

Note on the use of radioactive isotope to determine the available phosphorus in soils

Chai Moo Cho

Dept. of Agri. Chem., College
of Agriculture, S. N. U.
Suwon, Korea

Introduction

It has long been an object of many soil scientists to measure the available plant nutrient present in a soil. The most widely used pot-culture, though successful in showing whether the soil is deficient or adequate with respect to particular plant nutrient, takes long period of time, cumbersome and does not tell us how much of the element is present in the soil.

The chemical methods to determine, for example, the phosphorus in a soil show variable results depending upon the nature of the extracting solutions, time of extraction and soil to solution ratios (3, 6, 10, 16.).

Recently it was assumed that a plant is the sole object that determine the available plant nutrient in a soil since the plant actually absorbs the available form from a soil. On this basis, Fried and Dean (9) proposed the use of radioactive isotope to measure the available phosphorus in a soil. They assumed that the isotope dilution equation can be applied to the soil and plant. The assumptions in the use of isotope to measure available plant nutrient in a soil are (a) the applied radioactive fertilizer is 100% available to test-plant, (b) the test plant does not distinguish between radioactive and non-radioactive element and (c) the availability of radioactive fertilizer is not altered during the cropping period of the test plant. The use of water-soluble fertilizer will satisfy the assumption (a) and the assumption (b) is generally recognized to be fulfilled except very light elements were used. The assumption (c), however, is open to question. The present investigation was initiated to test the suitability of the isotope dilution principle applied to soil research using radioactive phosphorus. Various chemical methods were also used to compare the results so obtained with the A values.

EXPERIMENTALS

Description of soils

Five different soil samples representative of five different soil series were

taken from various part of Minnesota. Some chemical properties of the samples are shown in table 1.

Table 1. Some chemical properties of the soils

| Soils | Zimmerman loamy sand | Unclass, sandy loam | Fayette silt loam | Webster clay loam | Fargo clay |
|--|----------------------|---------------------|-------------------|-------------------|------------|
| PH | 5.9 | 5.8 | 6.2 | 7.2 | 7.5 |
| Cation exch. capacity (m. e. per 100g) | 2.59 | 7.37 | 11.05 | 47.50 | 34.88 |
| Pray No. 1 P (lbs/2m) | 77 | 280+ | 29 | 10 | 10 |
| NaHCO ₃ P (lbs/2M) | 24 | 72 | 16 | 36 | 28 |
| Morgan (lbs/2M) | 4 | 3 | 2 | 21 | 26 |

Greenhouse and laboratory study

Air dry soils passing 4 mesh shieve were filled to 63/4 inch pots. There were 4 replications. Every pot received adequate amount of nitrogen and potassium. Nitrogen was added in the form of ammonium nitrate and potassium as potassium chloride. Each pot received radioactive superphosphate at the rate of 40 lbs P₂O₅ per acre. The radioactivity of the phosphate was 0.15 mc. per gram of P₂O₅. Wheat, Selkirk, was grown on the pots and after 65 days of growth, plants were harvested and analyzed for phosphate. The phosphorus determination on both soils and plants were carried out colorimetrically by the method of Briggs(4). Radioactivity in the plant material was determined by the method of Mackenzie and Dean (12, 13) and A values were calculated from the equation.

Fixation capacity of the soils for added phosphate was determined by the method as described by Kurtz et al (11). Total phosphorus and chemically available phosphorus were also determined on these soils.

RESULTS

Greenhouse result

Yields of 14 wheat plants in grams and per cent P in plant material are shown in table 2.

Table 2 Yields and phosphorus contents of wheat grown on the soils

| Soils | Yields (g) | %P |
|----------------------|------------|-------|
| Zimmerman loamy sand | 12.0 | 0.195 |

| | | |
|---------------------|------|-------|
| Unclass. sandy loam | 8.1 | 0.224 |
| Fayette silt loam | 15.3 | 0.194 |
| Webster clay loam | 11.8 | 0.209 |
| Fargo clay | 11.7 | 0.233 |
| H. S. D. | 2.82 | 0.053 |

From the yield data, it is seen that the Fayette silt loam gave the greatest value and the Unclass. sandy loam the least. There were no significant differences among wheat grown on the Zimmerman loamy sand, Webster clay loam and Fargo clay.

