▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol.12, No.2, December 2001, pp. 130-139 ISSN 1021-1012

PYROPHOSPHATE AS A SOURCE OF PHOSPHORUS: HYDROLYSIS UNDER DIFFERENT CONDITIONS

Fiaz Ahmad[1] and William Ian Kelso[2]
[1]Central Cotton Research Institute, Multan, Pakistan. [2]Department of Soil Chemistry, University of North Wales, Bangor, UK.

Abstract: Polyphosphates are occasionally added to the soils as a phosphate source for plant nutrition. Polyphosphates (e.g. pyrophosphates) may be more economical due to their smaller volume and low transportation costs. Pyrophosphates (PP) are water-soluble and their condensed nature results in higher P analyses. However, it is observed that PP is a relatively ineffective source of P for plants prior to hydrolysis to the orthophosphate form. Hydrolysis of PP was, therefore, studied under different conditions. Pyrophosphate hydrolysis proceeded very slowly in solution media compared with that in the soil system. Added orthophosphate (OP), calcium carbonate ($CaCO_3$) and organic acids (rice straw extract) increased PP hydrolysis in solution. Hydrolysis of PP was more in soils subjected to submerged incubations as compared to moist incubations. In soil system addition of OP decreased PP hydrolysis both during submerged and moist incubations, whereas addition of organic acids (rice straw extract) along with OP increased PP hydrolysis. Increasing levels of temperature increased PP hydrolysis both in solution media and in soil system (submerged and moist incubations).

Keywords: Pyrophosphates, orthophosphates, hydrolysis, calcium carbonate, soil, submerged, moist.

INTRODUCTION

Orthophosphate (OP) is the major phosphate constituent of most phosphatic fertilizers and is well known as the main phosphate source in plant nutrition. The efficiency of applied phosphate is quite low in calcareous soils as added fertilizer is quickly immobilized by $CaCO_3$ and gradually deposited as water insoluble calcium compounds. The major primary product of the OP fertilizer in calcareous soils is dicalcium phosphate, which is subsequently transformed into octacalcium phosphate and the more basic hydroxyapatite [Griffin and Jurinak 1974].

Polyphosphates are occasionally added to the soils as a phosphate source for plant nutrition. During the last 50 years, there have been considerable increases in the fertilizer costs due to the increased demand of fertilizers for better crop production. This has drawn the attention of scientists to the use of economical fertilizers. Polyphosphates (e.g. pyrophosphates, etc.) may be more economical due to less volume and low transportation costs. Pyrophosphates are water-soluble and their condensed nature results in higher P analyses. In spite of their water solubility, pyrophosphates are not considered to be as efficient as orthophosphates in terms of plant nutrition.

It is well known that PP is a relatively ineffective source of P for plants prior to hydrolysis to the orthophosphate form [Sutton and Larsen 1964].

Generally the effectiveness of PP as a source of phosphorus for plants depends on its reactions with the soil constituents and the distribution of phosphorus between ortho- and pyro-phosphates at different times during the growing season [Hughes and Hashimoto 1971]. Studies on this aspect have revealed that PP hydrolysis in soils is a reaction of both chemical and bio-chemically mediated processes. Different factors, which are reported to enhance the PP hydrolysis, are the increases in temperature, H-ion concentration, enzymatic activity, colloidal gels, complexing cation concentrations and the ionic environment in the solution [Dick and Tabatabai 1986]. Other factors such as moisture content, soil texture and amounts of soil organic matter and their particular properties such as the molecular size and composition will also effect PP hydrolysis [Hons *et al.* 1986]. Pyrophosphate hydrolysis is catalyzed by the pyrophosphatase enzyme [Stott *at el.*1985], distributed within fauna, flora and soils. The activity of this enzyme decreases with an increase in the $CaCO_3$ levels due to the binding of the essential Mg^{2+} ions by $CaCO_3$ [Tabatabai and Dick 1979].

