CHAPTER II

HYDROLYSIS OF TRI- AND TETRAAMMONIUM PYROPHOSPHATES IN ARABLE AND FLOODED INDIAN SOILS
A. INTRODUCTION AND REVIEW OF LITERATURE

The use of polyphosphates (condensed phosphates) as sources of phosphorus for plants is receiving increasing attention in recent years. The availability of these condensed phosphates to plants depends upon the rate of hydrolysis of the pyrophosphate to orthophosphate in the soil as well as the relative distribution of ortho- and pyrophosphate present in the soil throughout the plant growing period because phosphorus uptake by plants is mainly from orthophosphate rather than from pyrophosphate. Van Wazer (1958) listed seven factors in decreasing order of importance in pyrophosphate hydrolysis, namely, temperature, pH, enzymes, presence of colloidal gels, complexing cations, phosphate concentration and ionic environment in solution. All these factors exist in the soil-plant system and are dependent upon changes in atmospheric conditions and especially in soil characteristics.

Rather limited work has been done in the past on the hydrolysis of tri- and tetraammonium pyrophosphates $\left[(\text{NH}_4)_3\text{H}_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}\right]$ and $(\text{NH}_4)_4\text{P}_2\text{O}_7$ in arable and flooded soils especially in tropical and sub-tropical soil types. However, a general review of existing literature on the rates of hydrolytic degradation of polyphosphates, with special reference to ammonium pyrophosphates including the influence of growing plants on pyrophosphate hydrolysis, is presented below:

A.1. Hydrolysis of polyphosphates in arable soils:

Van Wazer et al. (1955), Cleseer and Lee (1965), Van Wazer (1958) and Gilliam and Sample (1968) reported that the rates hydrolysis
of condensed phosphates in sterile systems follow first order reaction kinetics. Gilliam and Sample (1968) also reported that the rate of hydrolysis of \((\text{NH}_4)_3\text{H}_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}\) in sterile soils and in water were of about the same order of magnitude.

Gilliam and Sample (1968) carried out different experiments on the rate of hydrolysis of \((\text{NH}_4)_3\text{H}_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}\) in soils over a period of 45 days to examine whether microorganisms, extracellular enzymes, pH or other chemical factors in soils were responsible for the hydrolysis reaction. They observed that there was no effect of soil pH on the rate of hydrolysis in autoclaved soil samples and the rate of hydrolysis observed in sterile soils was generally similar to that in sterile water. However, the amount of hydrolysis which could be attributed to the chemical factors was significant in all the soils used.

Hashimoto and Wakefield (1974) reported on the rate of hydrolysis of ammonium pyrophosphate \((\text{NH}_4)_3\text{H}_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}\) in three soils at six temperatures over the range 5° to 40°C. The authors found that the rate of hydrolysis is dependent on both temperature and properties of the soil, and reported that the time required for hydrolysis of 50 percent of the pyrophosphate to orthophosphate was 25 to 60 days at 5° and 4 to 13 days at 25°C. Besides, they observed a moderate decrease in the rate of hydrolysis at temperatures between 25° and 40°C.

The hydrolytic degradation of other pyrophosphates e.g. sodium pyrophosphate (Blancher and Hossner, 1969b; Chang and Racz, 1977), sodium trimetaphosphate (Blancher and Hossner, 1969a and 1969b), potassium pyrophosphate (Savant and Racz, 1972a and 1972b), sodium
dihydrogen pyrophosphate (Sutton et al., 1966; Blancher and Hossner, 1969b; Juo and Maduakor, 1973) and sodium tripolyphosphate (Blancher and Hossner, 1969a and 1969b; Chang and Racz, 1977) in soils have been investigated. While the results of these studies reveal trends similar to those obtained with ammonium pyrophosphates the hydrolytic rate constants ($K$) and half-lives ($T_{1/2}$) show variable values depending on the pyrophosphate compound and the experimental soil conditions.

