

Chapter – II

Review of Literature

2. REVIEW OF LITERATURE

2.1 Phosphorus content in soil.

2.1.1 Total P

The total quantity of phosphorus in most soils is relatively small and it rarely exceeds 0.2% (Metson, 1961). It depends primarily on the parent material, degree of weathering and management practices. Dhir (1956) observed that Indian soils contain 165 to 1377 ppm total P with an average value of 474 ppm. The average values for black, alluvial, forest, desert and red soils were 419, 415, 1268, 240 and 376 ppm P, respectively.

According to Roy Chowdhuri and Datta (1964) total P in Indian soils varied from 130 to 1310 ppm. An appraisal of the total P content in soils by various workers have been summarised in Table 1. Tandon (1987) reported that total P content in Indian soils ranged from 100 to 2000 ppm. Chakraborty and Majumdar (1971) found that the total P in soils of Assam decreased in the following order: new alluvial, old alluvial, forest and hill soils. Agarwal and Goel (1960) observed that in alluvial soils of U.P., total P decreased with maturity of soil. Total P content of soil tended to increase with increase in the amount of organic matter and clay content (Williams and Saunder, 1956; Agarwal and Goel, 1960; Sharma, 1967; Khan and Mondal 1973; Chowdhury, 1988).

2.1.2 Forms of Phosphorus in Soil

Phosphorus in soil occurs almost exclusively as orthophosphate in which a central P atom surrounded by and bound to four oxygen atoms. This P in soils are derivative of phosphoric acid. The phosphates in soil present in two broad categories i.e. inorganic and organic. In inorganic forms, one to three of the H^+ ions of phosphoric acid are replaced by metallic cations, whereas in organic forms, one or perhaps more of the H^+ ions of the phosphoric acid is eliminated by an ester linkage, the remaining H^+ ions are replaced in part or completely by metallic cations.

The relative proportions of these two categories vary widely. Organic P tends to vary directly with content of organic matter present in soil and hence it is usually low in sub-soil and high in surface soil. The present study is concentrated on the inorganic forms of P present in soil. Thus, the review of literature is restricted to inorganic P fractions only.

2.1.2.1 Inorganic Phosphorus fractions

Inorganic forms of P present in soils may be classified according to their physical, mineralogical and chemical nature or combination of these, but till there is no consensus in this matter. Inorganic P occurs mainly as calcium phosphate (Ca-P) in alkaline and calcareous soils. As weathering proceeds and acidity develops in soils, the phosphate become increasingly bonded to aluminium and iron ions released from silicate minerals by weathering (Jackson, 1973).

Chang and Jackson (1957) developed a procedure for fractionation of soil P into the discrete chemical forms such as Ca-P, Al-P, Fe-P, reductant soluble (iron oxide coated) Fe-P and Occluded Al-P and Occluded Fe-P based on the selective solubility of soil P fractions in various extractants. Peterson and Corey (1966) modified Chang and Jackson (1957) procedure for routine fractionation of inorganic soil P. They recommended the use of constant suction pipettes, two molybdophosphoric reductants with different sensitivities and an isobutyl alcohol extraction for the determination of reductant soluble P which greatly increase the speed of P determination. Prakash (1975) suggested the use of alkaline ammonium fluoride (pH 8.5) instead of neutral NH_4F in Chang and Jackson's method for extracting Al-P fractions from soils containing high amount of iron oxides. Although there are some shortcomings as pointed out by Smith (1969), Rajendra and Sutton (1970) and Ponnampereuma (1972), the procedure of Chang and Jackson (1957) with some modifications provides an insight into the relative distributions of the various inorganic forms of phosphorus in soils.

Table 1. Total P content in some Indian Soils

State	Soil Type	Range (mgkg ⁻¹)	Mean (mgkg ⁻¹)	Reference
Pubjab	-	279-1048	497	Kanwar and Grewal (1959)
West Bengal	-	123-190	-	Adhikari and Si (1994)
	-	131-1120	436	Roy Choudhuri and Datta (1964)
	-	-	300	Desai and Ukil (1945)
	Rice Soil	177-544	-	Khan and Mondal (1973)
Assam	Acidic hill soil	175-1220	-	Roy Choudhuri and Datta (1964)
	Tea Soil	810-1162	925	Potgiri and Datta (1993)
Bihar	Alluvial soil	175-436	350	Roy Choudhuri and Datta (1964)
Maharashtra	Black Soils	-	1000	- DO-
	Lateritic soils	262-1520	-	Dongale and Kadrekar (1992)
U. P.	Alluvial		350	Roy Choudhuri and Datta (1964)
	Salt affected soil	325-610	-	Dongale (1993)
	Indo-Gangetic alluvial soil	300-488	-	Gupta and Misra (1964)
	Alluvial soil	405-530	-	Misra and Verma (1979)
	Sub-mountainous soil	180-275	-	Tyagi and Das (1969)

State	Soil Type	Range (mgkg ⁻¹)	Mean (mgkg ⁻¹)	Reference
Rajasthan	Alluvial Terai soil	100-760	350	Bhar and Tripathi (1973)
	Alfisol	173-620		Room Singh and Omanwar (1987)
	Inceptisol	148-560		DO
	Entisol	209-471		DO
	Central alluvial soils	291-1127	-	Tripathi and Dwivedi (1993)
	Western U.P. soil	375-700	502	Misra (1994)
	Desert soil	912-1484	-	Pareek and Mathur (1969)
Sikkim	Acid soil	1178-6450	-	Mehta <i>et al.</i> (1971)
		375-1650	-	Patiram and Prasad (1990)
Meghalaya	Acid Soil	375-1200	-	Patiram <i>et al.</i> (1993)
Tamil Nadu	Lateral	183-1304	557	Kothandaraman and Krishnamoorthy (1979)
	Alluvial	276-628	-	DO
	Black	311-494	-	DO
	Red	152-600	-	DO
H. P.	Hapludalfs	320-1159	622	(Sood, 1987)

Hsu and Jackson (1960) and Syers *et al.* (1970) showed that at the initial stage of weathering calcium and aluminium phosphates were more dominant than iron phosphates. With increase in the degree of weathering the phosphate present as calcium and aluminium phosphate gradually changed into iron phosphate form which has the least solubility among them (Chang and Jackson, 1957).

Different fractions of inorganic P vary from soil to soil and often related to soil physical properties. Fe and Al bound P has been found to be present in large amount in soils of lower pH and Ca-bound P in soils of higher pH (Kanwar and Grewal, 1959; Randhawa, 1967). Chang and Chu (1961) reported significant and positive correlation between clay and Fe-P, which they attributed to the fact that clay being rich in Fe, there is a possibility of added P or native P to be converted to Fe-P. Scheffer *et al.* (1960) analysed different particle size fractions of soils of Germany and found a tendency for accumulation of Fe-P and Al-P in finer fractions and Ca-P in coarser fractions. Schachtschabel and Heinmann (1964) reported that with an increase in soil pH, the Ca-P fractions increased and Fe-P fractions decreased.

The knowledge of the distribution of the specific chemical forms of inorganic phosphorus in soil is helpful in understanding the chemistry of soil phosphorus in assessing the availability of soil P to plants (Susuki *et al.*, 1963; Alben *et al.*, 1964; Smith, 1965; Singh *et al.* 1966). Chaudhuri (1964) reported that in red soils of upper Damodar Valley (Bihar) Fe-P and Al-P constituted 89.4 to 94.6% while Ca-P constituted only 1.4 to 5.9% of the total inorganic P. Dhar and Saxena (1966) showed that the native P occurred mostly as Fe-P in acid soils and Ca-P in alkaline soils, while neutral soils contain both in equal proportions. Sharma (1967) reported that in hill soils of Kangra and Kulu districts of Himachal Pradesh, Fe-P and Al-P together constituted 45 to 68% and Ca-P constituted 21 to 50% of inorganic P. Tyagi and Das (1969) found that in surface soils, P in combination with iron was the highest, whereas in sub-soils insoluble Ca-P was dominant. Chattapadhyya and Kar (1973) reported that in acidic soils of Bihar 70 to 90% of the total P was in inorganic form and the inorganic P was

distributed among the P fractions in the following order: Red -P > Fe-P > Ca-P > Al-P > Occl-P. Reductant soluble P accounted for about 50% of the total inorganic P. In tea growing soils of Assam, the contribution of different fractions towards inorganic P was in the decreasing order of Al-P, Fe-P, RS-P, Ca-P. In rice growing soils of West Bengal, Ca-P, Fe-P, Al-P, RS-P and Occl-P constituted about 46.6, 27.8, 16.2, 7.2 and 2.2% of total inorganically bound P (Khan and Mondal, 1973) respectively.