Pyrophosphate hydrolysis is also affected by soil moisture contents; flooded soils having more rapid hydrolysis than when at -33 kPa moisture potential [Hossner and Phillips 1971]. Half-life values of applied PP under submerged conditions ranged from about 0.5 to 4 days depending on other environmental factors. The half-life time required for PP hydrolysis under aerobic conditions varied from 4 to 100 days [Blanchar and Hossner 1969].

MATERIALS AND METHODS

EXPERIMENT I. PYROPHOSPHATE HYDROLYSIS IN SOLUTION

Hydrolysis of PP was studied in solution media incubated at three temperature levels for a period of 240 days with the following treatments.

1. PP (Potassium Pyrophosphate @ 1000 μg P ml^{-1} solution)
2. PPCa (Pyrophosphate + $CaCO_3$ @ 5g 100 ml^{-1} solution)
3. PPOa (Pyrophosphate + Organic acids*)
4. PPCaOa (Pyrophosphate + $CaCO_3$+ Organic acids)
5. PP+OP (Pyrophosphate 20 % + Orthophosphate 80 %)

*water extract of rice straw containing humic acids etc.

All the treatments were subjected to three temperature levels i.e. 5, 25 and 45°C respectively in a refrigerator, room temperature and incubator. Pyrophosphate solution was also incubated at three pH levels of 4.5, 6.5 and 8.5, adjusted with the addition of NaOH or diluted H_2SO_4.

Water Extract of Rice Straw

Rice straw (2 g) was added to 100 ml water in plastic bottle, shaken for one hour at 175 cycles per minute in a reciprocating shaker. The extract was filtered and retained for the treatments.

Experimental Procedure

Phosphate solution was prepared and a volume of 100 ml with a final concentration of 1000 ug P ml^{-1} was added in triplicate to 125 ml plastic bottles and kept at three different temperatures as mentioned above. Phosphate in solution was determined [Olsen and Dean 1965] after 30, 60, 90, 120 and 240 days. Small portion of each sample was used to hydrolyze the remaining PP in solution keeping at 95°C for 14 hours in the presence of 1ml H_2SO_4. Solution P was determined and considered as total P. Unhydrolyzed PP at each stage was determined by subtracting the solution P from the total P and the data are presented as percentage PP hydrolyzed in Table 1.

Table 1: Percent PP hydrolyzed in solution media as affected by different (a) Treatments (b) Temperature levels and (c) pH values

	Days of Incubation			
	30	60	120	240
Treatments		(a)		
T1	0.07	0.20	0.90	1.10
T2	0.63	1.50	3.07	3.77
T3	0.93	1.80	3.27	3.90
T4	1.50	2.47	4.77	6.27
T5	6.97	13.10	14.27	28.23
Temperature (°C)		(b)		
5	0.90	1.60	3.34	4.08
25	1.98	4.18	8.70	9.92
45	3.18	5.52	9.72	11.96
pH		(c)		
4.5	3.60	7.50	13.80	15.40
6.5	1.70	2.50	4.40	5.50
8.5	1.10	1.70	2.90	2.64

EXPERIMENT II. PYROPHOSPHATE HYDROLYSIS IN SOIL CONDITIONS

This experiment was conducted to see the effect of submerged and moist conditions at three temperature levels (5°C, 25°C, 45°C) on PP hydrolysis in Typic Haplorthod and Typic Haploxerult soils from UK and a Typic Camborthid Pakistani soil. The effect of OP and/or organic acids on PP hydrolysis under submerged and moist conditions was also included in studies. Physiochemical characteristics of the soils are given in Table 2.

Treatments

The following treatments were included for each soil.