A.2. Hydrolysis of polyphosphate in flooded soils:

Various physical, microbiological and chemical changes take place when soils are maintained under flooded conditions. The aerobic organisms do not exist in the absence of oxygen supply and the anaerobic organisms take over as the primary biological population in the decomposition of organic matter. Soils remain in the reduced condition because of chemical transformation of $\text{NO}_3^-$ to $\text{N}_2$, $\text{N}_2$ to $\text{NH}_3$, $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$, $\text{Mn}^{4+}$ to $\text{Mn}^{2+}$, $\text{SO}_4^{2-}$ to $\text{HS}_2$, $\text{CO}_2$ to $\text{CH}_4$ and $\text{H}^+$ to $\text{H}_2$. The redox potential of the submerged soils decreases from 0.2 to -0.4 V as compared to that of aerobic soil which lies in the range of 0.3 to 0.8 V (Ponnampereuma, 1972). The accumulated concentrations of different ions like $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\text{NH}_4^+$, molecules like $\text{H}_2\text{S}$, $\text{SiO}_2$, $\text{H}_2\text{CO}_3^-$ and anaerobic metabolism of microorganisms increase slowly in both solution and solid phases of flooded soils. The pH values of acidic soils increase and those of alkaline soils decrease, generally, up to three weeks but later the pH values under both conditions attain nearly neutrality (Ponnampereuma, 1955, 1972).
Very little previous information is available on the hydrolysis of polyphosphates under anaerobic soil conditions. While studying the hydrolysis of ($\text{NH}_4 \text{H}_{2}\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$) in four soils under flooded and 1/3 atmospheric moisture content, Hossner and Phillips (1971) found that hydrolysis was faster under flooded conditions but not at 1/3 atmospheric moisture content. The half-life values for applied pyrophosphate varied from 0.6 to 3.9 days in flooded soils.

The only other study on hydrolysis of pyrophosphate in flooded soils is the work of Racz and Savant (1972) who compared the rate of hydrolysis of $\text{K}_4\text{P}_2\text{O}_7$ in a noncalcareous soil maintained at field capacity moisture content and under flooded conditions. They found that the initial rates of hydrolysis were rapid and approximately the same in both cases. The rates of pyrophosphate degradation under arable as well as flooded soil regime followed first order kinetics.

A.3. Hydrolysis of polyphosphate in presence of plant growth:

In relation to the use of pyrophosphate compounds as fertilizers for plants grown in soils, it is important to consider the influence of plant roots and the rhizosphere microorganisms on the hydrolysis of pyrophosphates. While no studies on these aspects have been conducted with ammonium pyrophosphates the literature on other pyrophosphate compounds is briefly reviewed in the following paragraphs.

McGeorge (1939) and Tsue and Yoshida (1958) have suggested that the pyrophosphate was hydrolysed to orthophosphate by the phosphatases of roots or by the rhizoplane microbes prior to absorption and the presence of plant roots greatly accelerated the rate of hydrolysis.
Comparative studies on the rates of hydrolysis of polyphosphate \( \text{Na}_4\text{P}_2\text{O}_7 \) and \( \text{Na}_5\text{P}_3\text{O}_{10} \) solutions (pH 6.5) in presence of sterile and nonsterile 7 days old wheat and pea intact roots at \( 20 \pm 1^\circ\text{C} \) were carried out by Savant and Racz (1972c). They found that phosphatase enzymes present on the plant root hydrolyzed pyrophosphate and tripolyphosphate. This hydrolysis was greater in the presence of nonsterile roots than sterile roots. They also found that increasing the orthophosphate content in solution decreased the rate of conversion of orthophosphate from pyrophosphate and tripolyphosphate.

Subbarao et al. (1977) have examined the influence of concentration of pyrophosphate on the rate of hydrolysis and reasons for different trends of hydrolysis of polyphosphates \( \text{K}_4\text{P}_2\text{O}_7 \) and \( \text{Na}_5\text{P}_3\text{O}_{10} \) in presence of different root environments of corn and soybean using the split-root techniques to supply nutrients and to prevent precipitation reaction between phosphate sources and other nutrients. They found that the hydrolysis of polyphosphates took place faster in presence of corn roots rather than in the presence of soybean roots. The differences were attributed to the different phosphatase activities of the associated rhizoplane organisms or due to difference in weights and surface areas of corn and soybean roots in the phosphate solutions. In addition, they observed that pyrophosphate hydrolyzed more rapidly than tripolyphosphate and the rates of both polyphosphates at a substrate concentration of 75 ppm phosphorus followed zero-order kinetics in the presence of corn and soybean roots. Besides, these authors have also suggested that, as indicated by earlier studies of Savant and Racz (1972c) on hydrolysis of pyrophosphates and tripolyphosphates in Canadian soils, a higher (first)
order kinetics are followed at lower substrate (pyrophosphate) concentrations, while zero-order kinetics operate at higher substrate concentrations.