The per cent phosphorus in wheat were variable from soil to soil, but the differences were not significant at the 5% level. It is noticed that the wheat grown on Unclass. sandy loam, with least yield, has great value of % P while the Fayette silt loam showed reverse effect.

Phosphate fixation

Phosphate fixation experiment as mentioned earlier is useful in characterizing the soil properties. The amount of phosphate fixed by the soils after certain time intervals when monocalcium phosphate was added are shown in fig. 1.

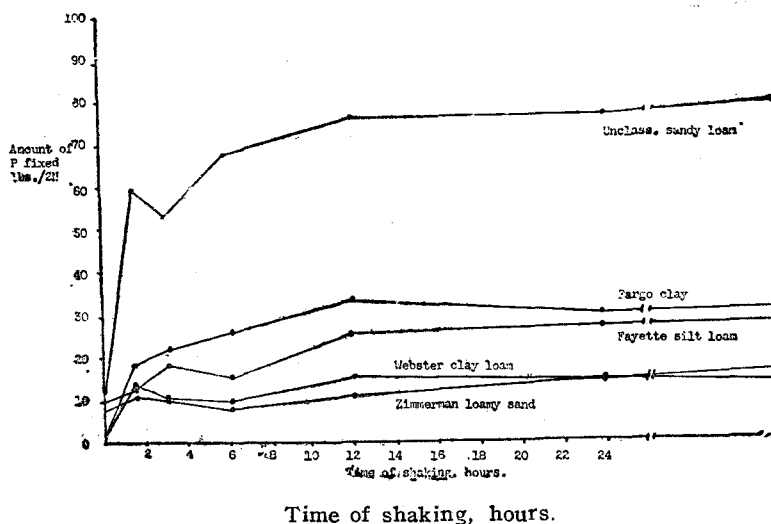


Fig. 1. The amount of phosphorus fixed by soils in various time intervals when added at the rate of 100 pounds of phosphorus per two million pounds of soils.

Fixation for zero time on the graph was obtained after mixing the soils and standard phosphate solution and immediate determination of phosphate on the supernatant. Data on the graph show that phosphate can be fixed by soils very rapidly as many others have shown (7, 8, 15, 17). The capacity to fix the

phosphate varies from soil to soil. The Unclass. sandy loam with lowest pH and medium textured, fixed the highest amount of phosphate. As the pH of the soils increased to near neutral the fixing capacity decreased and as the pH of the soil, the Fargo clay, was alkaline the fixing capacity became great again. The lowest fixing capacity of Zimmerman loamy sand seemed to be due to its coarse textural nature. If the phosphate fixation is first order reaction, the curves should be in the form of $C(1-e^{-kt})$, since the curves were drawn for amount of phosphate fixed. C is constant, K is rate constant and t is the time. The result is certainly in that form. From this consideration, it is seen that the rate constant of Unclass. sandy loam is the greatest and the Zimmerman loamy sand the least.

Available phosphorus results

Chemically extracted phosphorus and A values of the soils determined from radioactivity measurements of plant materials are shown in table 3.

Table 3 A values and chemically extracted available phosphorus of the soils after plant growth

| Soils | A value (lbs./2M) | Bray No1 (lbs./2M) | NaHCO ₃ (lbs./2M) | Morgan (lbs./3M) | Total (lbs./2M) |
|----------------------|----------------------|-----------------------|---------------------------------|---------------------|--------------------|
| Zimmerman loamy sand | 16.47 | 81 | 23 | 10 | 514 |
| Unclass. sandy loam | 45.78 | 287 | 63 | 5 | 1121 |
| Fayette silt loam | 22.52 | 55 | 12 | 4 | 757 |
| Webster clay loam | 12.07 | 35 | 51 | 33 | 993 |
| Fargo clay | 17.25 | 29 | 37 | 25 | 897 |

The Unclass. sandy loam had the highest while the plant grown on this soil showed the least yield. On the other hand the yields of wheat from Fargo clay, Fayette silt loam and Webster clay loam, though their A values were lower than Unclass. sandy loam, were greater than from Unclass. sandy loam. It should be pointed out here that the Unclass. sandy loam had the highest phosphate fixing capacity among all.