1. PP (Potassium Pyrophosphate @ 1000 µg P ml^{-1} of solution)
2. PPOP (Pyrophosphate 20 % + Orthophosphate 80 %)
3. PPOPOa (Oa = Rice Straw Extract 10 ml)

Experimental Procedure

Soil samples (10 g) from each soil type in triplicate were added into plastic bottles with phosphate solution, distilled water and/ or rice straw extract. A total volume of 10 ml in each bottle was achieved for the samples incubated under submerged conditions. The bottles were sealed and kept at three temperature levels of 5, 25 and 45°C respectively in a refrigerator, room temperature and an incubator. For the soils under moist conditions, a total volume of 1.5 ml was achieved by drying the samples at 32°C and then the bottles were sealed and kept in incubator as above. Sampling was done after every week and solution P determined. Total P in solution was determined after hydrolyzing the remaining PP in solution in the presence of 1 ml concentrated H_2SO_4 at 95°C for 14 hours. The effect of submerged and moist conditions on native soil P was eliminated by deducting the solution P in control samples from P treated samples. Unhydrolyzed PP was obtained by subtracting the solution P from the total P. Results are presented as percentage of PP hydrolyzed during 4 weeks of submerged and moist incubations.

Table 2: Some Physiochemical Properties of Soils

Soil Characteristics	Typic Haplorthod Soil (UK)	Typic Haploxerult Soil (UK)	Typic Camborthid Soil (Pakistan)
% Sand	72.86	36.28	12.10
% Silt	23.33	55.13	74.64
% Clay	3.91	8.6	13.26
Textural Class	Sandy loam	Sandy silt loam	Silt loam
% $CaCO_3$ equi.	0.00	1.05	14.00
pH	4.51	5.93	8.49
CEC (c moles kg^{-1} soil)	22.5	15.5	21.3
Exch. Ca^{++}(c moles kg^{-1} soil)	Nil	8.50	17.4
Exch. Mg^{++}(c moles kg^{-1} soil)	Nil	1.20	2.30
Free Fe Oxides (mg g^{-1} soil)	146.00	28.50	18.80
Organic Carbon (%)	3.15	2.70	0.70
$NaHCO_3$-P (mg kg^{-1} soil)	9.45	19.60	10.16
DTPA-Fe (mg kg^{-1} soil)	54.29	93.39	2.16
DTPA-Mn (mg kg^{-1} soil)	6.95	37.49	5.73
DTPA-Cu (mg kg^{-1} soil)	0.45	2.45	1.37
DTPA-Zn (mg kg^{-1} soil)	1.92	2.07	0.88

Methods for analysis: Phosphorus [Olsen and Dean 1965], Micronutrients (Fe, Mn, Cu and Zn) [Lindsay and Norvell 1978]

RESULTS AND DISCUSSION

PYROPHOSPHATE HYDROLYSIS IN SOLUTION

Hydrolysis of PP in solution was examined during a long incubation period of 240 days. It was found to be a slow process in solution media and only 1.0 percent hydrolysis in PP treatment was observed after 240 days (Table 1a). Addition of $CaCO_3$ and organic acids alone or in combined form increased PP hydrolysis. The combined effect of $CaCO_3$ and organic acids (T4) in hydrolyzing PP was more pronounced. Addition of $CaCO_3$ to PP solution (T2) might have caused a positive effect on chemical hydrolysis of PP. It has been reported that water soluble Ca^{2+} was involved in chemical hydrolysis of PP and tri-metaphosphate hydrolysis was shown to be catalyzed by Ca^{2+} in sterile water [Healy and Kilpatrick 1955]. The commercial grade lime used as Ca^{2+} source might also contain Mg^{2+}, which is required for the activation of PP in pyrophosphatase assays [Searle and Hughes 1977] and has been shown to promote chemical hydrolysis of polyphosphates in soils [Busman and Tabatabai 1985]. Addition of organic acids (rice straw extract) to PP solution (T3) also increased PP hydrolysis probably due to the effects on pH and/or due to the presence of pyrophosphatase enzyme in the extract [Tabatabai and Dick 1979], which catalyzed the hydrolysis of PP. Since PP hydrolysis is a reaction of both chemical and biochemically mediated processes [Dick and Tabatabai 1986] both types of hydrolysis might have taken place in this treatment. Maximum hydrolysis of PP was observed where OP was added with PP (T5), which was probably due to increased chemical hydrolysis.