B. MATERIALS AND METHODS

The preparation of triammonium pyrophosphate $\left(\text{NH}_4\right)_3\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$ and tetraammonium pyrophosphate $\left(\text{NH}_4\right)_4\text{P}_2\text{O}_7$:

All the salts used for the preparation of triammonium pyrophosphate monohydrate (TPP) and tetraammonium pyrophosphate (TAPP) were of A.R. grades. Both TPP and TAPP were prepared in the laboratory by ion exchange method described by Coates and Woodwards (1964) and Lehr et al. (1967).

B.1. $\left(\text{NH}_4\right)_3\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$: Dowex 10 W-XE, 50 - 100 mesh (H) resin in 55 x 3 cm column was used to prepare the triammonium pyrophosphate monohydrate from sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7\cdot\text{10H}_2\text{O}$). The resin was most rapidly reconditioned by treatment with the following reagents in order: 130 ml dilute HCl (1:1 conc. HCl : H$_2$O), 170 ml conc. HCl, water (until the effluent was neutral), 150 ml NH$_4$OH (1:3 conc. ammonia : H$_2$O), 300 ml water. The liquids were run through the column at approximately 5 ml/minute.

A saturated solution of $\text{Na}_4\text{P}_2\text{O}_7\cdot\text{10H}_2\text{O}$ (200 ml) was run through the conditioned ion exchange column at rate 1.5 ml/minute. The ammonium pyrophosphate solution was formed at pH 5.6 adjusted by dilute solutions of NH$_4$OH and HCl. For crystallization and recrystallization, ethyl alcohol was used.
B.2. (NH₄)₂P₂O₇: This compound was prepared by a method similar to that used for the preparation of TPP except that the pH was controlled at 8.0.

TPP contains 17.0% N and 57.48% P₂O₅ whereas TAPP 22.76% N and 57.71% P₂O₅.

B.3. Soils selected and their physico-chemical characteristics:

The soils used for all investigations were a red sandy loam (Rhodustalf) from Raigarh, Madhya Pradesh, a laterite (oxisol) from Ratnagiri, Maharashtra, an acidic coastal alluvium (Ha_plaquent) from Panaji, Goa, an alluvium (Ha_plaquent) from Delhi, an alluvium (Ha_plaquent) from Paderi, Uttar Pradesh and a medium black clay loam (Pellustert) from Trombay, Maharashtra. The selected soils are typical of major Indian soil types which occur extensively in the country. These soils were collected from the surface layer of 0 - 15 cm, brought to laboratory and passed through >20 mesh sieve for use in various studies. The physico-chemical characteristics of these soils were determined as follows and are reported in Table 1.

(i) Moisture equivalent was determined by the suction method of Bouyoucos (1935).

(ii) pH of the soil was determined by making a 1:2.5 soil water suspension and measuring the pH after one hour using a glass electrode pH meter with calomel reference electrode (Jackson, 1964).