The Bray No.1 phosphorus followed the similar pattern as A values. However, in this case the amount of phosphorus was more closely related with the pH of the soils. As the pH of the soils were low the great values of Bray No.1 P were observed and as the pH of the soils increased the phosphorus content also decreased. The Bray No.1 phosphorus was also not correlated with the plant yields.

NaHCO₃ phosphorus was not easily interpretable since its distribution in the

soils was variable and correlation with any soil factor does not seem to exist.

The Morgan phosphorus, mainly calcium phosphate (10), was observed to be present in high content in neutral to alkaline soils and its content decreased with the pH of the soils. This effect is almost reverse from what was observed from the Bray No.1 phosphorus.

The total phosphorus content of the soils was observed to be very high in every case. The Unclass. sandy loam had the highest of all and the most coarse textured Zimmerman loamy sand had the least.

Correlation analysis

To evaluate the methods of determining the available phosphorus in soils, the correlation analysis of the available phosphorus with plant yields and per cent P in plants were carried out. Greater the value of the correlation coefficient the better suited the method is. The results are shown in Table 4.

Table 4. Correlation of available phosphorus with plant yields and per cent P in plant.

| Methods | Yield (r) | % P in plant (r) |
|--------------------|-----------|------------------|
| Bray No.1 | -0.657 | +0.181 |
| NaHCO ₃ | -0.798 | +0.462 |
| Morgan | 0.0 | +0.157 |
| A value | -0.524 | +0.064 |

The results in table 4 indicates that none of the methods correlated well with plant yields nor per cent P. The poor correlation was due to high phosphate content on Unclass. sandy loam and poor yield from this soil. Another factor that contributed the poor correlation was due to exceptionally good growth of wheat on Fayette silt loam while the soil had relatively low available phosphorus.

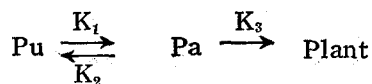
The poor correlation of A value deserves further analysis since many scientists use the A value as a standard for evaluating the available phosphorus status in soils.

Theoretical analysis of isotope dilution principle

It is known that the free iron and aluminum oxides, and calcium hydroxide and carbonates are fixed of added phosphates (1, 2, 5, 7, 14). The fixed phosphates are generally known to be relatively unavailable. The chemistry of the phosphates in soils is very much complicated and yet much is unknown. In this analysis it will be assumed that the soil phosphorus is in dynamic equilibrium between

unavailable form and available form and every transition from one to the other is first order reaction, including the absorption of available form by plant.

Schematically, following diagram will illustrate the pattern of absorption of available form by plant.



Where Pu; the amount of unavailable form, Pa; the amount of available form and k_1 , k_2 , and k_3 are rate constants for the reactions given.

Rate equations for the conversion processes can be written as follows.

$$\frac{dpu}{dt} = k_2 Pa - k_1 Pu \quad (1)$$

$$\frac{dPa}{dt} = k_1 Pu - k_2 Pa - k_3 Pa \quad (2)$$

$$\frac{dAp}{dt} = k_3 Pa \quad (3)$$

Ap; the amount of P absorbed by plant, t ; the time.

It should be pointed out here that the constant k_2 may take the form $k_2'F$, where F refers to the amount of phosphate fixing agent.

Pa is eliminated from eq. (1) and (2), then

$$\frac{d^2 pu}{dt^2} + (k_1 + k_2 + k_3) \frac{dpu}{dt} + k_1 k_3 Pu = 0 \quad (4)$$

The equation (4) has a solution as

$$P_u = C_1 e^{w_1 t} + C_2 e^{w_2 t} \quad (5)$$

$$\text{where } W_1 = -\frac{1}{2}(k_1 + k_2 + k_3) + \frac{1}{2}\{(k_1 + k_2 + k_3)^2 - 4 k_1 k_3\}^{1/2}$$

$$W_2 = -\left[\frac{1}{2}(k_1 + k_2 + k_3) + \frac{1}{2}\{(k_1 + k_2 + k_3)^2 - 4 k_1 k_3\}^{1/2}\right]$$

Substituting the value of Pu and $\frac{dpu}{dt}$ into eq. (1) gives the answer for Pa

$$Pa = \frac{(w_1 + k_1)}{k_2} C_1 e^{w_1 t} + \frac{(w_2 + k_1)}{k_2} C_2 e^{w_2 t} \quad (6)$$

Integration constants can be obtained from the condition that at $t = 0$ $P_u = P_u^0$ and $Pa = P_a^0$