Vijoyachandran and Raj (1973) noted that in some acid soils of South India, 40% of total P was reductant soluble while in highly weathered acid soils of Bihar over 50% of total P was present in occluded forms (Singh and Singh, 1977). Udo and Ogunwale (1977) observed that the relative abundance of the inorganic fractions were in the order of Occl-P > Fe-P > Al-P > Ca-P in six Nigerian soil profiles. Vantour and Carriera (1984) reported that the content of P fractions occurred in the following order: Al-P \approx Fe-P > Ca-P in red ferrallitic soils of Cuba and the fractions were found significantly correlated with soil pH and organic carbon. Liu *et al.* (1987) reported that inorganic P accounted for 78 to 98% of the total P in red and yellow soils in Yaan and Dukuo (Sichuan) with an average of 86%. Of the total inorganic P, 54 to 67% was in occluded form, 14 to 36% was associated with free Fe, 6 to 14% was in calcium phosphate forms and only 2 to 7% was associated with free Al. Among the different forms of inorganic P, Ca-P formed the dominant fraction followed by reductant soluble-P, Fe-P, Al-P in Alfisol, Inceptisol and Entisol of Uttar Pradesh (Singh and Omanwar, 1987).

Doddamani and Rao (1988) studied various inorganic P fractions and their distribution in some soil samples representing the typical Vertisols, Alfisols, Oxisols and Inceptisols in Karnataka. The distribution of P-fractions in the soil were observed in the order of

- i) Vertisols : Ca-P > Al-P > Red-P > Occl-P > Fe-P > Saloid-P
- ii) Alfisols : Al-P > Red-P > Fe-P > Ca-P > Occl-P > Saloid-P
- iii) Oxisols : Fe-P > Al-P > Red-P > Occl-P > Ca-P > Saloid-P
- iv) Inceptisols: Ca-P > Red-P > Al-P > Occl-P > Fe-P > Saloid-P

In a study, Brar and Vig (1990) found that Fe-P constituted the major fraction followed by Ca-P and Al-P in some benchmark soils of Punjab. Both Fe-P and Al-P significantly related to P-uptake and dry matter yield of wheat. Jaggi (1991) observed from his studies with some surface soil samples of Himachal Pradesh that pH showed a significantly negative correlation with Ca-P. Paramasivam (1991) studied the different fractions of inorganic P in soils from Tamil Nadu in relation to physical and chemical properties of soil and found that inorganic P fractions followed the order of Ca-P > Fe-P > Al-P > Saloid-P. There was a positive significant correlation of Saloid-P with clay and silt content. However, the distribution of Al-P, Fe-P, RS-P, Occl-P and Ca-P did not follow a definite pattern in some Vertisols of Karnataka (Viswanatha and Doddamani, 1991). Mamo and Haque (1991) found in some soils of Ethiopia that the relative abundance of the various inorganic P-fractions were in the order of Ca-P > Red-P > Fe-P > Al-P. Organic P, on an average, constituted $\approx 41\%$ of the mean total P content of the soils. Multiple correlation analysis of the data showed that the various P-fractions were significantly correlated with total-P in the soils.

Sharma and Tripathi (1992) noted that the dominance of reductant soluble P in some acid soils of North West India was probably the cause of negligible or no response to application of P-fertilizer in rice crop under low lying situations. The relative sequence of P-fractions indicated that the majority of soils studied were in advance stage of weathering whereas remaining were weakly weathered. Misra (1992) studied five established soil series of West Bengal and reported that Fe-P and Al-P were the dominant mineral P fractions in all the soil series. Dongale and Kadrekar (1992) reported that inorganic and organic P content in lateritic soils of Ratnagiri and Sindhudurg districts (South Konkan) of Maharashtra were 200 to 840 and 10 to 867, respectively. The inorganic and organic P accounted for 66% and 34% of the total P respectively. The relative dominance of various inorganic P-fractions was in the order: Residual P > Fe-P > Red-P > Occl-P > Al-P > Ca-P.

Srivastava and Srivastava (1993) explored the effect of pH on the changes in forms of P in saline-sodic soils and found that Ca-P was the

predominant form of P in the soil pH range of 7.2 to 10.3. Prakash *et al.* (1993) observed in some Alfisols of Karnataka that organic P was predominant and accounted for 33.7 to 47.5% of total P. Saloid-P, Al-P, Fe-P and organic-P were negatively correlated with pH, clay, silt+clay and sesquioxides whereas they were positively correlated with organic carbon, available-P, total P and reductant soluble P. Ca-P and occluded P showed reverse relationship with the said soil properties.

Tripathi and Dwivedi (1993) carried out a laboratory experiment to estimate the various fractions of native-P in some central alluvial soils of Farrukhabad (U.P.) and showed that total P, available P and inorganic-P (Saloid-P, Al-P, Fe-P & Ca-P) were highest in western low land soils and least in Ganga upland sandy soils. These fractions were significantly correlated with each other and also showed significant correlation with clay, silt+clay and organic matter. Inorganic fractions were in the order of Red-P > Fe-P > Al-P > Ca-P in some acidic upland Hapludalfs and low land Haplaquents from East Khasi hill district of Meghalaya (Patiram *et al.*, 1993). They also reported that Al-P and Fe-P were the main sources of available-P and there was more organic and total P in the Haplaquents due to deposition of erosional material from upland Hapludalfs. Haplaquents also contained more amorphous Fe and Al, Al-P and Fe-P.

Adhikari and Si (1994) reported the distribution of inorganic P-fractions in some acidic soils of West Bengal in the order of Saloid bound – P > Occl-P > Active-P. The relative amount of active P was of the order: Fe-P > Ca-P > Al-P. The variation in inorganic P content in these soils was considered to arise from the alluvial origin of soils. Rao and Chakraborty (1994) observed that the relative abundance of inorganic P in tea growing soils of Himachal Pradesh followed the order: Red-P > Fe-P > Ca-P > Al-P > Saloid-P in surface soils. Misra (1994) noted that the amount of organic P in the soils of western U.P. varied widely and constituted 6 to 25.7% of the total P. Ca-P was the dominant inorganic P and Al-P and Fe-P accounted for 3.0 to 12.2% and 2.9 to 13.1% of the total P, respectively.

2.2 Available Soil Phosphorus

2.2.1 Concept of Available Phosphorus

The term available phosphorus (P) refers to the inorganic form, occurring in the soil solution, which is almost exclusively 'Orthophosphate'. This 'Orthophosphate' occurs in several forms and combinations, and only a small fraction of the total amount present may be available to plants, which is of direct relevance in assessing the P fertility level.

The phosphate concentration in solution is governed by heterogeneous equilibria in which it takes part. Larsen (1967) represents this situation as: P adsorbed in solid phase \rightleftharpoons P in soil solution \rightleftharpoons P precipitated from solutions.

The phosphorus absorbed by plants comes from the soil solution in which it exists as inorganic 'orthophosphate' ions, viz. H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} . The most accessible ion is H_2PO_4^- , with the greatest activity coefficient followed by HPO_4^{2-} . The quantity of P accessible to the plants is influenced by a series of soil properties. The relative abundance of these ions is, however, relatively dependent on the soil pH. For soils having a pH between 4.5 and 7.5 ions of H_2PO_4^- as well as HPO_4^{2-} exist in soil solution. At a pH of 7.2, H_2PO_4^- and HPO_4^{2-} ions have on equal activity, and when the pH is strongly alkaline (>8.3) ions of HPO_4^{2-} predominate in solution. Above pH of 9.0, the trivalent ion (PO_4^{3-}) becomes more important than H_2PO_4^- , but even at a pH of 12, the HPO_4^{2-} concentration is still greater than that of PO_4^{3-} .

Soil phosphate is most conveniently divided into two categories – insoluble and readily soluble. The insoluble phosphate, which is not directly available to plants or micro-organism, usually comprises around 95 to 99% of the total soil phosphate. The insoluble inorganic phosphate in all soils is mostly attached to three elements, of which, Fe and Al are the main binding agents in acid soils and Ca in slightly acid to alkaline soils. The amount of the total insoluble soil phosphorus that is organic varies widely around 30 to 85% discounting extreme types of soils. It is particularly high in acid soils, usually related to the amounts of carbon and nitrogen in the soils.

According to Bray & Kurtz "The term available forms (of soil P) is restricted to those which are of most immediate significance to crop growth and whose variations in amount are responsible for variation in crop growth and response to added phosphates".

According to the latest compilation (Hasan, 1994) based on about 9.6 million soil test data for available soil P in Indian soils, it is seen that 49.3% of district and Union territories are in the low category, 48.8% in medium class and 1.9% of total districts have high P status (Table 2). However, this compilation gives only a trend because at least 30 million soil test results are required to get a comprehensive and broad based information for available P status. There is a need for P application for ensuring proper crop growth in nearly half of the districts in the country.

An appraisal of available P status in relation to the major soil groups or association indicates that generally the deep black soils, grey brown, desert and red loamy soils of semi-arid region have medium fertility level. Similarly, the soils of foothills alluvial strips of the northern region and coastal alluvium that are not sandy in nature largely depict medium available P status. The vast alluvial tracts of central, eastern and southern parts of the country, the latosol, medium black, red loamy soils of semi humid or humid regions and sandy coastal alluvium are usually low in available P.