Pyrophosphate hydrolysis increased with the increase in temperature from 5^oC to 45^oC (Table 1b). Increases in PP hydrolysis with an increase in the temperature from 5^oC to 35^oC have also been reported [Hons *at el.* 1986]. Hydrolysis of PP decreased with the increase in pH from 4.5 to 8.5 (Table 1c). Hydrolysis in sterile aqueous systems normally decreases with the increase in pH [Van Wazer *at el.* 1955], probably due to decrease in H^+ contribution for hydrolysis with the rise in solution pH.

HYDROLYSIS IN SOILS

Hydrolysis of PP in Typic Haplorthod and Typic Haploxerult UK soils and a Typic Camborthid Pakistani soil was observed during an incubation period of 4 weeks (Tables 3, 4 and 5).

In PP treatment maximum hydrolysis (63%) was observed in Typic Camborthid Pakistani soil and the minimum (58.5%) in Typic Haploxerult soil from UK. It may be suggested that less sorption of applied PP took place in the Typic Camborthid soil, which had pH values more than 7.0 and contained more $CaCO_3$ (14%) and less DTPA extractable Fe (2.16 mg kg^{-1} soil) compared with the other soils.

The sorption of applied PP in Typic Camborthid soil was probably controlled by extractable Fe and not by $CaCO_3$. More adsorption of applied PP in acidic soils than the calcareous soils has been reported [Hons *at el.* 1986]. It has been found that adsorbed PP hydrolyzed at a slower rate than non-adsorbed PP [Van Wazer *at el.* 1955]. They concluded that the fixation (adsorption and/or chemical precipitation) of PP reduces its enzyme-catalyzed hydrolysis. Therefore, it is most likely that soils with a low P-fixing capacity would hydrolyze PP at a higher rate than the soils with a high P-fixing capacity. The optimum pyrophosphatase activity occurs at pH values between 7 and 8 in soils [Dick and Tabatabai 1978]. Furthermore, alkaline soils tend to have both alkaline and acid phosphatase and acid soils to exhibit only acid phosphatase activity [Dick and Tabatabai 1986], which may partially account for increased hydrolysis in Typic Camborthid soil. The greater sorption of applied PP by Typic Haplorthod and Typic Haploxerult soils was not unexpected due to high Fe contents, which are known as active sorption

Table 3: Percent PP hydrolyzed in Typic Haplorthod soil during 4 weeks of incubation as affected by different (a) Treatments (b) Temperature levels

	Weeks of Incubation			
	1	2	3	4
Treatment Effect	(a)			
T1	26.7	40.5	50.7	59.9
T2	7.8	14.5	28.0	39.3
T3	10.5	17.2	32.3	47.3
Temperature Effect	(b)	(Submerged)		
5°C	10.3	20.0	28.7	44.0
25°C	18.7	26.3	43.3	56.0
45°C	29.3	36.3	55.0	62.0
	(Moist)			
5°C	6.0	13.3	22.7	34.0
25°C	10.3	22.0	34.3	46.7
45°C	15.3	26.3	38.0	48.0

Table 4: Percent PP hydrolyzed in Typic Haploxerult soil during 4 weeks of incubation as affected by different (a) Treatments (b) Temperature levels

	Weeks of Incubation			
	1	2	3	4
Treatment Effect	(a)			
T1	27.2	40.8	51.2	58.5
T2	5.9	13.3	25.0	41.8
T3	14.7	19.2	34.2	51.2
Temperature Effect	(b)	(Submerged)		
5°C	10.3	18.2	29.3	44.7
25°C	13.2	26.0	42.0	56.7
45°C	19.0	34.2	48.0	60.7
	(Moist)			
5°C	7.7	15.7	22.7	32.0
25°C	11.7	22.6	35.6	51.7
45°C	19.0	30.0	43.0	57.3

