERMINATION IN PLANT SAMPLES

P.K. Omanwar

July, 1968

- Grind the plant material to pass through a 40 mesh sieve.
- Weigh 0.05 g of plant material to the nearest 0.1 mg and transfer to a 20 ml pyrex test tube.
- Add 4 ml of ternary mixture of concentrated  $H_2SO_4$   $HClO_4$  (70%) and concentrated  $HNO_3$  (ratio 1:1:8).
- Mix the plant material with the mixture of acids.
- Put the tube in a 600 ml beaker containing 300 ml of fine sand so that 1/4th of the tube is buried in the sand.
- Put the beaker on the hot plate and cover it with a glass fume hood connected to water aspirator pump.
- Switch on the hot plate to heat the beaker to  $180^\circ C$ . Continue digestion at  $180^\circ C$  for about three hours or until the acid mixture is volatilized and the remaining solution is clear. Be sure of the temperature and disposal of the fumes.
- Remove the tube from the beaker when digestion is complete.
- Take up the residue from the digestion tube first with 5 ml of concentrated  $HCl$  and then with 5 ml 6 N  $HCl$ .
- Transfer the solution to a graduated centrifuge tube and rinse the tube with 6 N  $HCl$  to make up the volume to 25 ml. Never wash with distilled water.
- Stir the contents of the centrifuge tube with an air jet stirring rod.
- Centrifuge at 12,000 rmp (or more) for 10 minutes to get a clear solution.
- Decant the supernatant liquid into a clean bottle and stopper it firmly. This is the main stock solution.
- Transfer an appropriate quantity of this solution to a 25 ml flask.

- Adjust the pH to 5.0 using p-nitrophenol indicator. (Colorless below 5.0).
- Add 4 ml of reagent 'A' of the ascorbic acid method.
- Make up the volume with distilled water.
- Read the absorbance at 882 mμ using a spectrophotometer. Calculate the ppm of P in solution using a standard curve.

#### PRECAUTIONS

1. Perchloric acid is a very strong oxidizing agent. There is always some danger of explosion. Use face mask and hand gloves. Do most of the work in the fume hood.
2. After every two or three runs wash off the hood and clean the tubing to avoid deposition of acid fumes.
3. Perchloric acid attacks every metal except stainless steel. Use either glass or stainless steel water aspirator.

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APPENDIX D

A MICRO AND RAPID METHOD FOR MEASURING

$P^{32}$  IN PLANT SAMPLES

In the measurement of available phosphorus of soils by the "A" value technique, many plant samples must be analyzed for  $P^{32}$ . Therefore a simple and rapid method for measuring  $P^{32}$  in the plant samples is desirable.  $P^{32}$  content of plant samples has been determined in the solid<sup>13</sup> as well as liquid<sup>2</sup> forms. Hall and MacKenzie<sup>1</sup> discussed the advantages and disadvantages of measuring  $P^{32}$  in the solid and liquid forms and recommended the preparation of  $P^{32}$  samples in the solid form. The usual method for measuring  $P^{32}$  in plant material using the solid form is to prepare briquets or to place the loose powdered plant material<sup>3</sup> into planchets to an "infinite" thickness. The first method requires a large amount of plant material and equipment to press the plant material into briquets. The second method may result in contamination of the window of the Geiger tube with the loose plant material. Moreover the limited space between the sample holder and ultra thin window of gas flow counters attached to automatic sample changers now being widely used do not permit the use of very thick briquets. Since the samples are automatically moved to the detector, the uniformity of the loose plant material in the planchet may be disturbed. To avoid contamination of the window of the Geiger tube with radioactive material, a binder such as collodion solution can be used<sup>4</sup>. Such a solution is not desirable for measuring isotopes emitting soft beta particles

because of self absorption. Therefore, we attempted to devise a micro and rapid method by using water as a binder for plant material.

To test the method, we ground oven dry (70° C) unlabelled plant material to 40 mesh. We transferred 0.05, 0.10, 0.15 and 0.30 g of plant material to stainless steel, cup shaped planchets of 2.54 cm diameter. To each of the planchets, we added about a millilitre of distilled water. The plant material was mixed with the water by tapping and rotating the planchets. Then 0.1 millilitre of radioactive ( $P^{32}$ ) solution was added to the two planchets containing 0.05 g of plant material. Likewise, 0.2 millilitre was added to the 0.10 g, 0.3 millilitre to the 0.15 g and 0.6 millilitre to the 0.30 g samples. The planchets were then tapped and rotated again to mix the radioactive solution with the slurry of the plant material. The samples were kept for 15 minutes to obtain a equilibrium between the solution and plant material. After equilibration the planchets were transferred to a hotplate to evaporate the water. Slow evaporation of water allowed the plant material to stick together as well as to adhere to the bottom of the planchets. When the water was completely evaporated, we found that a fine cake of the plant material was formed and attached to the bottom of the planchets. The planchets were then cooled and the  $P^{32}$  activity was measured using a gas flow counter equipped with automatic sample changer and print out attachment. After completion of the counting, the Geiger tube was checked for contamination of radioactive material. We found the same background count rate before and after the counting and hence concluded

that the Geiger tube was not contaminated with radioactive material.