2.2.2 Existing Rapid Chemical Methods of Determining Available Phosphorus

Phosphorus determination for soils was greatly expedited by the development of sensitive colorimetric methods. The following are the widely used methods:

- I. Chlorostannous–reduced molybdophosphoric blue colour method, in a sulphuric acid system.
- II. Chlorostannous–reduced molybdophosphoric blue colour method, in a hydrochloric acid system.

- III. Molybdenum-reduced molybdophosphoric blue colour method, in a sulphuric acid system.
- IV. 1, 2, 4 – aminonaphthosulfonic – reduced molybdophosphoric blue colour method, in a perchloric or sulphuric acid system.
- V. Vanadomolybdophosphoric yellow colour method, in nitric acid system.

The determination of P from soil involves two steps i.e. i) Extraction, ii) Development of colour by any one above described method and colorimetric reading. The success of available P determination lies on the choice of right type of extractant. The followings are the different types of extractants used by different workers.

- i) 0.5 (M) NaHCO_3 at pH 8.5 – Olsen method (Olsen *et al.*, 1954).
- ii) 0.025 (N) HCl in 0.03 (N) NH_4F – Bray-I (Bray and Kurtz, 1945)
- iii) 0.1 (N) HCl in 0.03 (N) NH_4F – Bray-II (Bray, 1948)
- iv) 0.002 (N) H_2SO_4 – Truog (Truog, 1930)
- v) $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$ (pH 4.8) – Morgan method (Morgan, 1941)
- vi) 0.05 (N) HCl+ 0.025 (N) H_2SO_4 (pH-1.2) – Mehlich-1 Method (Nelson *et al.*, 1953)
- vii) 1(M) NH_4HCO_3 + 0.005 M DTPA (pH 7.6) – AB-DTPA method (Sultanpour and Schwab, 1977).
- viii) 1% Citric acid - Dyer (Dyer, 1894).

Mehlich (1978) evaluated a new extractant for simultaneous extraction of several plant nutrients over a wide range of soil properties. The new extractant composed of 0.2 (N) NH_4Cl + 0.2 (N) HOAC + 0.015 (N) NH_4F + 0.012 (N) HCl at approximately pH 2.5 and compared with other extractants. P uptake by millet was highly correlated with the phosphorus extracted by the new extractant, Bray-I, DA [0.05 (N) HCl – 0.025 (N) H_2SO_4] followed by Olsen.

Table 2. Distribution of Indian districts and Union territories into fertility classes according to the status of available phosphorus in soil

State/Union territory	No. of districts for which soil tests obtained	Fertility classes		
		Low	Medium	High
Andhra Pradesh	21	17	04	-
Arunachal Pradesh	05	-	05	-
Assam	09	1	06	02
Bihar	26	12	14	-
Chandigarh	01	01	-	-
Dadar & Nagar Haveli	01	-	01	-
Delhi	01	01	-	-
Goa	01	01	-	-
Gujrat	19	14	05	-
Harayana	11	02	09	-
Himachal Pradesh	11	02	07	02
Jammu & Kashmir	10	01	09	-
Karnataka	19	16	03	-
Kerala	10	03	07	-

State/Union territory	No. of districts for which soil tests obtained	Fertility classes		
		Low	Medium	High
Madhya Pradesh	45	15	30	-
Maharashtra	25	17	08	-
Manipur	01	01	-	-
Meghalaya	02	02	-	-
Mizoram	01	01	-	-
Nagaland	06	06	-	-
Orissa	13	05	08	-
Pandicherry	01	01	-	-
Punjab	12	02	10	-
Rajasthan	26	02	21	03
Tamil Nadu	13	08	05	-
Uttar Pradesh	55	41	14	-
West Bengal	15	04	11	-
Tripura	03	03	-	-
Total	363	179 (49.3)	177 (48.8)	7 (1.9)

Figure in parenthesis indicates percentage.

2.2.3 Quantification of Contribution of Various Inorganic P-Fractions towards Available P

Kanwar *et al.* (1979) analysed soil samples for inorganic and available P values by the procedure of Bray and Kurtz, Olsen *et al.* and Morgan. The Al-P and Fe-P fractions made significant contribution to Olsen P and Bray P. Patiram *et al.* (1990) studied various extractants for available P in acid soils of Sikkim and observed that Al-P contributed more towards P availability to maize than the other two forms of P (Fe-P and Ca-P). Mehlich extractant proved the best among the extractants used. A significant positive relationship between Olsen-P and inorganic P fractions in Karail, red, alluvial and *terai* soils of Uttar Pradesh was reported by Verma *et al.* (1991).

Mamo and Haque (1991) estimated available-P in the soils of Ethiopia by eight chemical methods (Bray-I, Olsen, Dabin, Truog, Bray-II, Waren and Cooke, Williams and Stewart and Egner). The P values extracted by all methods except for the Bray-I were significantly correlated with Al-P and the same by the Olsen and Dabin methods were also correlated with Fe-P as well as with Al-P. P estimated by Truog, Bray-II, Waren and Cooke, Williams and Stewart, and Egner methods were also significantly correlated with Ca-P.

Patiram *et al.* (1993) reported that the amounts of available P extracted in some acid soils of Meghalaya was in the order: Bray-2 > Mehlich > Olsen > Bray-1. Mehlich extractant was recommended for the upland Hapludalfs and Mehlich and Bray-2 for lowland Haplaquents. It was also reported that Al-P and Fe-P were the main sources of available-P.

Rao and Chakraborty (1994) evaluated available-P using the extractants, viz, Mehlich-1, Mehlich-3, Bray-2, and Olsen in relation to inorganic-P fractions in tea growing soils of Himachal Pradesh. Stepwise regression analysis showed that Al-P and Ca-P were the predominant fractions contributing towards availability of phosphorus.

Singh *et al.* (1996) studied P-availability in Alfisols of varying agroclimatic region in India and found that of the P-extracted by various extractants, the water extractable -P ($r=0.70^*$), Olsen-P ($r=0.66^*$), Kumar's extractant-P ($r=0.70^*$) and

P-extracted by Soltanpur and Schwab's method ($r=0.70^*$) correlated with saloid bound-P which was the important source of plant available P in soil. Available-P status as estimated by different extractants and its relationship with different inorganic-P forms in Vertisols located in different agro-climatic zones of Northern Karnataka was reported by Giridhara Krishna and Satyanarayan (1996). The P-extracting power of different extractants was in the order: Truog > Bray-1 > Olsen > Datta and Kamath > Morgan. Olsen and Bray-1 extractants were consistent in extracting P from specific P fractions than the other three extractants.

The relationship between indices of P-availability and different forms of P in soils of Bihar Plateau was studied by Binod *et al.* (1998). Results indicated that Bray P_1 and Bray P_2 extractable-P were positively and significantly correlated with Al-P, Fe-P and Occl.-P. Ravindra and Ananthanarayana (1999) tried to assess the available-P status of the acid soils of Karnataka by seven extractants, viz. Bray-1, Bray-2, Truog, Mehlich-1, Mehlich-3, Olsen and Morgan. The extracted amounts of P by various extractants were correlated with inorganic-P fractions. The extracting power of different extractants was in the order of Bray-2 > Truog > Mehlich-3 > Bray-1 > Olsen > Mehlich-1 > Morgan. Simple correlation studies revealed that Bray-1 had a better correlation with saloid-P ($r=0.44^{**}$), Al-P ($r=0.56^{**}$) and Fe-P ($r=0.48^{**}$). In multiple regression analysis 63% of the variation in Bray-1 P was explained by Al-P +Fe-P. Dhillon *et al.* (2001) reported that both Al-P and saloid-P controlled P availability in soils of pearl millet growing areas of Punjab and among the various soil test methods to extract available P, Olsen's method was found to be the most suitable in modified form by changing shaking time (16 hours) and soil solution ratio (1:100). The amount of P released by different extractants followed the order: Nelson (HCl+H₂SO₄) > Hunter (NaHCO₃+EDTA+NH₄F) > Olsen (NaHCO₃) > Bray-1 (NH₄F +HCl) was observed by Ghosh and Singh (2002). Among the various extractants Nelson method showed the highest significant correlation both with relative yield and uptake of P by maize grown in acidic soils of Uttaranchal hills.

2.2.4 Crop Preference for Different P Fractions

Several reports are available where in different crops have been reported to utilise more of particular inorganic form (s) of P in soil. It was also found that the crops have preferred one or more inorganic forms. Some of references have been listed in Table 3.

2.2.5. Correlation of Different Methods of Determining Available Phosphorus with Crop Response

Soil chemists for a long time have been concerned with advising farmers how much fertilizer it is economically justifiable to give a crop on a particular field and have devoted a great deal of time for upward of a century, devising simple reliable methods to help them.