(iii) Free calcium carbonate content in the soil was estimated according to the method described by Piper (1950).
<table>
<thead>
<tr>
<th>Soil</th>
<th>pH (1:2.5)</th>
<th>Moisture equivalent (%)</th>
<th>Electric conductivity (mmhos/cm)</th>
<th>Org.C (%)</th>
<th>AV.P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; (Kg/ha)</th>
<th>AV.K&lt;sub&gt;2&lt;/sub&gt;O (Kg/ha)</th>
<th>Total N (%)</th>
<th>Cation exchange capacity (meq %)</th>
<th>Ex.Ca (meq %)</th>
<th>Ex.Mg (meq %)</th>
<th>Free CaCO&lt;sub&gt;3&lt;/sub&gt; (%)</th>
<th>Biological activity (mg CO&lt;sub&gt;2&lt;/sub&gt;/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red sandy loam (Rhodustalf), Raigarh</td>
<td>5.5</td>
<td>22.93</td>
<td>0.12</td>
<td>0.66</td>
<td>1.6</td>
<td>138.5</td>
<td>5.04</td>
<td>1.02</td>
<td>0.61</td>
<td>0.50</td>
<td>7.61</td>
<td></td>
</tr>
<tr>
<td>Laterite (Oxisol), Ratnagiri</td>
<td>6.1</td>
<td>33.29</td>
<td>0.28</td>
<td>0.90</td>
<td>21.6</td>
<td>367.4</td>
<td>0.086</td>
<td>19.00</td>
<td>3.57</td>
<td>1.93</td>
<td>2.45</td>
<td>13.94</td>
</tr>
<tr>
<td>Acidic coastal alluvium (Haplaquent), Panaji</td>
<td>6.2</td>
<td>26.07</td>
<td>0.13</td>
<td>0.70</td>
<td>4.5</td>
<td>72.3</td>
<td>12.94</td>
<td>2.22</td>
<td>0.92</td>
<td>1.00</td>
<td>7.68</td>
<td></td>
</tr>
<tr>
<td>Alluvium (Haplaquent), Paderi</td>
<td>7.5</td>
<td>25.13</td>
<td>1.10</td>
<td>1.63</td>
<td>37.6</td>
<td>222.8</td>
<td>0.090</td>
<td>23.74</td>
<td>8.66</td>
<td>4.11</td>
<td>2.75</td>
<td>14.43</td>
</tr>
<tr>
<td>Alluvium (Haplaquent), Delhi</td>
<td>7.7</td>
<td>23.00</td>
<td>0.27</td>
<td>0.74</td>
<td>54.9</td>
<td>373.4</td>
<td>0.071</td>
<td>27.56</td>
<td>10.70</td>
<td>3.24</td>
<td>2.25</td>
<td>11.45</td>
</tr>
<tr>
<td>Medium black clay soil (Pellustert), Trombay</td>
<td>8.0</td>
<td>44.79</td>
<td>0.43</td>
<td>0.67</td>
<td>22.9</td>
<td>319.2</td>
<td>0.045</td>
<td>40.50</td>
<td>19.53</td>
<td>18.40</td>
<td>8.62</td>
<td>18.84</td>
</tr>
<tr>
<td>Deep black clay loam (Pellustert), Poona</td>
<td>9.0</td>
<td>37.16</td>
<td>0.46</td>
<td>0.85</td>
<td>9.2</td>
<td>542.1</td>
<td>61.50</td>
<td>25.00</td>
<td>6.17</td>
<td>16.12</td>
<td>19.40</td>
<td></td>
</tr>
</tbody>
</table>
(iv) Cation exchange capacity of soils was determined by leaching the soil with normal ammonium acetate as described by Jackson (1964).

(v) Exchangeable calcium and magnesium were determined according to the method described by Cheng and Bray (1951).

(vi) Organic carbon content and available potassium were determined by the method described by Jackson (1964).

(vii) Available phosphorus was estimated by the method of Olson et al. (1954).

(viii) Total nitrogen in the soil was determined according to the method of Steyermark (1961).

(ix) Total soluble salts were determined by the use of an electric conductivity bridge (Jackson, 1964).

(x) Biological activity of the soils was determined according to the procedure of Sutton and Larsen (1964).

The medium black clay soil is clay to clay loam in structure, containing 2:1 layer type minerals (montmorillonite/illite), having high base exchange capacity, alkaline pH, high biological activity and deficient in phosphorus content but having medium potassium content. The laterite soil forming from lateritic rocks is rich in hydrated oxides of iron and aluminium, containing 1:1 type layer mineral (kaolinite), having peculiar soil formations specific for the tropics with intermittently moist climate and is light red in colour, light textured, well drained, porous, poor in base exchange capacity along with magnesium and calcium.
carbonate and acidic in reaction. Both the alluviums (Delhi and Paderi) are derived from the continuous deposition of the river system of the Ganges, varying in texture from drift sand to loams and shift clay, with a mixture of clay minerals of kaolinite and degraded illite, having medium type base exchange capacity and pH ranging from acidic to alkaline. The climate of the alluvial region varies from semiarid to subhumid. The acidic coastal alluvium (Panaji) is freely permeable, excessively drained, having a slightly lower cation exchange capacity than alluvium and is slightly acidic in reaction. This soil contains more kaolinitic clay minerals than illitic. The red soil is derived from the crystalline and metamorphic rocks and is light textured and acidic in reaction. It contains considerably lower amounts of calcium, magnesium and phosphorous and low base exchange capacity. Its clay fraction is predominantly kaolinitic.