Also it is noticed that

$$P_a^0 = Pa^{\neq 0} + Pa^{*0} \quad \text{and } Pa^{\neq 0} = \frac{k_1}{k_2} P_u^0$$

where $Pa^{\neq 0}$ is the amount of initially present available P

Pa^{*0} is the amount of available radioactive P added to soil

When the integration constants so obtained are substituted into eq. (5) and (6),

$$Pu = \frac{1}{w_1 - w_2} \left[k_2 Pa^{*o} (e^{w_1 t} - e^{w_2 t}) + Pu^o (w_1 e^{w_2 t} - w_2 e^{w_1 t}) \right] \quad (7)$$

$$Pa = \frac{Pa^{*o}}{w_1 - w_2} \left\{ k_1 (e^{w_1 t} - e^{w_2 t}) + (w_1 e^{w_1 t} - w_2 e^{w_2 t}) \right\} \\ + \frac{Pa^{\ddagger o}}{w_1 - w_2} \left\{ (w_1 e^{w_2 t} - w_2 e^{w_1 t}) + k_3 (e^{w_2 t} - e^{w_1 t}) \right\} \quad (8)$$

The amount of phosphorus absorbed by the plant Ap becomes

$$\frac{dAp}{dt} = K_3 Pa \\ Ap = \frac{k_3 Pa^{*o}}{w_1 - w_2} \left\{ (k_3 + w_1) (1 - e^{w_2 t}) - (k_3 + w_2) (1 - e^{w_1 t}) \right\} \\ + \frac{Pa^{\ddagger o}}{k_1 (w_1 - w_2)} \left\{ w_2 (w_2 + k_3) (1 - e^{w_1 t}) - w_1 (w_1 + k_3) (1 - e^{w_2 t}) \right\} \quad (9)$$

Splitting the terms in the equations into radioactive term and non-radioactive term leads to

$$Pa^* = \frac{Pa^{*o}}{w_1 - w_2} \left\{ (w_1 e^{w_1 t} - w_2 e^{w_2 t}) + k_1 (e^{w_1 t} - e^{w_2 t}) \right\} \\ Pa^{\ddagger} = \frac{Pa^{\ddagger o}}{w_1 - w_2} \left\{ k_3 (e^{w_1 t} - e^{w_2 t}) + (w_2 e^{w_1 t} - w_1 e^{w_2 t}) \right\} \\ Ap^* = Pa^{*o} + \frac{Pa^{*o}}{w_1 - w_2} \left\{ k_3 (e^{w_1 t} - e^{w_2 t}) + (w_2 e^{w_1 t} - w_1 e^{w_2 t}) \right\} \\ Ap^{\ddagger} = Pa^{\ddagger o} + Pu^o - \frac{Pa^{\ddagger o}}{k_1 (w_1 - w_2)} \left\{ (w_2^2 e^{w_1 t} - w_1^2 e^{w_2 t}) - k_3 (w_2 e^{w_1 t} - w_1 e^{w_2 t}) \right\}$$

The isotope dilution equation used to determine the available phosphorus, if written in different form, becomes

$$\frac{A}{B} = \frac{(1-y)}{y} = \frac{Ap^{\ddagger}}{Ap^*}$$

where Y is the fraction of P in plant derived from radioactive phosphorus

B is the amount of radioactive fertilizer applied to the soil and is equal to Pa^{*o}

A is the available P present in the soil and is equal to $Pa^{\ddagger o}$

Now the ratio of non-radioactive available P to radioactive available P becomes

$$\frac{Ap^{\ddagger}}{Ap^*} = \frac{Pa^{\ddagger o} + Pu^o - \frac{Pa^{\ddagger o}}{k_1 (w_1 - w_2)} \left\{ (w_2^2 e^{w_1 t} - w_1^2 e^{w_2 t}) - k_3 (w_2 e^{w_1 t} - w_1 e^{w_2 t}) \right\}}{Pa^{*o} + \frac{Pa^{*o}}{w_1 - w_2} \left\{ k_3 (e^{w_1 t} - e^{w_2 t}) + (w_2 e^{w_1 t} - w_1 e^{w_2 t}) \right\}} \quad (10)$$

The equation (10) is now used to interpret the experimental cases.