Initially they looked for a chemical that would dissolve the same amount of phosphate from the soil as would the plant roots, ignoring the fact that different plants extract different amounts of phosphate from the same soil. But they soon realised that any standardised chemical extraction technique which placed the soils in order of crop responsiveness to phosphate was all that was needed, so recent work has been concerned with determining the correlation co-efficient either between the amounts or the logarithm of the amount, of phosphate extracted using various techniques and either the responsiveness of a crop to a phosphate fertiliser or the yield or phosphate uptake of a crop grown on a range of soils, usually the representative of a region or a country. The crops may either be grown in field trails or in pots in a green house, and the method of evaluation of available nutrient is most suitable that gives the highest correlation co-efficient. Various studies have been made in different places from time to time and some of such works are reported below.

Kanapathy *et al.* (1973) investigated on seven soils with ragi as test crops in pot experiments and analysed for P by twelve different methods, of which, Bray and Kurtz No.2 extractant and Olsen's method appeared to be most satisfactory, but nearly all the methods showed good correlation. A preliminary

Table 3. Association of soil P fractions with nutrition of crops

Crop	Soil	Preferred fraction (s) ^P	Reference(s)
Maize	Alluvial	Al-P, Fe-P	Datta and Khera (1969), Goswami and Singh (1979)
Rice	Alluvial	Al-p, Fe-P, Ca-P	Ramamoorthy and Bisen (1979)
Rice	Red & Black	Fe-P	Rajakkannu and Ravi Kumar (1978)
Rice	Alfisol	Al-P, Fe-P	Verma and Tripathi (1981)
Wheat	Alluvial	Al-P, Ca-P, Fe-P	Ramamoorthy and Basin (1979)
Wheat	Alluvial	Al-P, Ca-P	Sharma and Dev (1974)
Pearl millet	Alluvial	Al-P	Rao <i>et al.</i> (1984)
	Red	Red-P	Goswami and Singh (1979)
Red gram	Alluvial	Organic-P	Jain (1979)
Lentil	Acid	Al-P	Sharma <i>et al.</i> (1985)
Jute	Alluvial	Al-P	Doharey <i>et al.</i> (1980)
Coffee	Lateritic	Al-P, Red-P	Iyenger <i>et al.</i> (1982)
Sunflower	Red	Al-P, Ca-P, Red-P	Rao <i>et al.</i> (1984)
Black gram	Red	Al-P, Ca-P, Red-P	Rao <i>et al.</i> (1984)

field tests with paddy confirmed the suitability of the former extractant, which has been officially adopted in Thailand for available-P determination.

Ekpete (1976) reported that P extracted from waterlogged and air dry samples of unfertilized traditional swamp rice soils using Bray-1, Bray-2, Truog, EDTA and Olsen method and data were correlated with percentage dry matter yield, P-uptake for unfertilized soil and available-P obtained from rice tops grown under waterlogged condition in the green house. The Olsen method was the most effective in extracting P from both air dry and waterlogged soil.

Bowman *et al.* (1978) reported that Olsen-P, Colwell-P, total exchangeable-P and resin extractable-P were evaluated in terms of total plant P-uptake in a three years continuous green house study of 23 high P calcareous and neutral soils. All methods were highly correlated with the total P-uptake by 5 to 8 successive green house crops (Sudan grass, sorghum, and barley). The Olsen-P procedure extracted an average of nearly 50% of the total plant P while Colwell procedure extracted nearly 80%.

Bates (1990) conducted a green house experiment in Ontario soils and five chemical soil-P extractants were compared. The correlation of extractable-P to plant uptake resulted in r^2 values of 0.74, 0.73, 0.54, 0.65 and 0.66 for the NaHCO_3 , AB-DTPA, Bray-Kurtz- P_1 , Bray-Kurtz- P_2 , and Mehlich-3 extractants, respectively. Adding soil pH the equation improved the prediction of plant P-uptake resulting in R^2 values of 0.80, 0.80, 0.70, 0.73 and 0.75 for said extractants respectively. The two alkaline extractants were equally effective and superior to three acidic extractants, with the Bray – Kurtz- P_1 extractant being least effective.

Among the various inorganic P-fractions and organic P, only Ca-P was significantly and positively related to cumulative P-uptake by five crops ($r=0.478$) showing the importance of Ca-P for the evaluation of P-availability over an extended period of cropping for the soils of Western U.P. (Misra, 1994). A comparison among seven methods of measuring available soil P in wheat growing valleys of Himachal Pradesh was studied by Jaggi *et al.* (1990) and found that Bray P_1 method was assessed to be the best, followed by Olsen as

well as Truog method. Among inorganic-P fractions, Al-P and saloid-P accounted for major variations in available-P extracted by these methods and yield parameters of wheat.

Dhillon *et al.* (1998) conducted a pot experiment with berseem on 19 soils collected from flood-plain areas of Punjab to evaluate various P-availability indices. Amongst different extractants for soil P, Olsen's method was found to be the most suitable. Both Al-P and Ca-P controlled P, availability to berseem in these soils but Al-P seemed to be more important as it correlated significantly with available-P extracted by most of the extractants tested and various yield and P-uptake parameters. A pot experiment was conducted with 20 soils to evaluate various P-availability indices by Dhillon *et al.* (2001) and showed that dry matter yield and P-uptake increased with rise in soil P. Both Al-P and saloid-P controlled P-availability in these soils as they correlated significantly with various plant parameters. Among the various methods to extract available P, Olsen's method was found to be the most suitable in modified form.

2.3 Adsorption Desorption Behaviour of Phosphorus

2.3.1 Phosphate Sorption

2.3.1.1 Concept of P-fixation

The removal of phosphate (P) from soil solution when a soluble phosphate is brought into contact with soil has been termed 'phosphate fixation'. A knowledge of the mechanism of phosphate fixation in soils is necessary to understand both the nature of P-transformation in soil and the availability of the added phosphate (in the form of fertilizer) to plants.

During the earlier part of this century, there was confusion about the mechanisms of P-fixation as to whether such fixation was due to chemical precipitation, adsorption or both. The precipitation has attributed largely to the presence of calcium and magnesium ions in calcareous soils and iron and aluminium ions in acid soils (Kelly and Midgley, 1943).

Hemwall (1957) observed that P is fixed by clay minerals by way of reacting with soluble aluminium which originates from the exchange sites or from lattice dissociation of the clay minerals to form highly insoluble aluminium phosphate compound (Variscite). Experimental results also indicated that the rate of 'fixation' was dependent upon the rate at which clay replenishes the solution with soluble aluminium.

Gebhardt and Coleman (1974) suggested three separate reactions mechanisms to describe the phosphate retention by allophanic soils, viz, i) precipitation of phosphate as variscite or strengite type of compound, ii) specific, inner sphere, adsorption of H_2PO_4^- on a protonated surface, iii) adsorption of phosphate ions accompanied by that of Na^+ ion (NaH_2PO_4 was used as P source).

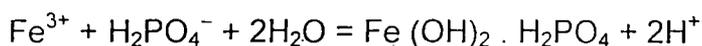
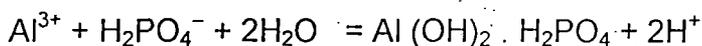
P-fixation in acid soils involves both adsorption and precipitation reaction, although the former appears to be dominant over short reaction periods (Rajan and Watkinson, 1976; Mehadi and Taylor, 1988).

In acid soils, P adsorption is generally attributed to hydrous oxides of iron (Fe) & Aluminium (Al) and to (1:1) layer lattice clays, particularly in tropical soils with low pH (Sanyal and De Datta, 1991).

2.3.1.2 Mechanism of Fixation of P in Acid Soil

2.3.1.2.1 Precipitation of phosphate from soil solution

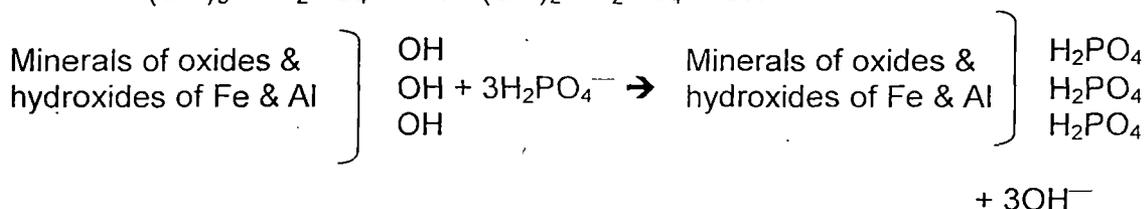
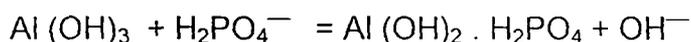
In organic soil containing less amount of inorganic constituents, the fixation of phosphorus is less even though the soil is strongly acidic. In an inorganic soil having very low pH, the concentration of Fe, Al and Mn both in exchangeable phase and in soil solution is high which form insoluble compounds with phosphate ions. The type of compounds formed is not yet clearly understood but by potentiometric fixation and x-ray defraction studies it has been identified that probably Fe and Al – oxy and hydroxy phosphates are formed which may be represented as follows:



The phosphate ion may also be adsorbed on the colloidal constituents of the soil. In mild acidic soil the amount of phosphorus may be fixed in the form of dicalcium phosphate.