The hydrolytic degradation of both triammonium pyrophosphate and tetraammonium pyrophosphate were examined under arable conditions in six soils, namely, red sandy loam, acidic coastal alluvium, medium black clay loam, laterite and two alluviums. Five grams soil was taken in a 50 ml plastic tube and kept at moisture equivalent for 24 hours. The TPP or TAPP containing 0.5 mg phosphorus was then added to the soil. Subsequently, samples were mixed thoroughly and incubated at constant room temperature (24 ± 1°C) at its moisture equivalent which was then maintained by replenishing daily the water lost through evaporation. For each series of phosphorus treated samples, there was an equivalent
number of controls (no phosphorus). The control samples were prepared in exactly the same manner as treated samples. Three samples of each treatment were taken for analysis on different sampling dates, namely, 2, 5, 10, 15, 20 and 24 days of incubation.

Similarly, the hydrolysis of both TPP and TAPP was examined in two soils, namely, medium black clay loam and acidic coastal alluvium under flooded regime at different periods, namely, 2, 5, 10, 15, 20 and 24 days of incubation at room temperature (24 ± 1°C). Five grams of the soil sample was weighed into a 50 ml tube. This soil sample was kept under flooded condition (4 cm column of water above the soil surface to ensure reduced conditions) prior to addition of pyrophosphates. At the end of 4 days, the free water from the moist soil was drawn off and 0.5 mg phosphorus each of TPP or TAPP was applied to the soils. The sample was thoroughly mixed and water was added to replace that drawn off previously. Soil moisture level was maintained by replenishing daily the water lost through evaporation. Four replicates of each treatment were kept for analysis at the different sampling dates.

Phosphorus was extracted from the samples as outlined by Gilliam and Sample (1968). The extraction of soil samples from each of the treatments was accomplished by thoroughly mixing the soil with about 10 ml of 0.1 N H₂SO₄ and transferring the mixture to a Buchner funnel. The soil was leached with small portions of 0.1 N H₂SO₄ until a total of 65 ml had been used. The soil sample was then leached with 30 ml of 1 N H₂SO₄ until a total solution of 125 ml had been utilized. The two filtrates were then combined together and charcoal was mixed
with it to absorb organic matter. The combined solution was then filtered in a 250 ml volumetric flask and the last washings were made 2 to 4 times with distilled water. The leaching and filtration procedures were completed within one hour to avoid further hydrolysis. The hydrolysed phosphorus in the extract was immediately determined by the method described by Watanabe and Olsen (1965). Total phosphorus in each of the extracts was determined by taking an aliquot of 2 to 2.5 ml adding 5 to 6 drops of conc. H₂SO₄ and heating for 16 hours at 80 - 90°C to ensure complete hydrolysis of pyrophosphate. The nonhydrolysed pyrophosphate content in the extracts was obtained by subtracting the hydrolysed phosphorus (orthophosphate) from total phosphorus. Necessary corrections were applied to take account of the very small amounts of orthophosphate present in the original pyrophosphate compound added to soil.

Since hydrolytic degradation of ammonium pyrophosphate was observed to follow first order kinetics, the data were processed to compute the hydrolytic rate constants (K) and half-lives (T½) of orthophosphate formation in soils under both nonflooded and flooded conditions. The K and T½ values were calculated as follows:

\[ K = \frac{2.303}{t} \log \frac{C_0}{C} \]

\[ T_{\frac{1}{2}} = \frac{0.693}{K} \]

where, \( K \) = hydrolytic rate constant,
\( t \) = time in hours,
\( C_0 \) = initial concentration of phosphorus in polyphosphate form (nonhydrolysed phosphorus),
C = the phosphorus concentration in the form of pyrophosphate (nonhydrolysed) at time t in hours and

T₂ = total time required in days for 50 per cent transformation of pyrophosphate to orthophosphate.

C. RESULTS AND DISCUSSION

The hydrolytic degradation of both TPP and TAPP results in the formation of orthophosphates as indicated below:

\[
\text{(NH}_4\text{)}_2\text{HPO}_4 \quad \text{NH}_4\text{H}_2\text{PO}_4
\]

\[
\text{(NH}_4\text{)}_3\text{P}_2\text{O}_7 \quad \text{NH}_4\text{H}_2\text{PO}_4
\]
Data on the comparative rates of hydrolysis of TPP (Fig. 1 and 2) and TAPP (Fig. 3 and 4) in six arable soils during the incubation periods ranging from 0 to 24 days indicated that the rates of hydrolysis of pyrophosphates follow first order kinetics and present a linear relationship between the logarithm of amount of unhydrolysed phosphate and time. Similar patterns of hydrolysis were obtained for TPP (Fig. 5) and TAPP (Fig. 6) in two soils under flooded conditions. The data clearly indicated that the rates of hydrolysis in red sandy loam, acidic coastal alluvium and laterite soils were lower than those in medium black soil and both alluvial soils. The observed deviation of the values for the two longest experimental periods of 20 and 24 days in some of the soils (Fig. 1 - 6) may be attributed to either fixation of pyrophosphates in soils or formation of complexes with pyrophosphates.