The data (Table 1) clearly show that the loss of counts with increasing thickness up to 0.15 g plant material per planchet is less than 5%. This means that the losses due to self absorption of beta particles were negligible. A thickness of more than 0.15 g plant material per planchet causes a considerable loss of counts due to self absorption. The satisfactory duplicates indicate a good reproducibility of the method.

We measured the  $P^{32}$  content of the many plant samples from our "A" value experiment using this method. The only major operation in the method is to transfer a weighed quantity of powdered plant material to the planchet. The use of an automatic sample changer and print out attachment made it possible to stack 50 planchets at one time and greatly reduced the time otherwise required to handle the many samples.

#### SUMMARY

A rapid method for measuring  $P^{32}$  in ground, undigested plant material is described.

#### ACKNOWLEDGEMENTS

The authors wish to acknowledge financial assistance from the Canadian Commonwealth Scholarship and Fellowship Committee and National Research Council.

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Table 1 Data on Self Absorption

Sample No.	Plant material g/planchet	Radioactive solution ml/planchet	Counts per minute corrected for background	Average counts per minute and average deviation	Percent loss based on the first sample
1 a	0.05	0.1	869	886±17	0.0
b	0.05	0.1	903		
2 a	0.10	0.2	1687	1700±13	4.2
b	0.10	0.2	1713		
3 a	0.15	0.3	2552	2591±38	2.6
b	0.15	0.3	2629		
4 a	0.30	0.6	4819	4796±23	10.9
b	0.30	0.6	4773		

method the absorbance readings were made on the remaining set, using the same path length and spectrophotometer.

Examination of the two standard curves (Fig. 2) indicated clearly that a satisfactory standard curve was obtained by the isobutanol extraction method, and the sensitivity of the ascorbic acid method was increased by a factor of approximately four.

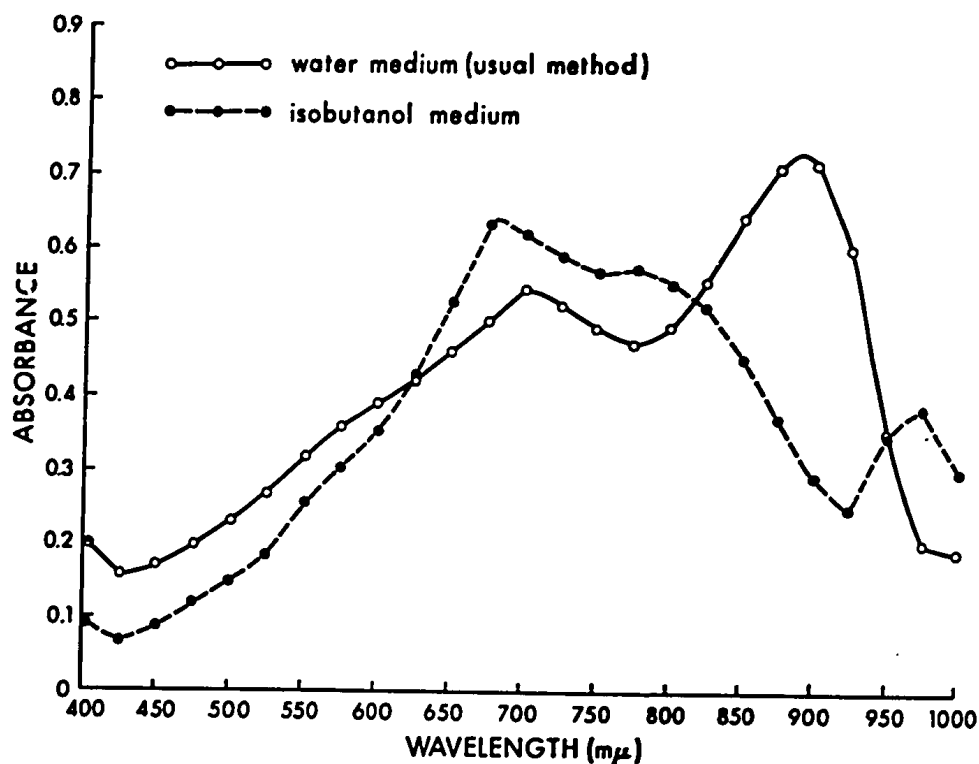


FIG. 1. The absorption curves for the ascorbic acid-reduced molybdophosphoric acid in water medium (usual method) and in isobutanol medium (0.1 ppm of P; 10-cm cells).