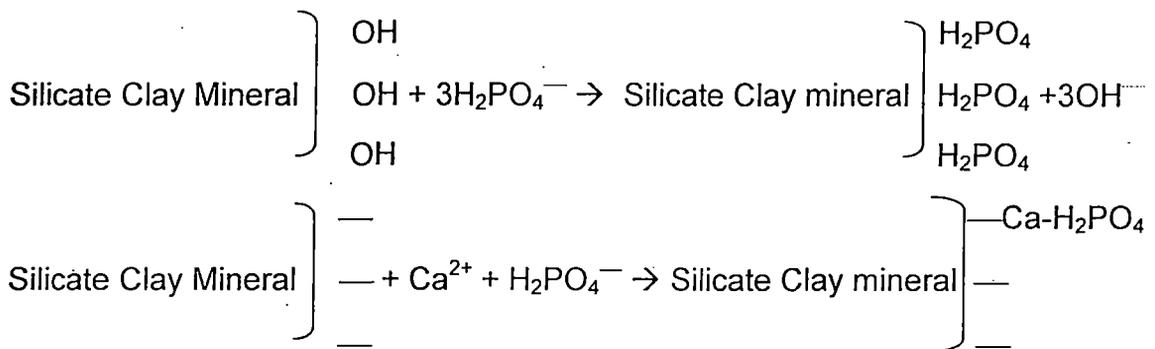
2.3.1.2.2 Interaction with hydrated sesquioxides

In acid soils considerable amount of hydrated oxides of Fe, Al and Mn are present in colloidal form which adsorbed phosphate ions of their surface. The compounds formed are similar to those formed in precipitation reaction and the reaction shown schematically with only $\text{Al}(\text{OH})_3$ as hydrated oxides of Al.



2.3.1.2.3 Interaction with silicate clay minerals

In mild acidic soil phosphorus may be fixed by the clay minerals forming clay – Ca – H₂PO₄ linkage. Silicate clay minerals also retain phosphate by the mechanism of anion exchange where hydroxyl ion of aluminium atom exposed at the broken edge or on the planar surface is replaced by the phosphate ions. P fixation is more by 1:1 type of clay minerals having low Si : sesquioxide ratio than 2:1 type of clay minerals having high Si : sesquioxide ratio and the reaction was shown schematically as follows:



2.3.1.3 Phosphate Sorption Characteristics of the Soil

Phosphate adsorption which refers to the process in which phosphate ions are removed from solution and retained on the surface of soil particles determines the behaviour of labile inorganic P in soil. Thus, the extent of P adsorption affects both the availability of phosphate to plants and the effectiveness of phosphatic fertilizer. Different ways of measuring and describing phosphate adsorption have been reported.

2.3.1.4 Adsorption Isotherms

The relation between the amount of substance (adsorbate) adsorbed by an adsorbent (clay surface, fine particles of minerals, colloidal forms of Fe & Al and organic matter) and the equilibrium pressure (or concentration) of the adsorbate at constant temperature is known as the adsorption isotherm. The main motivations for describing adsorption curves are to i) identify the soil

constituents participating in adsorption (Adams *et al.*, 1987; Longanathan *et al.*, 1987), ii) predict the amount of fertilizer needs of soils to meet the demand of plant for an optimum yield (Fox and Kamprath, 1970; Fox 1974; Fox and Kang 1978; Roy and De Datta, 1985; Greenland and De Datta, 1985; Klages *et al.*, 1988), and iii) study the nature of adsorption process to learn more about the mechanism of the process (Barrow, 1984; Sanyal and De Datta, 1991).

Several adsorption models have been used by different authors to describe the adsorption of phosphate by soil surface.

Langmuir model

There have been many attempts to fit the results of P adsorption studies on soils, clays and sediments to the simple Langmuir equation (Olsen and Watanabe, 1957; Bache and Williams, 1971; Vig and Dev, 1984; Bennoah and Acquaye, 1989; Sanyal *et al.*, 1993).

An equation of phosphate adsorption equation following the Langmuir isotherm reads

$$\frac{x}{m} = \frac{K_1 K_2 C}{1 + K_2 C} \quad \dots (1)$$

Where 'x' is the amount of phosphate adsorbed by 'm' g of soil and 'C' is the equilibrium phosphate concentration in soil solution. 'K₁' and 'K₂' are constants. Linearization transformation of equation (1) leads to

$$\frac{C}{x/m} = \frac{1}{K_1 K_2} + \frac{C}{K_1} \quad \dots (2)$$

Here, the constant 'K₁' is designated as Langmuir adsorption maximum for phosphate (LAMP), and 'K₂' is related to the corresponding binding energy. This equation (Equation-2) is based on the assumptions that the energy of adsorption is constant which implies uniform states and no interaction between the adsorbed phosphate species, that the adsorption is on localised situation which implies no transitional motion of adsorbed molecules, and that maximum possible adsorption corresponds to a complete monomolecular layer.

The Langmuir plot of 'C/(x/m)' against 'C' should give a straight line and the linear regression can then be used to estimate the appropriate adsorption parameters.

The major advantage of the Langmuir equation is that the 'adsorption maxima' can be calculated (Olsen and Watanabe, 1957). However, a close fit to simple Langmuir equation is generally obtained at low concentration (<15mg/l) only a limited range. In fact, the 'adsorption maximum' calculated from observations at low concentrations is sometimes exceeded at higher concentrations (Barrow, 1978; Harter, 1984; Sanyal and De Datta, 1991; Sanyal et al., 1993). A curved relationship between 'C/(x/m)' and 'C' over a wide range of concentrations implied that the binding energy is not constant, but rather is a function of adsorption (Bach and Williams, 1971; Barrow, 1978).

Gunary (1970) modified the simple Langmuir equation and expressed it as:

$$\frac{C}{x/m} = A + BC + D\sqrt{C} \dots (3)$$

where 'A', 'B', and 'D' are co-efficient. Comparison with equation (2) shows that this is equivalent to adding a square root term to describe the curvature observed when 'C/(x/m)' is plotted against 'C'. He interpreted this curvature as meaning that the soil would adsorb a small amounts of phosphate firmly, a slightly greater amount less firmly and so on.

Sposito (1980) also criticized the validity of the two (or three) surface Langmuir equation as a physical model for P sorption by soils. He pointed out that the adjustable parameters in the two-surface Langmuir equation cannot be interpreted in terms of surface reactions without additional independent evidence that adsorption on two kinds of surface sites is actually involved in the ion sorption reaction.

Freundlich Model

Freundlich equation was widely used to describe P adsorption in soils (Russell and Prescott, 1916; Mead, 1981; Le Mare, 1982; Polyzopoulos et al., 1985; Buchter et al., 1989; Sanyal and De Datta, 1991; Sanyal et al., 1993). The equation may be written as

$$x/m = KC^{1/n} \quad (n>1) \dots (4)$$

where 'x/m' the amount of P adsorbed per unit mass of soil, 'C' is the concentration of P in equilibrating solution and 'K' and 'n' are constants

dependent on the given adsorption process and temperature of study. A linear version of equation (4) is :

$$\log (x/m) = \log K + 1/n \log C \dots (5)$$

A plot of $\log (x/m)$ against $\log C$ should give a straight line and the adsorption parameters can be estimated from linear regression.

Although this equation does not provide any measure of an 'adsorption maximum', the Freundlich co-efficient, K , may be regarded as a hypothetical index of P adsorbed from a solution having unit equilibrium concentration. Thus, the co-efficient ' K ' may be taken to provide a measure of relative phosphate sorption capacity of different soils (Biggar and Cheung, 1973). Freundlich equation implies the affinity (bonding energy) decreased exponentially with increasing surface coverage, a condition which is perhaps nearer to reality than the assumption of constant binding energy as in the simple Langmuir equation.

Barrow (1978) pointed out the reason of deviation in the plot of the simple Freundlich equation [eg. Plot of $\log (x/m)$ against $\log C$] due to neglect of the native phosphate which could take part in adsorption process along with the added P . Thus denoting the native P as Q , equation (4) may be rewritten as

$$x/m + Q = K.C^{1/n} \quad (n > 1) \dots (6)$$

$$\text{or, } x/m = KC^{1/n} - Q \quad (n > 1) \dots (7)$$

Tempkin Model

The Tempkin equation can be derived from the Langmuir equation by including the condition that adsorption energy decreases linearly with the surface coverage (Bache and Williams, 1971; Barrow, 1978; Sanyal *et al.*, 1991). The adsorption then varied with the equilibrium concentration in a complex manner, but for middle range of surface coverage, the equation reads

$$x/m = K_1 \ln (K_2 C) \dots (8)$$

where ' K_1 ' and ' K_2 ' are constants and (x/m) is the specific phosphate adsorption by the given soils, while ' C ' is the equilibrium phosphate concentration in solution phase.