C.1. The hydrolysis of pyrophosphate in arable soils:

K and \( T_{1/2} \) values for orthophosphate formation under arable conditions in six soils are reported in Table 2. The K-values for hydrolytic degradation of TPP in the acidic soils, namely, red, laterite and acidic coastal alluvium, range from \( 1.14 \times 10^{-3} \) h\(^{-1} \) to \( 1.44 \times 10^{-3} \) h\(^{-1} \) and their corresponding \( T_{1/2} \) for orthophosphate formation vary from 25.25 to 20.00 days. The K-values in alkaline soils, namely, the two alluviums and medium black clay loam, vary from \( 2.58 \times 10^{-3} \) h\(^{-1} \) to \( 3.22 \times 10^{-3} \) h\(^{-1} \) with their corresponding \( T_{1/2} \) of 11.32 to 9.0 days. These results indicate that the rates of hydrolysis of TPP in alkaline soils were higher than those in acidic soils by a factor of two.
Fig. 1(a), 1(b). Hydrolysis of (NH₄)₃PO₄·7·H₂O in aerable soils.
Fig. 2(a), 2(b). Hydrolysis of (NH$_4$)$_3$P$_2$O$_7$·H$_2$O in aerable soils.
Fig. 3(a), 3(b). Hydrolysis of \( (NH_4)_4P_2O_7 \) in aeolian soils.
Fig. 4(a), 4(b). Hydrolysis of (NH₄)₂P₂O₇ in aerable soils.
Fig. 5(a), 5(b). Hydrolysis of $(\text{NH}_4)_3\text{PO}_4\cdot\text{H}_2\text{O}$ in flooded soils.
Fig. 6(a), 6(b). Hydrolysis of $\left(\text{NH}_4\right)_2\text{P}_2\text{O}_7$ in flooded soils.
Table 2

Kinetic rate constants (K) of hydrolysis of TPP and TAPP with their half-live values (T<sub>1/2</sub>) in arable and flooded soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;HP&lt;sub&gt;0.7&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;P&lt;sub&gt;0.27&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K (x 10&lt;sup&gt;-3&lt;/sup&gt; h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>T&lt;sub&gt;1/2&lt;/sub&gt; (days)</td>
</tr>
<tr>
<td>Red sandy loam</td>
<td>1.44</td>
<td>20.00</td>
</tr>
<tr>
<td>Laterite</td>
<td>1.15</td>
<td>25.22</td>
</tr>
<tr>
<td>Acidic coastal alluvium</td>
<td>1.14</td>
<td>25.25</td>
</tr>
<tr>
<td>Alluvium, Paderi</td>
<td>3.22</td>
<td>9.00</td>
</tr>
<tr>
<td>Alluvium, Delhi</td>
<td>2.58</td>
<td>11.32</td>
</tr>
<tr>
<td>Medium black clay loam</td>
<td>2.73</td>
<td>10.60</td>
</tr>
<tr>
<td>Acidic coastal alluvium</td>
<td>1.67</td>
<td>17.27</td>
</tr>
<tr>
<td>Medium black clay loam</td>
<td>3.17</td>
<td>9.30</td>
</tr>
</tbody>
</table>
Similarly, $K$-values for TAPP in acidic soils varied from $1.27 \times 10^{-3} \, h^{-1}$ to $1.48 \times 10^{-3} \, h^{-1}$ and values of $T_{1/2}$ ranged from 22.80 to 19.50 days whereas in alkaline soils the $K$-values of this compound were in the range of $2.77 \times 10^{-3} \, h^{-1}$ to $3.51 \times 10^{-3} \, h^{-1}$ with their corresponding $T_{1/2}$ values varying from 10.42 to 9.23 days.

A comparison of the data on TPP and TAPP reveals that the rates of hydrolysis of TAPP were marginally higher than those of TPP. The maximum hydrolysis for both pyrophosphates were observed in alluvium (Paderi) followed by medium black clay and alluvium (Delhi), and the rates of hydrolytic degradation of both pyrophosphates were lower in acidic soils than those obtained in alkaline soils.