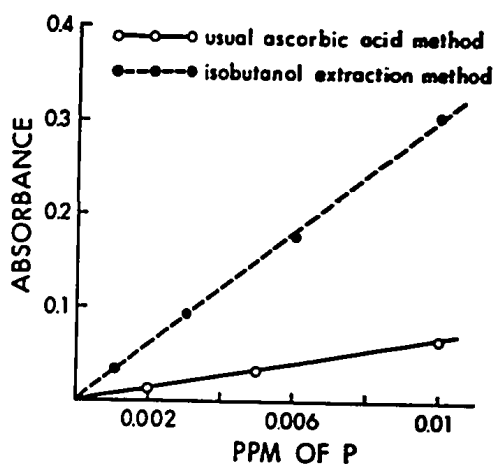


FIG. 2. The calibration curves for the usual ascorbic acid method and isobutanol extraction method (10-cm cells; Cary spectrophotometer).

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To test the general applicability of the method to soil solutions, an unfertilized carbonated soil (pH 7.8) from the Lethbridge Research Station was selected. The soil contained 5 ppm of  $0.03\text{ N NH}_4\text{F} + 0.03\text{ N H}_2\text{SO}_4$ -soluble P, but it was not possible to measure accurately the calcium chloride-soluble P by the usual ascorbic acid method. A 200-ml  $\text{CaCl}_2$  extract of this soil (soil to solution ratio 1:1) was obtained and phosphorus was determined by the modified ascorbic acid method described above. The concentration of phosphorus in the soil extract was found to be 0.0051 ppm of P.

It is concluded from the data that concentrating the molybdophosphoric acid in isobutanol makes it possible to increase the sensitivity of the ascorbic acid method so that it becomes suitable for very dilute solutions.

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### MODIFICATION OF THE ASCORBIC ACID METHOD FOR DETERMINING PHOSPHORUS IN DILUTE SOLUTIONS<sup>1</sup>

In the measurement of the phosphate potential ( $\frac{1}{2}$  pCa + pH<sub>2</sub>PO<sub>4</sub>) of soils, solutions of extremely low phosphorus concentration pose an analytical problem. Methods of solving this problem are to use either more sensitive methods such as activation analysis, or to modify the existing colorimetric methods. In the past, colorimetric methods for dilute solutions have been modified by adding a phosphorus standard to the test solutions, by concentrating the test solutions by ion exchange resins (2) or evaporating before adding the complexing reagent, or by concentrating the colored complex after adding the complexing reagent. Some workers (4, 6) have used isobutanol for concentrating the unreduced molybdophosphoric acid in the chlorostannous method. The ascorbic acid method (3, 5) has been successfully used in this laboratory for determining total (1) and calcium chloride-soluble phosphorus of soils. We studied the feasibility of improving the sensitivity of the ascorbic acid method by concentrating the molybdophosphoric acid complex in isobutanol.

Preliminary observations, based on absorbance readings, showed that extracting the ascorbic acid-reduced molybdophosphoric acid was superior to extracting the unreduced molybdophosphoric acid. Therefore, the subsequent studies were restricted to extracting reduced molybdophosphoric acid.

It was necessary to determine if the absorption maximum of the ascorbic acid-reduced molybdophosphoric acid was different in isobutanol from that in water (usual medium). To do this, we used the ascorbic acid method (5) to develop the color in two 50-ml samples containing 0.1 ppm P. After more than 30 minutes, one of the samples was transferred to a separatory funnel containing 40 ml of isobutanol and the mixture was shaken for a few seconds. The aqueous layer was discarded and the isobutanol layer was made up to 50 ml with isobutanol. Absorption curves of the unextracted water solution (usual medium) as well as the isobutanol medium (as described) were determined over the range 400–1000 m $\mu$ , using a Cary spectrophotometer with a 10-cm path length.

The absorption curve (Fig. 1) for the usual method had a maximum at 882 m $\mu$  and was similar to the one published by Murphy and Riley (3). The absorption curve of ascorbic acid-reduced molybdophosphoric acid in isobutanol was clearly different. The maximum absorption peak was found to be at 690 m $\mu$ , with a second, smaller absorption peak at 975 m $\mu$ .