The major advantage of this model is that it can describe phosphate adsorption by soils over a wide range of phosphate concentration in soil solution.

Moreover, it can also compare the relative phosphate sorption capacity of various soils, corresponding to an empirically observed equilibrium phosphate concentration (e.g. 0.2 ppm P) that lead to optimum crop growth (Roy and De Datta, 1985; Klages et al., 1988; Sanyal et al., 1993). Furthermore, for phosphate adsorption in soil, the intensity factor is, in fact, the chemical potential of P in equilibrium solution. The latter is a logarithmic function of P activity in soil solution.

However, Kamprath and Watson (1980) were of the opinion that some cautions must be exercised to use such adsorption isotherms of calculate P fertilizer requirements from the amounts required to raise P concentration in the soil solution to a predetermined level. Thus, this approach considers only the intensity factor for solution P while disregarding other factors that affect P uptake by roots (e.g. buffer capacity of soils and the transport of solution P to the root zone) (Olsen and Khasawneh, 1980; Sanyal and De Datta, 1991). In addition, this model is of less value, especially when the soils contain large amounts of native P relative to the amount adsorbed. One way of overcoming this problem is to measure the slope of the adsorption isotherm at the required concentration rather than the amount adsorbed (Barrow, 1978). The slope is a much more permanent soil characteristic than either the existing phosphate content (native phosphate), which varies with manurial treatment, or the amount sorbed from a given solution, which also depends on the amount of the added phosphate, and on other experimental factors. The slope actually provides the phosphate buffer capacity of soil which regulates the availability of P to plant.

2.3.1.5 Some Comparative Studies on Phosphate Adsorption Isotherms

Polyzopoulos *et al.* (1985) demonstrated that P adsorption data from 14 representative Alfisols of Greece may be described by the simple and two surface Langmuir equation, and also the Freundlich and Tempkin equations, with the Freundlich and the two-surface Langmuir equations proving slightly superior. The Freundlich equation, being simpler, was preferred by these authors.

Berigari (1988) carried out an adsorption study in some typical soils of Iraq and the data conformed to the linear plots of Freundlich, Langmuir and Tempkin equations with highly significant positive correlation. Superior fit of the data, however, was observed with the Freundlich equation which is simple in form.

Sanyal *et al.* (1993) used the Tempkin, Freundlich and Langmuir adsorption isotherms to study the equilibrium P sorption and release behaviour in some acidic soils of contrasting properties. The authors found that the Freundlich equation gave the best fit of equilibrium P sorption data. The Freundlich equation was preferred over other adsorption equations by several workers also due to its simpler nature (Barrow, 1978; Ratkowsky, 1986).

P adsorption-desorption studies of some Alfisols of varying agro-climatic region in India was carried out by Singh *et al.* (1996) and showed that the adsorption data significantly fitted to modified Freundlich, Freundlich and Langmuir equations. Toor *et al.* (1997) fitted P adsorption data to Langmuir, Freundlich and Tempkin adsorption equations for some soils and found that Freundlich equation explained better the P adsorption behaviour than the Langmuir equation as evidenced by higher correlation co-efficient values (ranged from 0.934 to 0.998). P adsorption increased with increase in equilibrium P concentration.

Biswas *et al.* (1999) noted that the Freundlich equation gave a better fit of the equilibrium sorption data than did Langmuir and Tempkin equations for some soils of Central India. The fitness of data into these equations did not change when the sorption data from different background electrolytes (CaCl_2 , KCl, and NaCl) were used and this indicated the fact that the mechanism of sorption did not alter due to presence of different cations. P sorption data were satisfactorily described by Freundlich and Langmuir adsorption isotherms in eight acidic surface soils (Saha *et al.*, 1999).

2.3.1.6 Factors Affecting Phosphate Adsorption

Many soil properties influence P adsorption by soils, soil minerals and sediments. These include the nature and amount of soil components (e.g. clay, organic matter, and hydrous oxides of iron and aluminium, CaCO_3 for calcareous soil), background electrolyte- its concentration and valency of the constituted cations, pH of the adsorption solution and lastly the soil temperature.

2.3.1.6.1 Iron and aluminium oxides and hydroxides

Amorphous iron and aluminium hydroxides have less well-defined surface than the crystalline hydrous oxides. Among the different soil properties tested for P sorption, acid ammonium oxalate extractable (amorphous) iron and aluminium proved to be an important criterion, governing P adsorption in several acidic soils (Juo, 1981; Borggaard, 1983; Loganathan *et al.*, 1987; Adams *et al.*, 1987; Wada *et al.*, 1989; Buchter *et al.*, 1989; Sanyal *et al.*, 1993; Yuan and Lavkulich, 1994).

Rajan (1975 a,b,c) and Rajan and Perrott (1975) showed that low concentration of phosphate were adsorbed by anion exchange on silica, alumina and soil allophanes.

Larsen *et al.* (1959) studied effects of Fe and Al on the adsorption of P by two organic soils as well as humic acid extracted from the corresponding soils. They demonstrated that large contents of sesquioxides (of Fe and Al) affect positively the P fixation capacity of the soils studied, and also overshadowed the negative (opposite) effects of humic acid content.

Saunders (1965) found significant correlation between phosphate retention and oxalate-extractable Fe and Al contents of some New Zealand soils.

Sree Ramulu *et al.* (1967), while studying P-fixation by 12 acid soils, worked out a significant correlation ($r=0.77$) between P fixation and dithionite extractable Fe. But regression analysis showed that soils which contained kaolinite as the only clay mineral fixed more P. They also worked out a highly significant correlation ($r=0.95$) between P fixation and oxalate-extractable Fe for all but one the soils studied. Finally, Sree Ramulu *et al.* (1967) concluded that the oxalate reagent removes only those forms of Fe present in the soils which

are active in P fixation, but dithionite removes Fe forms which are not active in P fixation. While Vig and Dev (1984) showed that sesquioxides provide major site for P sorption, and the sesquioxides removed by citrate dithionite affect P sorption more than that affected by oxalate extractions. The results also indicated that a higher percentage of sorbed P was in Fe and Al forms.

Loganathan *et al.* (1987) studied P sorption by 42 samples of highly acidic surface soil samples of West Africa. The results showed that the sorption capacities were significantly correlated with different forms of Fe and Al. In addition, amorphous Al appeared to be the predominant soil component influencing P sorption in all the three soil groups used, although on a per unit weight basis, exchangeable Al influenced the P sorption most. Liu *et al.* (1987) found that the amount of P sorbed by the soils correlated significantly with free Fe, Al and clay contents in the red and yellow soils of Sichuan. P adsorption and P-fixation in Alfisols and adjoining Entisols collected from different altitudes of East Kashi hills of Meghalaya was studied (Munna *et al.*, 1987). P adsorption at 0.2 ppm P equilibrium concentration, buffering capacity and adsorption maxima were correlated positively with exchangeable Al and extractable Al in Alfisols and Entisols. Besides the above, the clay was also associated with P adsorption in Entisols. P fixation capacity was correlated significantly with exchangeable, amorphous bound Al and total Fe in Alfisols but with total Fe and amorphous bound Al in Entisols.

Upadhyay *et al.* (1993) studied the adsorption of P by ten soils of the NorthWestern Himalayas. While adsorption maxima were observed to be positively correlated with clay, CBD- Fe_2O_3 and Al_2O_3 , they showed negative correlation with pH, CaCO_3 and Olsen P content of the soils. The P-sorption capacity was significantly correlated with clay and silt contents and with oxalate extractable Al_2O_3 for soils in Nigeria.

2.3.1.6.2 Organic matter

Several scientists have reported significant positive correlation between soil organic matter content and P sorption by soil (Singh and Tabatabai, 1977; Bennoah and Acquaye, 1989; Sanyal and De Datta, 1991; Sanyal *et al.*, 1993).

The role of organic matter in augmenting P sorption in soil has often been attributed to the association with and possible stabilization of the soil organic matter by the 'free' sesquioxides. These organic compound with aluminium and iron could be envisaged as a complex gel, a phospho-silico-hydroxy humate of iron and aluminium (Saunders, 1965). Thus, Wada and Gunjigake (1979) observed that P adsorption by volcanic soils was correlated with organically bound aluminium, and to a lesser extent, with iron extracted by sodium pyrophosphate.

Bennoah and Acquaye (1989), while studying the P sorption characteristics of the selected major Ghanaian soils worked out a significant positive correlation between sorption maximum and organic carbon. A similar relationship has been reported for the Malaysian soils (Ahmad and Foster, 1983). The authors (1989) further demonstrated that iron and aluminium intimately associated with organic matter could sorb much more P than can the same amount of free Fe_2O_3 and Al_2O_3 alone. However, other workers, among them Agboola and Ayodele (1983), found no correlation between sorption maxima and organic carbon.