Regarding the observed rates of hydrolysis of TPP under arable conditions in the present study, the work of Hashimoto and Wakefield (1974) on Davidson clay loam, Hartsells loam and Norfolk sand/loam from Alabama, USA, which is the only report available in literature on comparative $T_{1/2}$ values of this compound, indicates that $T_{1/2}$ values were in the range of 4 to 13 days at 25°C.

Juo and Maduakov (1973) reported that under field moisture capacity, the half-lives ($T_{1/2}$) of sodium pyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$) in the tropical surface soils of Nigeria, which were generally slightly acidic in nature, were in the range of 4 to 14 days whereas the values of $T_{1/2}$ ranged from 16 to more than 64 days in the corresponding subsoil samples. Thus, the $T_{1/2}$ values (19 to 26 days) obtained for both pyrophosphates in Indian acidic soils during the present investigation are somewhat higher than $T_{1/2}$ values reported for Nigerian soils. The
variations noted above may be, at least in part, due to the differences in the pyrophosphate compounds used in the two studies.

In summary, under arable conditions the extent of hydrolysis of pyrophosphates was generally greater in soils having higher organic carbon, biological activity, cation exchange capacity and pH. Generally, similar observations were made in earlier studies by Gilliam and Sample (1968), Hossner and Phillips (1971), Sutton and Larsen (1964) and Sutton et al. (1966).

C.2. Hydrolysis of pyrophosphates in flooded soils

The kinetic rate constants (K) of hydrolysis along with their corresponding half-life values ($T_{1/2}$) for both TPP and TAPP under flooded conditions in contrasting soils, namely, acidic coastal alluvium and medium black clay soil, are reported in Table 2. The data indicate that the values of K for ammonium pyrophosphates ranged from $1.67 \times 10^{-3} \text{ h}^{-1}$ to $3.17 \times 10^{-3} \text{ h}^{-1}$ for TPP and $1.55 \times 10^{-3} \text{ h}^{-1}$ to $3.12 \times 10^{-3} \text{ h}^{-1}$ for TAPP. The corresponding $T_{1/2}$ values for orthophosphate formation ranged from 17.27 to 9.3 days for TPP and from 18.60 to 9.26 days for TAPP.

In general, the rates of hydrolysis of both pyrophosphates in acidic soils were lower than those in alkaline soils. The most important observation made in these experiments was that soil pH per se did not influence the chemical hydrolysis in the arable and non-arable soils. Similar observation was made by Gilliam and Sample (1968). This is in contrast to the large effects normally noted in solution (Van Wazer et al. 1955). The K-values reported here for TPP were in the range of 1.24 to
8.58 \times 10^{-3} \text{ h}^{-1} (2.09 \text{ to } 14.3 \times 10^{-5} \text{ min}^{-1}) \text{ which were obtained in}
flooded soil at 25°C by Hossner and Phillips (1971). In addition,
Clesceri and Lee (1965) presented data to show first order rate constants
of pyrophosphate hydrolysis in sterile lake water to be 1.08 \times 10^{-3} \text{ h}^{-1}
(1.8 \times 10^{-6} \text{ min}^{-1}) \text{ which were slightly lower than the reported values,}
possibly because in the referenced study biological activity did not
play an important role in conversion of pyrophosphate to orthophosphate.

The rates of hydrolysis of both pyrophosphates were higher in
flooded soils than those maintained at moisture equivalent probably due
to an increase in pyrophosphatase activity in the anaerobic soils.
Similar results were also obtained by Racz and Savant (1972c) on the
rates of hydrolysis of K_4P_2O_7 in the moist and flooded soils at room
temperature.

The present findings clearly suggest that in arable and flooded
soils examined nearly all of the ammonium pyrophosphates incorporated
into soils would have completely hydrolysed within 5 half-lives i.e.,
45 to 150 days in arable soils and 45 to 120 days in non-arable soils.
Further, as a result of the enhanced rate of hydrolysis in the vicinity
of the root surface due to the association of rhizoplane organisms
(McGeorge, 1939; Gilliam, 1970; Juo and Maduakor, 1973; Subbarao et al.
1977), the half-lives of the two pyrophosphates incorporated into the
soil are likely to be reduced in the presence of growing plants and the
hydrolysed phosphorus in orthophosphate form would be available for
plants during the initial period of growth when phosphorus requirement
of crops is maximum.