Table 5: Percent PP hydrolyzed in Typic Camborthid soil during 4 weeks of incubation as affected by different (a) Treatments (b) Temperature levels

	Weeks of Incubation			
	1	2	3	4
Treatment Effect	(a)			
T1	41.3	50.7	58.3	63.2
T2	8.0	15.3	27.3	38.2
T3	18.3	27.0	38.5	49.7
Temperature Effect	(b)	(Submerged)		
5°C	17.3	26.0	34.0	41.7
25°C	22.7	38.3	52.0	62.7
45°C	26.0	44.0	59.7	67.7
	(Moist)			
5°C	9.2	15.0	22.7	28.7
25°C	14.8	30.0	39.0	51.0
45°C	19.0	32.7	41.0	50.3

for applied PP and/or OP. Polyphosphate hydrolysis is shown to be negatively correlated with dithionite extractable iron [Busman 1984]. Addition of OP with PP in all the soils decreased PP hydrolysis in contrast to its addition in the solution media. Inhibition of PP hydrolysis by OP has also been reported [Stott *et al.* 1985]. The exact mechanism by which OP inhibits PP hydrolysis is not yet known. It has been suggested that competition between OP and PP ions for sorption sites might be involved in inhibition process. It has been reported that borate (BO_3^{2-}), arsenate (ASO_4^{3-}), molybdate (MoO_4^{2-}), vanadate (VO^{3-}) and tungstate (WO_4^{2-}), which have similar ionic structure as OP, act as competitive inhibitors of pyrophosphatase in soils [Stott *et al.* 1985]. Addition of organic acids along with OP increased PP hydrolysis in all the soils studied. Organic ions might have competed with PP and/or OP ions for the sorption sites in the soils resulting in the less sorption of applied PP and hence more hydrolysis. Moreover, the addition of organic acids might also have increased the activity of pyrophosphatase enzyme [Tabatabai and Dick 1979].

Hydrolysis of PP increased with the temperature and moisture contents in all the three soils studied. The effect of temperature levels was similar both under submerged and moist incubations. Maximum hydrolysis was observed at 45^{o}C and minimum at 5^{o}C in all the soils. Increases in PP hydrolysis with the increase in temperature from 5^{o}C to 35^{o}C have also been reported [Hons *at el.* 1986]. This increase in temperature to 35^{o}C probably increased the microbial and enzymatic activities, which ultimately favored PP hydrolysis.

The data regarding the effect of submerged and moist incubations on PP hydrolysis in all the soils is presented in Fig. 1. The hydrolysis of PP showed similar trend in the soils studied. The hydrolysis was more in submerged incubations than in moist incubations. In submerged incubations about 23, 15 and 32 % more hydrolysis was observed in Typic Haplorthod, Typic Haploxerult and Typic Camborthid soils respectively. The greater rate of PP hydrolysis under submerged conditions compared with the moist conditions may be due to changes in physical, chemical and microbiological processes that take place under these conditions. Changes that could affect rates of PP hydrolysis when a soil is flooded include rise in pH in acid soils and solubilization of Mn and Fe [Patrick and Fontenot 1976]. Soil pH may affect the hydrolysis reaction by affecting enzymatic activity such as ionization states of enzymes and substrates [Dick and Tabatabai 1987]. Increased solubilization of metals (e.g. formation of Fe^{2+}) would also decrease sorption of linear polyphosphates thus leaving them susceptible for hydrolysis reactions [Dick and Tabatabai 1986].

CONCLUSIONS

1. Hydrolysis of PP was negligible in solution compared with that in the soils.
2. Added OP, $CaCO_3$ and organic acids (rice straw extract) increased PP hydrolysis in solution.
3. Hydrolysis increased with a rise in the temperature and decreased with a rise in solution pH.