Patiram *et al.* (1990), while studying the effect of different soil parameters on P adsorption by some acid soils showed that P buffering capacity and P sorbed at 0.2ppm equilibrium solution P were positively and significantly correlated with organic carbon content, amorphous and crystalline forms of Al and Fe, while pH had an inverse relationship.

In a recent study Douli and Dasgupta (1998) observed sorption maxima, bonding energy and buffering capacity of four ferroginous soils (Alfisols) of eastern India had significant positive relationship with organic carbon suggesting the role of organic carbon in P sorption characteristics.

Moreover, reduction of P sorption by organic matter in soils has also been reported (Yaan, 1980; Sibanda and Young, 1986; Anderegg and Naylor, 1988) This can be explained by a possible competition between P and organic matter for common sorption sites on, for instance, hydrous oxides of iron and aluminium.

In a study, Sanyal *et al.* (1993) showed that P sorption per unit weight of clay and organic matter content increased with a decrease in clay or soil organic matter content. Sanyal *et al.* (1993) proposed that intimate clay – organic complexes, formed through cationic bridges, could possibly render some of the active surfaces of both the soil components for P fixation inaccessible.

2.3.1.6.3 Clay

The reaction of phosphate with clay minerals in soil has also received a great deal of attention from soil scientists. It is becoming increasingly evident that clay fix P by the same mechanisms as iron and aluminium compounds do. As a matter of fact, it is probably the aluminium in and on the clay that is responsible for the P fixing properties of clay.

Some clay minerals have a pH dependent charge which occurs at the edges of the crystals where $[Al(OH)(H_2O)]^{n+}$ groups are exposed. The $[Al(OH)_2]^+$ groups are the sites that accept a proton at low pH to lead to positive sites (Bolland *et al.*, 1976). At low solution concentrations, phosphate is adsorbed on some clay mineral surface (Kuo and Lotse, 1972), but at high phosphate concentration precipitation occurred, resulting in the formation of new crystalline phases such as taranakite.

Kuo and Lotse (1972) suggested that phosphate exchanged with Al (H₂O) groups on kaolinite rather than Al (OH)₂ since

- (i) adsorption increased with decrease in pH, and
- (ii) no release of (OH) was observed.

Hydrous oxides of iron and aluminium have been found to occur as fine coating on surface of clay minerals in soils (Greenland *et al.*, 1968; Haynes, 1983). These coatings, having large active surfaces, affect greatly the adsorption by such soils.

Several authors have found significant correlations between P sorption parameters and clay content of the soils studied (Fox and Kamprath, 1970; Dolui and Gongopadhyaya, 1984; Loganathan *et al.*, 1987; Wada *et al.*, 1989; Bennoah and Acquaye, 1989; Sanyal and De Datta, 1991; Sanyal *et al.*, 1993).

This effect of clay on P sorption may possibly be attributed to large specific surface area of the former.

Das *et al.* (1993) studied the effect of soil characteristics on phosphate fixing capacity of some acidic soils of Orissa. The amount of P fixed at four different levels of added P (25, 50, 100 and 150 ppm) and maximum P fixing capacity of these soils showed highly significant positive correlation with clay, free oxides, total exchangeable cations, and negative correlation with the available P content of the given soils.

Adepoju (1993), in the P-sorption studies of forest and Savanna soils of Nigeria found that quantities of added P sorbed by the Inceptisols and Ultisols of the forest zone were significantly higher than that by the Entisols and Alfisols of the Savanna zone. It was also found that P sorption capacity had positive correlation with clay content, exchangeable Al and oxides of Fe and Al.

Milap chand *et al.* (1995) conducted a laboratory experiment of some soils of North –West India and observed that P adsorption in soils decreased with the decrease in CEC, clay, organic carbon and CaCO_3 contents, while equilibrium solution P concentration decreased significantly with the increase in clay, organic carbon, oxalate extractable Fe and Al in soils. The combined effect of clay and extractable Fe explained about 98% of variations both in adsorbed P and in solution P concentration. The soils having higher clay content, CaCO_3 or extractable Fe and Al exhibited high adsorption suggesting the role of these soil constituents in P adsorption (Singh *et al.*, 1996; Toor *et al.*, 1997).

However, Sanyal and De Datta (1991) and Sanyal *et al.* (1993), while working with the soils of south and south East Asia, reported a contradictory relationship between the amount of P fixed and the clay content. Earlier, Fox and Kamprath (1970) also observed similar trends and proposed on easier access of P to clay surfaces when the clay is dispersed through media like sand. Sanyal *et al.* (1993) proposed that intimate clay organic complexes, formed through cationic bridges, might have rendered some of the active surfaces of both the colloidal components of the experimental soils inaccessible for P sorption. They

showed that the Langmuir adsorption maximum per unit surface area of the given soils was negatively correlated with the surface area of the soils studied.

2.3.1.6.4 pH and supporting electrolyte concentration

Several soil scientists observed a strong negative correlation between adsorption parameters (e.g. Freundlich K, Langmuir adsorption maxima) and soil pH (Adams and Odam, 1985; Bolan *et al.*, 1988; Mehadi and Taylor, 1988; Sanyal *et al.*, 1993).

However, an opposite effect of pH had also been observed on P sorption in soils. Thus, a considerable controversy regarding the pH effect exists (Sanchoz and Uehara, 1980; Probert, 1980; Haynes, 1982, 1984; Barrow, 1985, 1990). A decrease in adsorption with pH was reported when dilute solutions of NaCl or KCl were used to measure P adsorption (Barrow, 1984). But when dilute CaCl₂ solutions or concentrated solutions of KCl or NaCl were used, P retention by a limed soil increased (Amarasiri and Olsen, 1973; Barrow, 1984; Naidu *et al.*, 1990). Barrow (1990) was of the opinion that the reaction between P and soil is reaction between charged particles (phosphate ions) and variable charge surfaces and that both the ions present and the charge and the potential of the surface vary with pH and, in addition, the charge and the potential of the surface area affected by the electrolyte present. If the surfaces reacting with P are mainly negative (-) as they are for most soils at common pH values, then increasing the concentration of cations, or increasing the valence of the cations, makes the electric potential less negative and increased P sorption. The higher the pH, the greater this effect. Thus, Barrow (1990) concluded that for realistic assessment of the effect of changing pH on P sorption by a particular soil, measurement of both the concentration and composition of soil solution is necessary.

With increase in pH, the charge and the electrostatic potential of positive sites on variable charge materials in soil decreases, causing a fall in P retention. However, at higher pH (>5.0), the concentration of deprotonated H₂PO₄⁻ (i.e. HPO₄²⁻ ion) increases, and the existing theories (Bowden *et al.* 1980; Barrow,

1984) treat HPO_4^{2-} ion as the dominant adsorbable species (e.g. on goethite). This encourages the P adsorption by goethite at higher pH upto a pH of 7.0 (which is the value of pK_2 of H_3PO_4). Thus, P sorption by goethite (Bowden *et al.*, 1980) and amorphous hydroxy-Al surfaces (Kwong *et al.*, 1979) decreases relatively slowly upto pH 7.0, and rapidly beyond pH 7.0.

The net effect of these opposite tendencies is usually governed by the nature of the supporting electrolyte in which pH effects on P adsorption are measured (Sanyal and De Datta, 1991). Electrolyte concentration and valency of cation affect the electrostatic potential on the surface. An increase in concentration of the electrolyte, especially if the cation is polyvalent, renders the potential on the surface less negative (Bowden *et al.*, 1980; Barrow, 1990), and the effect of higher pH in bringing down P adsorption is less marked.

Four different supporting media (10^{-2}M CaCl_2 , 10^{-4}M CaCl_2 , $3 \times 10^{-2}\text{M}$ NaCl & 10^{-4}M NaCl) were used to study P sorption characteristics of arid and semiarid soils of Punjab (India) (Chowdhary *et al.*, 1993). Phosphate sorption was highest in 10^{-2}M CaCl_2 and lowest in 10^{-4}M NaCl . Greater adsorption in 10^{-2}M CaCl_2 solution eventually was due to an additional effect of Ca^{2+} on P sorption by alkaline soils.

Bala *et al.* (1995) also found that P adsorption increased with increase in ionic strength. At a particular molarity, P adsorption was higher in the presence of CaCl_2 as compared with NaCl .

Biswas *et al.* (1999), while studying in the effect of pH, ionic strength and electrolyte composition on P sorption by some soils of Central India, found that P adsorption was the highest in CaCl_2 medium followed by KCl and NaCl . In the pH range of 4 – 8.5, the amount of P sorbed decreased with increase in pH. The effect was much more pronounced in dilute solutions and solution containing monovalent than divalent cations.