Case 1. If the plant is grown for very long period of time, then $t \rightarrow \infty$ and the ratio is

$$\frac{Ap^*}{Ap^*} \approx \frac{Pa^{*0} + Pu^0}{Pa^{*0}} \gg \frac{Pa^{*0}}{Pa^{*0}} = \frac{A}{B}$$

From this it is seen that as the plant is grown for very long time the ratio of phosphorus in plant derived from both sources becomes equal to the ratio of total phosphorus to applied radioactive phosphorus. This clearly indicates that the A value is greatly over-estimated.

Case II. If the soil has a high phosphate fixing power, then $k_2 \gg k_1$ or k_3 . In this case, $w_1 \cong 0$, $w_2 \cong -k_2$ and $w_1 t \cong 0$ then

$$\frac{Ap^*}{Ap^*} = \frac{k_2 Pa^{*0} (k_1 + k_2 - k_2 e^{w_1 t} - k_3 e^{w_1 t})}{k_1 Pa^{*0} (k_2 + k_3 e^{w_1 t} - k_3 e^{w_2 t} - k_2 e^{w_1 t})}$$

If the time of experiment is not too short, then $e^{w_1 t}$ and $e^{w_2 t}$ become much smaller than unity. If these terms are neglected,

$$\begin{aligned} \frac{Ap^*}{Ap^*} &\approx \frac{k_2 Pa^{*0} (k_1 + k_2 - k_2 e^{w_1 t} - k_3 e^{w_1 t})}{k_1 Pa^{*0} (k_2 + k_3 e^{w_1 t} - k_3 e^{w_2 t} - k_2 e^{w_1 t})} \approx \frac{k_2^2 Pa^{*0}}{k_1 k_2 Pa^{*0}} \\ &= \frac{k_2 Pa^{*0}}{k_1 Pa^{*0}} = \frac{Pu^0}{Pa^{*0}} \gg \frac{A}{B} \end{aligned}$$

The approximation becomes closer to true as the value of k_2 becomes larger. This indicates that as the soil has higher phosphate fixing power, the greater the A value of that soil. This interpretation is consistent with the result of A values. The Unclass. sandy loam had the highest phosphate fixing power and highest A value while the wheat grown from that soil had the poorest yields.

Case III. If the available phosphorus added to soil is not fixed, then $k_2 = 0$. From eq. (1)

$$Pu^* = Pu^0 e^{-k_1 t}$$

$$Pa^* = Pa^{*0} e^{-k_3 t}$$

$$Pa^* = \frac{k_1 Pu^0}{(k_3 - k_1)} (e^{-k_1 t} - e^{-k_3 t}) + Pa^{*0} e^{-k_3 t}$$

$$Ap^* = Pa^{*0} (1 - e^{-k_3 t})$$

$$Ap^* = \frac{Pa^{*0}}{k_3 - k_1} \{k_3 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_3 t})\} + Pa^{*0} (1 - e^{-k_3 t})$$

therefore

$$\frac{Ap^*}{Ap^*} = \frac{Pa^{*0}}{Pa^{*0}} \left\{ 1 + \frac{\{k_3 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_3 t})\}}{(1 - e^{-k_3 t}) (k_3 - k_1)} \right\}$$

If $k_3 > k_1$ as generally is the case for showing P deficiency symptom at later part of plant growth, then

$$(k_3 - k_1) > 0 \quad e^{-k_1 t} > e^{-k_3 t}$$

and

$$\frac{Ap^*}{Ap^*} = \frac{Pa^{*0}}{Pa^{*0}} + \text{positive term} > \frac{Pa^{*0}}{Pa^{*0}}$$

If $k_1 > k_3$; the case when the soil supplies adequate available phosphorus

$$\frac{Ap^*}{Ap^*} = \frac{Pa^*}{Pa^*} + \frac{Pa^*}{Pa^*} \cdot \frac{\{k_1(1 - e^{-k_3 t}) - k_3(1 - e^{-k_1 t})\}}{(k_1 - k_3) 1 - e^{-k_3 t}}$$

since the second term of the right of the equation is also positive term, the A value is also over-estimated. In this latter case, however, since $k_3 < k_1$ the term $e^{-k_3 t}$ in the denominator is greater than former case. As a result the degree of over estimation is greater than former case. In another word, as the soil has higher phosphate supplying power, the greater the A value becomes. It is surprising that the A values are over-estimated even though the soil does not fix the added radioactive phosphate. Case V. If $K_1 = K_2 = 0$, the case when the phosphate is neither fixed nor released from the soil.