To compare the sensitivity of the usual ascorbic acid method with the proposed method of concentrating the reduced molybdophosphoric acid in isobutanol, two sets of appropriate phosphorus standards were made in 200 ml of water and the color was developed by the usual ascorbic acid method (5). The colored complex from one of the sets was extracted in 50 ml of isobutanol and the absorbance readings were made on this isobutanol extract at 690 m $\mu$ , using a 10-cm cell in a Cary spectrophotometer. For the usual ascorbic acid

<sup>1</sup>Contribution from the Department of Soil Science, University of Alberta, Edmonton, Alberta. This investigation includes a portion of the thesis to be submitted by the author in the partial fulfilment of requirements for Ph.D. degree at the University of Alberta.

method the absorbance readings were made on the remaining set, using the same path length and spectrophotometer.

Examination of the two standard curves (Fig. 2) indicated clearly that a satisfactory standard curve was obtained by the isobutanol extraction method, and the sensitivity of the ascorbic acid method was increased by a factor of approximately four.

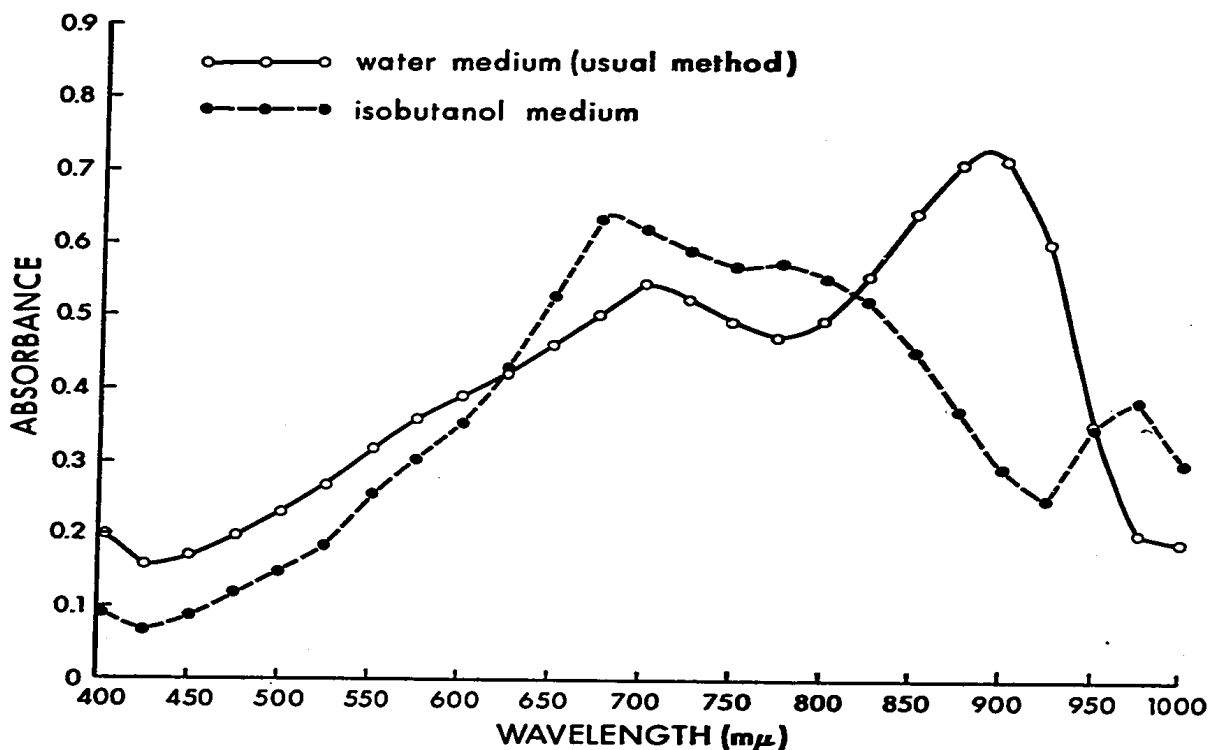


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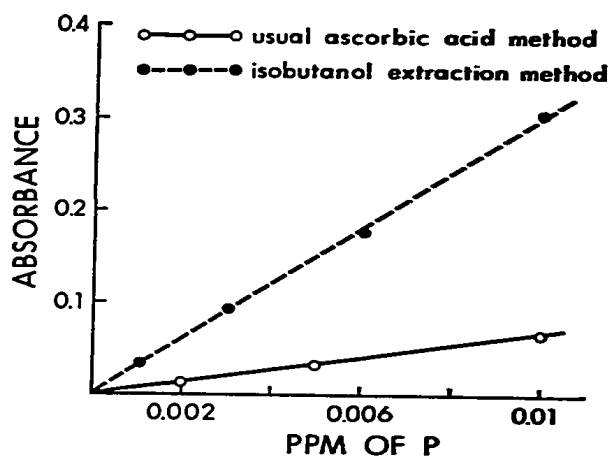


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Received November 20, 1968.