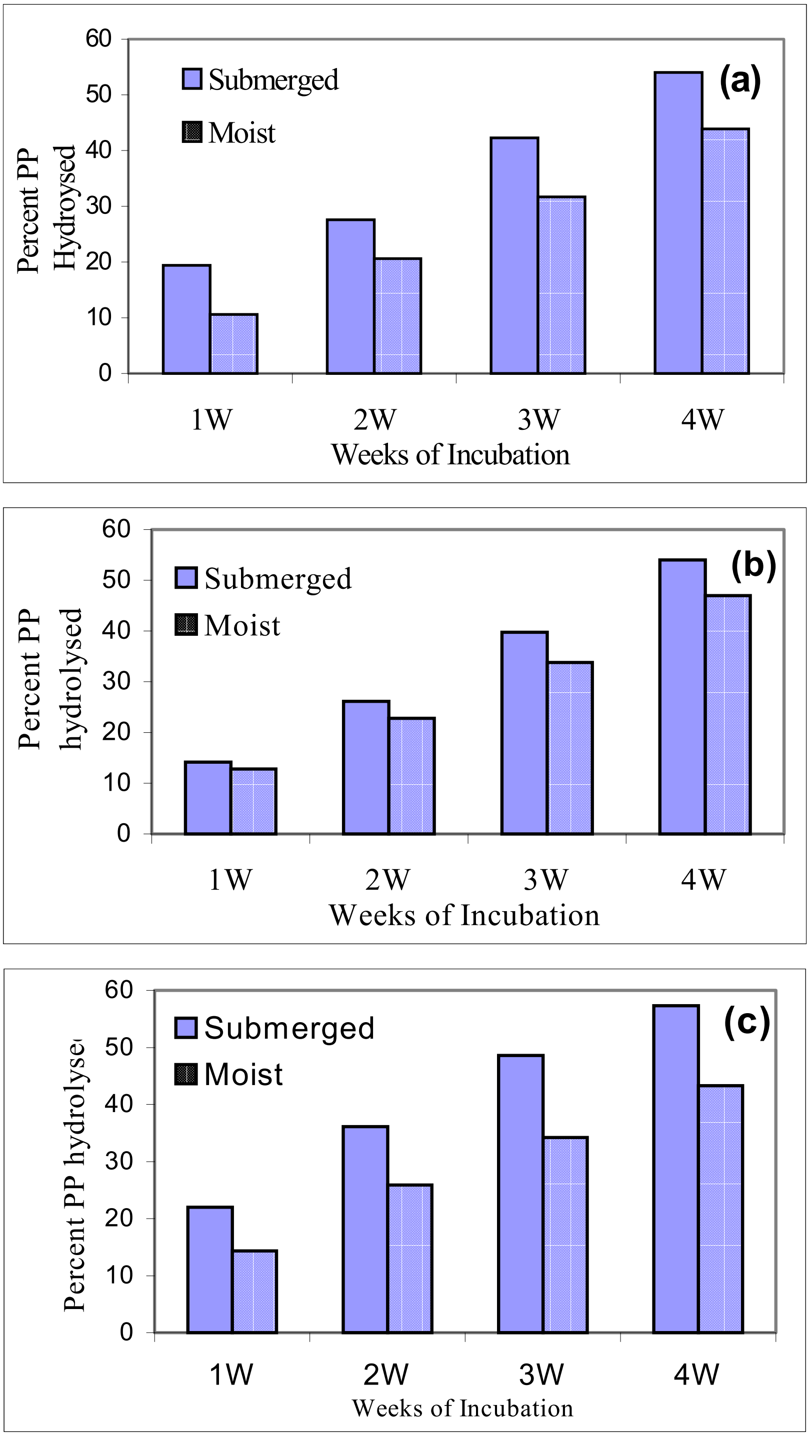

Fig. 1: Effect of submerged and moist incubations on PP hydrolysis in (a) Typic Haplorthod (b) Typic Haploxerult and (c) Typic Camborthid soils.

4. Hydrolysis increased both in solution and soils with the increase in temperature to 45ºC and it was more in submerged than that in moist incubations.
5. Addition of OP to PP solution decreased hydrolysis in the soils, whereas addition of organic acids along with OP increased hydrolysis.