The solution of the equation gives

$$Pa^* = Pa^{*0} e^{-k_3 t}$$

$$Pa^* = Pa^{*0} e^{-k_3 t}$$

$$Ap^* = Pa^{*0} (1 - e^{-k_3 t})$$

$$Ap^* = Pa^{*0} (1 - e^{-k_3 t})$$

and

$$\frac{Ap^*}{Ap^*} = \frac{Pa^*}{Pa^{*0}} = \frac{A}{B}$$

In this case the equation $A = B (1 - y/y)$ holds. In another word, the isotope dilution principle can be applied to determine the available phosphorus in a soil only when there is no fixation nor release of the phosphate from the soil.

CONCLUSION

Wheat was grown on five different soils with varying degree of phosphate fixing capacity to determine the A value. Plant yields and per cent phosphorus in plant were used to evaluate the degree of suitability of various chemical methods and A value.

None of the chemical methods were well correlated with the plant factors.

Since A value gave anomalous result, theoretical analysis of applicability of the isotope dilution principle was carried out. It was found that as the soil has the higher phosphate fixing capacity for added phosphate, greater the A value. The A value become also greater with the time of plant growth. It was pointed out that the isotope dilution principle can be successfully applied only when where is no chemical change between radioactive form and different-phased non-radioactive form.

From the experiment and theoretical analysis, it can be said that wheat can grow on a soil with smaller than 15 pounds of P_2O_5 per acre if adequate supply of

phosphorus is continually maintained from soil phosphorus (unavailable form);

Literature cited

1. Bass, G.B. and D. H. Sieling
Method for determining relative phosphate fixing capacity of acid soils
Soil Sci. 69; 269 (1950)
2. Black, C. A.
Phosphate fixation by kaolinite and other clays as affected by pH, phosphate concentration, and time of contact
Soil Sci. Soc. Amer. Proc. 7; 123 (1943)
3. Bray, R. H. and S. R. Dickman
Adsorbed phosphates in soils and their relation to crop responses
Soil Sci. Soc. Amer. Proc. 6; 312 (1941)
4. Briggs, A. P.
A modification of the Bell-Doisy phosphate method
J. Biol. Chem. 53; 13 (1922)
5. Cole, C. V. and M. L. Jackson
Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils
Soil Sci. Soc. Amer. Proc. 15; 84 (1951)
6. Cooke, C. W.
Fixation of phosphate during the acid extraction of soil
J. Soil Sci. 2; 254 (1951)
7. Davis, F. L.
Retention of phosphates by soils. 1
Soil Sci. 56; 457 (1943)
8. Ford, M. C.
The nature of phosphate fixation in soils
J. Amer. Soc. Agron. 25; 134 (1933)
9. Fried, M. and L. A. Dean
A concept concerning the measurement of available soil nutrients
Soil Sci. 73; 263 (1952)
10. Ghani, M. O.
Fractionation of soil phosphorus. 1.
Indian J. Agr. Sci. 13; 562 (1943)
11. Kurtz, L. T., E.E. Deturk, and R.H. Bray
Phosphate adsorption by Illinois soils
Soil Sci. 61; 111 (1946)
12. Mackenzie, A. J. and L. A. Dean
Procedure for measurement of P 31 and P 32 in plant material

- Analyt. Chem, 20; 559 (1948)
13. Measurement of P 32 in plant material by the use of briquet
Analyt. Chem. 22; 489 (1950)
14. McGeorge, W. T. and J.F. Breazeale
Phosphate solubility studies on some unproductive calcareous soils
Ariz. Agr. Expt. Sta. Tech. Bull. 35, (1931)
15. Moser, F.
Fixation and recovery of phosphate from some lateritic soils
Soil Sci. Soc. Amer. Proc. 6; 328 (1941)
16. Olsen, S. R., C. W. Cole, F. S. Watanabe and L. A. Dean
Estimation of available phosphorus in soils by extraction with NaHCO_3
Agron. J. 46; 175 (1954)
17. Toth, S. J.
Anion adsorption by soil colloid in relation to changes in free iron oxides
Soil Sci. 44; 299 (1937)