## APPENDIX F

### MOVEMENT OF PHOSPHORUS TO BARLEY ROOTS GROWING IN SOIL

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#### ABSTRACT

A plant growth room experiment was conducted using seven soils of Alberta with a treatment of 300 ppm of P on four of the soils. The contributions to the movement of P to the roots were calculated according to the method of Barber and co-workers, with some modifications. Results of the experiment showed clearly that movement by mass flow was the most important process of P transport to roots in soils treated with 300 ppm of P. Apparent diffusion was found to be the major process of P movement to roots in untreated

soils, which included two soils with naturally high levels of available P. Root interception was found to be of least importance in P movement to roots. Since the concentration of P in soil solution affected the amounts of P reaching the roots by diffusion, mass flow or root interception, the importance of the determination of soil solution P is emphasized. A correlation of 0.86 was obtained between the yield and soil solution P concentration of the untreated soils.

#### INTRODUCTION

In a soil-plant system, ions must move to the roots before they can be absorbed. Barber and co-workers (2, 7, 10, 11) have shown that three processes involved in the movement of ions to roots are mass flow, diffusion, and root interception. They studied the relative importance of the three processes in supplying Ca, Mg, K, Na, Mn, Fe, B, Cu, Zn, Al, Sr, and Mo to roots growing in soil. Shapiro *et al.* (16) thought that the most probable mechanism for the movement of P to roots was mass flow. Olsen *et al.* (12) and Lewis and Quirk (8), however, favored ion diffusion as the major mechanism. Bouldin (3) argued that the P concentration of soil solution would need to be greater than 2 ppm if all of the P moved to the roots by mass flow. Fried and Broeshart (4) suggested that the soil solution would have to contain 20 ppm of P to account for the entire uptake of P by mass flow. Obviously, the relative importance of mass flow and diffusion in P movement to the roots cannot be stated categorically.

Therefore, we conducted this project in order to increase our knowledge of the role of mass flow and diffusion in P movement to roots, to suggest improvements in the procedures used for calculating the contribution of mass flow and root interception in P movement, and to study the effect of adding P to soils on the contribution of mass flow and diffusion of P to the roots.

#### MATERIALS AND METHODS

The seven soils we used were collected from the Ap horizons. Portions of four of the soils received a treatment of 300 ppm of P in the form of  $\text{KH}_2\text{PO}_4$  solution which was sprayed on to the soil and mixed in thoroughly. All soil samples were stored in plastic bags at 75% available moisture and at 4.5 C until required.

To characterize the soils, some physical and chemical determinations were made. The particle size analysis was done by the pipette method. Organic carbon content was calculated as the difference between total and carbonate carbon content in soils. The pH was measured using the glass electrode in a 1:1 soil-water system. Total phosphorus was determined by digesting the soil with  $\text{HF}$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  (1). The available P was determined by the method of Miller and Axley as outlined by Robertson (14).



Table 1. Some characteristics of soils used in this study

Order	Great group	Subgroup	Series	Texture	P treatment (ppm)	pH	Organic C (%)	CaCO <sub>3</sub> equivalent (%)	Total P (ppm)	Avail. P (ppm)	Solution P (ppm)
Chernozemic	Brown	Orthic	Maleb	L	0	7.1	1.19	0.14	435	12.0	0.16
Chernozemic	Dark Brown	Calcareous	—	L	0 300	7.8 7.5	2.44 —	7.12 —	615 —	9.0 143.5	0.09 17.11
Chernozemic	Dark Brown	Carbonated	—	SCL	0 300	7.8 7.0	1.36 —	3.03 —	556 —	5.5 165.0	0.02 28.09
Chernozemic	Black	Eluviated	Angus Ridge	L	0 300	6.3 6.0	5.69 —	0.12 —	925 —	11.5 162.5	0.07 44.65
Chernozemic	Black	Solodic	—	L	0	5.2	3.64	0.08	864	60.0	0.31
Luvisolic	Gray Wooded	Orthic	Cooking Lake	L	0 300	5.8 5.6	1.44 —	0.09 —	355 —	7.5 170.5	0.04 35.99
Luvisolic	Gray Wooded	Orthic	Glory	Sil	0	6.5	2.23	0.11	880	48.5	0.19

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To estimate the soil solution P concentration at field capacity, the stored soils (storage time of 10 months) were extracted with 0.01 M  $\text{CaCl}_2$  solution, using four soil to solution ratios (1:1, 1:1.25, 1:2.5, and 1:5). Phosphorus was determined in the extracts and the P concentrations of the extracts were plotted against the extraction ratios (grams of soil in 100 ml 0.01 M  $\text{CaCl}_2$  solution). The curve was then extrapolated to the moisture content at field capacity (15). The modified ascorbic acid method (13) was used to measure accurately the extremely low P concentration found in some soil solutions.