References

Blanchar, R.W. and Hossner, L.R. (**1969**) "Hydrolysis and sorption of orthophosphate, pyrophosphate and trimetphosphate anions added to an Elliot soil", *Soil Sci. Soc. Am. Proc*., 33, 141-144.

Busman, L.M. (**1984**) "Behaviour of polyphosphates in soils" Ph.D. Thesis, Iowa State University, Ames, Iowa, USA.

Busman, L.M. and Tabatabai, M.A. (**1985**) "Hydrolysis of trimetaphosphate in soils", *Soil Sci. Soc. Am. J.,* 49, 630-636.

Dick, R.P. and Tabatabai, M.A. (**1986**) "Hydrolysis of polyphosphates in soil", *Soil Science*, 142(3), 132-140.

Dick, R.P. and Tabatabai, M.A. (**1987**) "Factors affecting hydrolysis of polyphosphates in soils", *Soil Science*, 143 (2), 97-104.

Dick, W.A. and Tabatabai, M.A. (**1978**) "Inorganic pyrophosphatase activity of soils", *Soil Biol. Biochem*., 10, 59-65.

Griffin, R.A. and Jurinak, J.J. (**1974**) "Kinetics of the phosphate interaction with calcite", *Soil Sci. Soc. Am. Proc.* 38, 75-79.

Healy, R.M. and Kilpatrick, M.L. (**1955**) "A kinetic study of the hydrolysis of trimetaphosphates", *J. Am. Chem. Soc.,* 77, 5258-5264.

Hons, F.M., Stewart, W.M. and Hossner, L.R. (**1986**) "Factor interactions and their influence on hydrolysis of condensed phosphates in soils", *Soil Science*, 25, 242-255.

Hossner, L.R. and Phillips, D.P. (**1971**) "Pyrophosphate hydrolysis in flooded soil", *Soil Sci. Soc. Am. Proc.,* 35, 379-383.

Hughes, J.D. and Hashimoto, I. (**1971**) "Triammonium pyrophosphate as a source of phosphorus for plants", *Soil Sci. Soc. Am. Proc*., 35, 643-647.

Lindsay, W.L. and Norvell, W.A. (**1978**) "Development of a DTPA soil test for zinc, iron, manganese and copper", *Soil Sci. Soc. Am. J.,* 42, 421-428.

Olsen, S.R. and Dean, L.A. (**1965**) "Phosphorus" In: C.A. Black *et al*., (Ed.), *Methods of Soil Chemical Analysis* Part 2, *Agronomy*, Am. Soc. of Agron. Inc., Madison, USA, 9, pp. 1035-1049.

Patrick, W.H. and Fontenot, W.J. (**1976**) "Growth and mineral composition of rice at various moisture tensions and oxygen levels", *Agron. J.,* 68, 325-329.

Racz, G.J. and Savant, N.K. (**1972**), "Pyrophosphate hydrolysis in soil as influenced by flooding and fixation" *Soil Sci. Soc. Am. Proc.,* 36, 678-682.

Searle, P.G.E. and Hughes, J.D. (**1977**) "Cation activation of pyrophosphatase from soil microorganisms", *Soil Biol. Biochem.*, 9, 153-156.

Stott, D.E., Dick, W.A. and Tabatabai, M.A. (**1985**) "Inhibition of pyrophosphatase activity in soils by trace elements" *Soil Science*, 139(2), 112-117.

Sutton, C.D. and Larsen, S. (**1964**) "Pyrophosphate as a source of phosphorus for plants", *Soil Science*, 97, 196-201.

Tabatabai, M.A. and Dick, W.A. (**1979**) "Distribution and stability of pyrophosphate in soils", *Soil Biology and Biochemistry*, 11, 655-659.

Van Wazer, J.R., Griffith, E.J. and McCullough, J.F. (**1955**) "Structure and properties of the condensed phosphates", *J. Amer. Chem. Soc.*, 77, 287-291.