2.3.1.7 Solution P Concentration

The concentration of P in soil solution is an estimate of intensity of P nutrition. The change in equilibrium P in soil solution has been used as a

criterion for characterizing available P status of soil. The intensity factor has been varyingly defined as phosphate potential or equilibrium phosphate potential or phosphorus concentration in soil (Ramamoorthy and Subramanian, 1960; and 1982; Sarkar *et al.*, 1986; Muralidharu and Omanwar, 1987; Patiram, 1990).

Decrease in phosphate potential with P addition has been reported (Biswas *et al.*, 1979). Further, availability of phosphorus in solution increased with water solubility of P fertilizer applied. Patiram (1990) reported equilibrium phosphate potential to be negatively related to soil pH and positively to amorphous iron and aluminium in soil.

The degree of saturation of soil complex with P has been found to be major intensity regulator governing mobility, availability and solubility of soil P and regulating its removal. Investigations have shown (Biswas *et al.*, 1979; Patiram and Rai, 1987) significant correlation between plant P uptake and equilibrium phosphate potential. Importance of intensity factor in early stages of plant growth has been stressed by Patiram and Rai (1987).

2.3.1.8 Phosphate Buffering Capacity

Phosphate buffering capacity of soil characterizes the dynamic relation between labile solid phase (Quantity) and solution phase phosphate (Intensity) from which plants take up their supply. It is measured from slope of the sorption isotherm or quantity-intensity isotherm and it varies according to the solution concentration at which isotherm slope is measured. Various indices used to express this parameter are: i) the slope at a standard equilibrium concentration of 0.2 mg ml^{-1} (Saxena, 1979; Jalali and Sharma, 1991); ii) the slope at a standard equilibrium concentration of $0.3 \text{ } \mu\text{g ml}^{-1}$ (Singh *et al.*, 1971); iii) the maximum slope of the isotherm as solution concentration tends to ∞ ; iv) ratio between the change in quantity factor and intensity factor designated as differential buffering capacity (Pati Ram, 1990).

A close linear relationship existed between P buffering capacity and ability of soil to sorb phosphate (Brar and Vig, 1988). Sandy soils have less P buffering capacity whereas fine textured soils have more (Lakshmi *et al.*, 1987). The

buffering capacity of acid and neutral soils is a function of amounts of crystallinity of hydrated oxides of Fe and Al (Pati Ram 1990). In calcareous soils, the amount of exchangeable calcium and CaCO_3 determine the P buffering capacity. Differential P buffering capacity in soils from North West India showed a significant relation with total Fe and Al, organic carbon and clay (Randhawa *et al.*, 1993), in Sikkim soils with organic carbon content (Pati Ram, 1990) and in four ferruginous soil of eastern India with clay and organic carbon content (Douli and Dasgupta, 1998). Studies conducted by Lakshmi *et al.*, (1987) revealed PBC per unit clay to be more in red soils than in black and alluvial soils.

Intensity is inversely related to P buffering capacity of Randhawa *et al.*, 1993); so soils with high buffering capacity will have less amount of P concentration in soil solution for exploitation by plant roots.

From the literature reviewed, it is clear that availability of P to plants is controlled by the mutual interplay of factors such as quantity, intensity and phosphate buffering capacity. These factors along with kinetic factors determine the diffusive flux of P to growing roots. Attempts have therefore been made (Vig *et al.*, 1978; Sharma *et al.*, 1993) to predict the availability of applied P to crops through the combined use of all these factors in a dimensionless parameter known as supply parameter (SP): $(qc)^{1/2} / (K_1K_2)^{1/4}$.

The supply parameter of phosphorus has been found to bear a close linear relationship with cumulative P desorbed (and Vig *et al.*, 1978; Brar *et al.*, 1986; Bahl *et al.*, 1986; Singh and Sarkar, 1991; Kumar and Singh, 1998) indicating thereby its usefulness for predicting response to applied P. Investigations have shown that the highest (82-86%) variations in P uptake by wheat crop could be accounted for by the use of P supply parameter (Brar *et al.*, 1986). Damodar Reddy *et al.* (1999) observed a highly significant and positive relation between supply parameter and available P.

2.3.2 Phosphate Desorption

Availability of soil P has also been characterised on the basis of P desorbed. Desorption is the reverse phenomena of adsorption and describes the

release of P into soil solution. Phosphorus desorption from soil colloids is one of the series of rate factors that govern P uptake by plants. The desorption of phosphate from soil has been described by Langmuir equation and first order kinetics (Bahl, 1990). Parabolic and radial diffusion equations have also been successfully used to describe release of surface adsorbed phosphate from soil (Krishnappa *et al.*, 1975; Vig and Dev, 1979; Biswas and Ghosh, 1987; Bahl, 1990; Sharma *et al.*, 1993) suggesting that relationship of cumulative P desorbed to $t^{1/2}$ is diffusion controlled.

Bahl (1990) observed that the amount of desorbed P depends upon the texture and type of soil, its P status and cropping sequence followed. Light textured soils desorbed more P than fine textured. Desorption of phosphate has also been reported to be more in alkaline soils than in acid soils (Vig and Dev, 1979). Residual built up P in soil affects the release of P from soil. The rate of release of phosphate and diffusion co-efficient have been found to increase with build up P. The desorption mechanism possible involves rapid dissolution of amorphous P compounds and the slow dissolution of crystalline P compounds. Phosphate in recently fertilized soils is at least thousand times more mobile than the residual build-up from long-term experiments.

The results obtained by Dhillon *et al.* (1986) and Sharma *et al.* (1993) indicated that rate of P release increased with P status of soil and decreased with cropping. A significant linear relationship existed between cumulative desorbed P and dry matter yield and P uptake by crops (Vig and Dev, 1979; Singh and Sarkar, 1991; Bahl *et al.*, 1986), indicating that rate of release of P from solid phase was important in determining P uptake by crops. Phosphate uptake by growing plants has been reported to be less dependent on initial solution P concentration than on the rate of phosphate release/replenishment (Brar and Vig, 1988). Singh *et al.* (1996) showed that a substantial part (42-60%) of P sorbed by some Alfisols of varying agro-climatic region in India was desorbed during two successive desorptions with 0.5 M NaHCO₃ (pH 8.5). The first desorption released considerably more P than the second.

Toor *et al.* (1997) studied adsorption-desorption behaviour of phosphorus of some soils and found that P desorption was far less compared to the P adsorption indicating lower P concentration in soil solution for plant use at a point of time. Dolui and Dasgupta (1998) reported that the amount of P desorbed by the extractant increased with the increase in amount of P sorbed.

Desorption of once- adsorbed P from soils and clays had often been shown to be irreversible leading to a large hysteresis effect (Madrid and Posner, 1979; Olsen and Khasawneh, 1980; Okajima *et al.*, 1983; Mouat, 1983). The desorption isotherm was thus displaced to the left of the sorption isotherm. Such hysteresis effect leads to an overestimation of the replenishing ability of soils to supply P to the soil solution, when P sorption isotherms are used for the purpose (Okajima *et al.*, 1983; Sanyal *et al.*, 1993; Saha *et al.*, 1999). Although Munns and Fox (1976) and Madrid and Posner (1979) found that the resulting degree of hysteresis decreases with longer time allowed after P addition, Ryden and Syers (1977) found the irreversibility of P desorption from soils and hydrous ferric oxide gel to increase with increasing time above 30h. The predominant view at present is to treat such irreversibility as arising from the incomplete attainment of equilibrium during the slower reaction phase of adsorption (Okajika *et al.*, 1983; Barrow, 1983 b, 1985).

Moreover, it has also been suggested that because adsorption equilibrium was slow, an apparent readsorption during the desorption step is possible (Barrow, 1983 b). The diffusive migration of initially adsorbed P beneath the adsorbing surface has also been cited as a probable reason for apparent irreversibility of P desorption (Barrow, 1983 b, 1985). In the event of the latter happening, a part of the adsorbed P would no longer be in equilibrium with the solution, hence, the irreversibility. Indeed, both sorption and desorption continue for long periods, although the rate of change may become too slow (Barrow, 1979 a; Bache and Ireland, 1980). Thus, it was shown that the plots of desorbed P against concentration were continuous with those of newly adsorbed P, but that the plots for originally added P did not coincide with either of these (Barrow, 1983 b), Madrid and Posner (1979) also demonstrated that when the total of

adsorption and desorption time is long enough both adsorption and desorption points tend to lie on a single curve that corresponds to the isotherm calculated according to the Stern model of double layer theory. Kuo *et al.* (1988) observed recovery of sorbed P from several soils, having contrasting properties, by using NaHCO_3 , NaOAC or $\text{NH}_4\text{F-HCl}$ extraction, was strongly dependent on P sorption capacity, but not on the buffer capacity of the soils or the bonding energy estimated by the application of Langmuir equation. However, Sanyal *et al.* (1993) and Saha *et al.* (1999) observed that the extent of hysteresis effect in the phosphate sorption-desorption behaviour was high in soils exhibiting strong phosphate sorption characteristics.