After the soils were stored for 9 months, a plant growth experiment was conducted in a growth room. Three pots were filled (2000 g oven dry basis), with each of the 11 soils (seven untreated and four P-treated). Conquest barley was seeded and after emergence was thinned to six plants per pot. Sufficient N, K and S were added to all pots and the soil moisture was controlled by weighing and watering the pots to the field capacity. Fifty grams of perlite were placed over the pots to reduce evaporation losses. Pots without barley plants were used to estimate evaporation losses. To estimate the seed contribution of P, barley was grown in pots containing only perlite. Three weeks after emergence, the plants were harvested. The roots were separated from the soil and the root volume was measured with a pycnometer. Fresh root weights were determined after blotting the roots with paper towels. The tops and roots were dried at 70 C, weighed, and ground. The samples were digested with  $\text{HNO}_3$ - $\text{HClO}_4$ - $\text{H}_2\text{SO}_4$  (5) and P was determined by the ascorbic acid method (17).

We calculated the movement of P by mass flow to the roots, using a modification of the method of Barber and co-workers (10). They estimated the soil solution concentration by using a saturation extract whereas we thought it more correct to obtain the P concentration at field capacity, the upper limit of watering in the plant growth experiment. The procedure for estimating the P concentration at field capacity is described above.

To estimate the contribution of root interception in P supply to the roots, we multiplied the soil solution concentration by the total root volume. For calculating the contribution of diffusion of P to roots, we followed Barber's approach of subtracting the mass flow and root interception contributions from the total uptake of nutrient. We corrected for the contribution of seed P by subtracting from the total uptake, the P contained in the plants growing in perlite.

## RESULTS AND DISCUSSION

The soils (Table 1) had a wide range of available P (5.5–170.5 ppm), total P (355–925 ppm), solution P (0.02–44.65 ppm),  $\text{CaCO}_3$  equivalent (0.08–7.12%), organic C (1.19–5.69%) and pH (5.2–7.8). Thus, the soils provided a wide spectrum of characteristics to study the movement of phosphorus in soils.

The yield data show that generally the higher the dry matter of the tops, the higher the dry matter of the roots and the volume of the fresh roots (Table 2). A treatment of 300 ppm of P on four soils resulted in a distinct yield increase of both tops and roots. We noted that two untreated soils (Solodic Black and Glory), naturally high in available P, gave as high yields as any P-treated soils. The total volume occupied by the roots in a pot was very small and varied from 8 to 26 cc.

Table 2. The dry matter of tops and roots, volume of fresh roots and transpiration ratios in the growth room experiment

Soil	Phosphorus treatment (ppm)	Dry matter (g/pot)		Volume of fresh roots (cc/pot)	Transpiration ratio (g H <sub>2</sub> O/g tops)
		Tops	Roots		
Maleb	0	1.65	1.59	12	341
Calcareous Dark Brown	0	1.46	1.45	12	292
	300	3.55	2.22	18	354
Carbonated Dark Brown	0	0.75	0.78	8	310
	300	3.05	2.89	26	326
Angus Ridge	0	1.38	1.23	11	277
	300	2.73	2.24	19	453
Solodic Black	0	3.04	2.15	22	400
Cooking Lake	0	1.44	2.11	17	251
	300	3.47	3.00	26	313
Glory	0	3.38	1.85	19	367

### Mass flow

The data (Table 3) show that the contribution of mass flow to the transport of P to roots is 4% or less for the untreated soils. For treated soils the range is from 74 to 192%. More than 100% contribution implies the accumulation of P at the root surface, since the supply of P by mass flow alone was greater than the total uptake. Under such conditions the concentration gradient is away from the surface of the roots. No diffusion of P to roots can occur but back diffusion of P can be expected. In contrast to treated soils, the untreated soils, no matter whether high or low in available P, could not supply more than 4% of P to roots by mass flow movement. The distinct increase in the mass flow contribution in the treated soils clearly shows the greater importance of mass flow of P in soils supplied with high doses of phosphatic fertilizers. Further, it is very likely that mass flow of P to roots may be the major process of P movement in the case of band placement of phosphatic fertilizers where a high concentration of P is expected. Our results suggest that mass flow is the major process supplying P to the roots when the soil solution P concentration is about 17 ppm or more (Calcareous Dark Brown treated with 300 ppm; Tables 1 and 3). However, in the case of soils naturally high in available phosphorus (Solodic Black and Glory), where low rates of phosphatic fertilizers are usually applied, the mass flow of P to the roots seems to be relatively unimportant.

### Root interception

The contribution of root interception is no greater than 3% (Table 3), and in the case of untreated soils it is much less than one percent. Thus root interception is not an important process in P transport. This conclusion is not surprising in view of the definition of root interception used in this paper. We are of the opinion that the maximum contribution of root interception is the quantity of ions in the volume of soil solution equal to the root volume. We think that any ions comprising part of the solid phase, or sorbed on to it, must pass into solution before

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Table 3. The uptake of P by tops and roots and estimation of the contribution of mass flow, root interception and diffusion of P uptake by Conquest barley grown on seven untreated and four treated soils

Soil	Phosphorus treatment (ppm)	Uptake of P (mg/pot)	Mass flow of P		Root interception of P		Diffusion of P	
			mg/pot	% of total P uptake	mg/pot	% of total P uptake	mg/pot	% of total P uptake
Maleb	0	3.19	0.09	3	<0.01	<<1	3.10	97
Calcareous Dark Brown	0	3.60	0.04	1	<0.01	<<1	3.56	99
	300	29.19	21.47	74	0.30	1	7.42	25
Carbonated Dark Brown	0	0.10	<0.01	4	<0.01	<<1	0.10	96
	300	32.57	27.86	86	0.73	2	3.98	12
Angus Ridge	0	3.66	0.03	1	<0.01	<<1	3.63	99
	300	28.67	55.14	192	0.83	3	—	—
Solodic Black	0	13.07	0.40	3	<0.01	<<1	12.66	97
Cooking Lake	0	4.19	0.02	<1	<0.01	<<1	4.17	100
	300	38.88	39.12	101	0.95	2	—	—
Glory	0	14.62	0.23	2	<0.01	<<1	14.39	98

moving toward the absorption sites of the roots. Following Low (9), we doubt that the absorption sites (6) approach the solid phase closely enough to permit direct contact exchange. If this is the case, their movement has to be ascribed to either mass flow and/or diffusion. This is in contrast with Barber's group (2, 7, 10, 11) who include sorbed ions in the root interception contribution.

### Diffusion

Our data (Table 3) indicate that the apparent diffusion of P to the roots is the major process of P movement in soils receiving no P treatment. It is interesting to note that even in soils (Solodic Black and Glory—Table 1 and 2) which gave yields equivalent to that of P-treated soils, the contribution of the apparent diffusion to P transport is more than 96%.

Since the contribution of diffusion is calculated by difference (total uptake minus mass flow and root interception), the errors in estimating mass flow and root interception are likely to affect to a great extent the amount of P calculated as diffusing to roots. However, there are many problems in estimating directly the amounts of P diffusing to the roots. Fried and Broeshart (4) reported that the published values of the P diffusion coefficient varied by a factor of  $10^7$ . The determination of the effective absorbing surface area of roots and root hairs growing in soils, the magnitude of the concentration gradient and the distance over which the concentration gradient exists are some of the difficult parameters to measure with any great degree of accuracy. Since the maximum mass flow and root

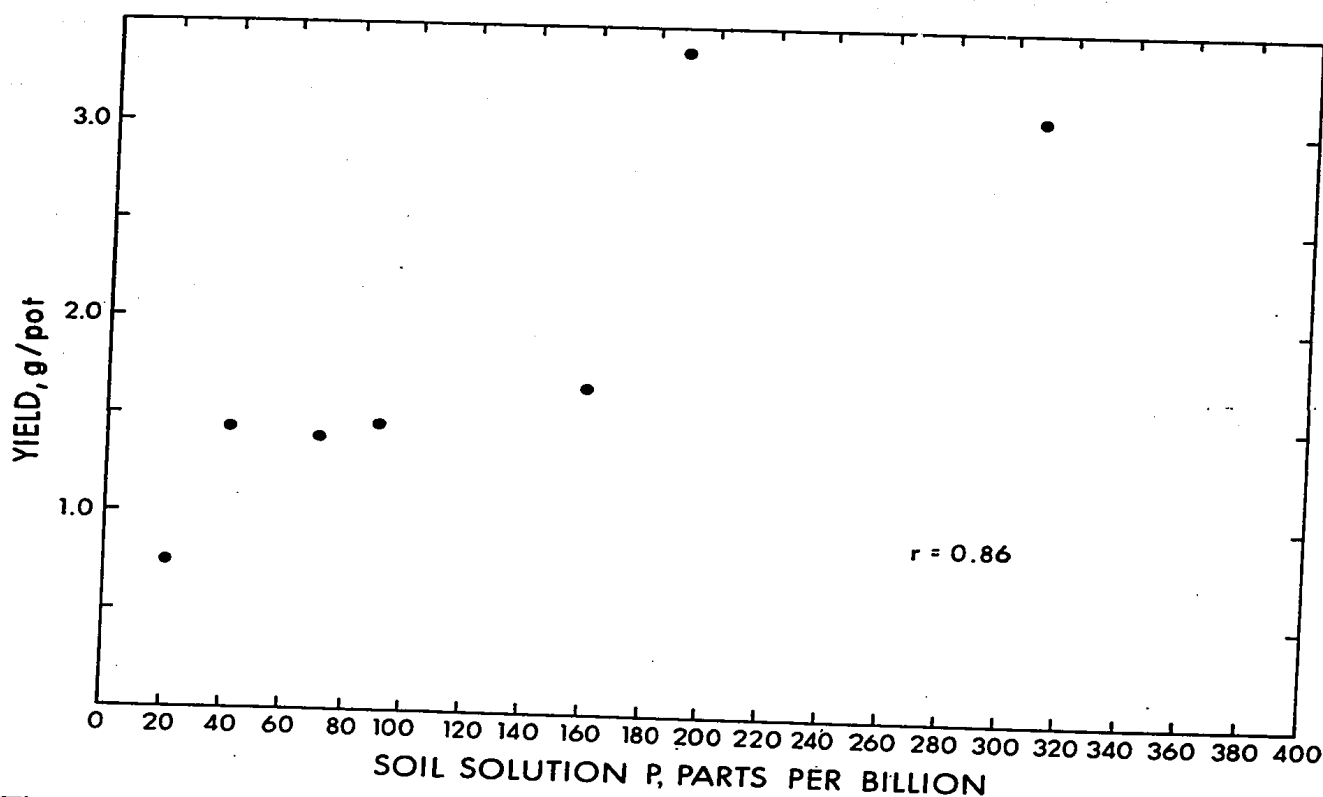


Fig. 1. Relationship between barley yields and soil solution P concentration of the untreated soils.

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OMANWAR AND ROBERTSON—MOVEMENT OF P

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interception contributions can be estimated more precisely, the indirect estimation of P diffusion appears satisfactory.

### Phosphorus concentration and movement

Since the soil solution P concentration is a component of mass flow, root interception and diffusion, one would expect it to be an important factor in the delivery of P to the roots no matter which process is involved. We found a correlation of 0.86 ( $P = 0.02$ ) between the yield and the soil solution P concentration of the untreated soils (Fig. 1). Using the same yield data, a correlation of 0.82 ( $P = 0.05$ ) was obtained between the P uptake and the soil solution concentration of the untreated soils. Although the soil solution P concentration is found to be very important in the delivery of P ions to the roots, other factors may also be important. These include: variations in evapotranspiration; the "rhizosphere effect" which may alter the soil solution concentration and/or nutrient uptake; the extent of root development; and thermal gradients which affect water movement.

### CONCLUSION

- (1) Mass flow of P to the roots is the most significant process in the transport of P in soils treated with high doses of P, and it is likely to be an important process in soils where phosphatic fertilizers are band placed.
- (2) Apparent diffusion to the roots is found to be a major process of P transport in the untreated soils which we studied.
- (3) Root interception as calculated is not important in the overall P transport process.
- (4) Since the apparent diffusion of P appeared to be the major process supplying P to the roots in untreated soils, a study of P diffusion, particularly on P deficient soils, is worth considering.
- (5) Since the soil solution P concentration affects the amounts of P moving to roots by mass flow, diffusion and root interception, the importance of determining P in the soil solution is emphasized.

### ACKNOWLEDGEMENTS

The authors wish to acknowledge financial assistance from the Canadian Commonwealth Scholarship and Fellowship Committee and National Research Council.

This investigation includes a portion of the thesis to be submitted by the senior author for the partial fulfilment of requirements for the PhD. degree at the University of Alberta.

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**APPENDIX F**

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APPENDIX G

Inorganic P Forms of the Phosphated Soils

Soils	P treatment ppm of soil	Inorganic P forms ppm of soil		
		Al-P	Fe-P	Ca-P
Calcareous Dark Brown	0	19	3	216
Calcareous Dark Brown	100	45	9	278
Calcareous Dark Brown	300	81	13	324
Carbonated Dark Brown	0	16	7	224
Carbonated Dark Brown	100	47	12	246
Carbonated Dark Brown	300	106	29	236
Eluviated Black (Angus Ridge)	0	31	46	75
Eluviated Black (Angus Ridge)	100	91	79	70
Eluviated Black (Angus Ridge)	300	176	104	83
Orthic Gray Wooded (Cooking Lake)	0	10	32	28
Orthic Gray Wooded (Cooking Lake)	100	54	79	20
Orthic Gray Wooded (Cooking Lake)	300	153	113	30