

## Reaction products of triammonium pyrophosphate in different Indian soils

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**Abstract.** Studies were undertaken on the isolation and identification of reaction products of triammonium pyrophosphate (TPP), the major non-orthophosphate constituent of ammonium polyphosphate newly introduced in India, in representative soils of the alfisol, oxisol, entisol, mollisol and vertisol groups of India. Saturated solution of TPP were reacted with soils for periods of 30 minutes and one day with corresponding precipitation times of 15 days, three months and one year to isolate reaction products which were identified by X-ray diffraction technique, infra-red spectroscopy and chemical analyses. Six reaction products, namely,  $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$ ,  $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{FeNH}_4\text{P}_2\text{O}_7$  and  $\text{NH}_4\text{Al}_{0.33}\text{Fe}_{0.67}\text{P}_2\text{O}_7$  were identified in different soils;  $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$  and  $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  occurring in abundance in most soils. Significant hydrolytic degradation of pyrophosphate reaction products to orthophosphate was not observed.

Complementary studies where TPP in solid form was applied to soil, and reaction formed at and around the site of TPP placement were identified after six weeks incubation also showed the formation of  $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$  and  $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  in the soils examined.

High-analysis, bi-nutrient ammonium polyphosphate fertilizer (containing 12% N and 25% P), is being produced on an experimental scale in India for agronomic testing before eventual commercial production. It contains 40 per cent of its phosphorus as triammonium pyrophosphate (TPP) [ $(\text{NH}_4)_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ], 54 per cent as monammonium orthophosphate (MAP) [ $\text{NH}_4\text{H}_2\text{PO}_4$ ], 5 per cent as pentammonium tripolyphosphate [ $(\text{NH}_4)_5\text{P}_3\text{O}_{10}$ ], and 1 per cent as higher polyphosphates. Of these constituents, TPP and MAP have a high degree of water solubility.

Water soluble phosphates added to soils undergo rapid transformation to compounds which persist over extended periods in soils. Identification of such reaction products helps to elucidate the fate of water soluble phosphate fertilizers in different soils, and this information is useful for evaluation of the efficiency of these fertilizers. The fate and reaction products of ammonium polyphosphate fertilizers in soils of the temperate regions has been intensively studied [7, 9, 10, 15, 20, 23, 25]. However, little comparable information exists on the persistent reaction products of ammonium

polyphosphate fertilizers in sub-tropical and tropical soils which form the predominant soil groups of India. Studies were, therefore, undertaken on the isolation and identification of reaction products of triammonium pyrophosphate in Indian soils of the alfisol, oxisol, entisol, mollisol and vertisol groups. These investigations form part of an on-going programme on the evaluation of triammonium pyrophosphate, which as indicated earlier is the major non-orthophosphate constituent of the newly introduced ammonium polyphosphate fertilizer, in terms of its agronomic efficiency for cereal crops [1, 5, 17, 18, 21, 22, 18] and its behaviour in principal Indian soil types.

### Materials and methods

TPP was prepared in the laboratory by the ion exchange method described by Coates and Woodward [4] and Lehr et al. [13]. Dowex 10W -  $\times$  8, 50-100 mesh ( $H^+$ ) resin in  $55 \times 3$  cm column was used to prepare the TPP from sodium pyrophosphate ( $Na_4P_2O_7 \cdot 10H_2O$ ). The resin was reconditioned by treatment with the following reagents in order: 130 ml dilute HCl (1:1 Conc. HCl:  $H_2O$ ), 170 ml Conc. HCl, water (until the effluent was neutral), 150 ml  $NH_4OH$  (1:3 Conc. ammonium :  $H_2O$ ), 300 ml water. The liquids were run through the column at approximately 5 ml/minute. A saturated solution of  $Na_4P_2O_7 \cdot 10H_2O$  (200 ml) was run through the conditioned ion exchange column at the rate of 1.5 ml/minute. The triammonium pyrophosphate solution was formed in the effluent at pH 5.6 adjusted by dilute solutions of  $NH_4OH$  and HCl. Ethyl alcohol was used to crystallize triammonium pyrophosphate. This product contained 17% N and 25.1% P with 24.72% P as pyrophosphate and 0.38% P as orthophosphate.

The soils used for the study were a red sandy loam (Rhodustalf) from Raigarh, Madhya Pradesh, a laterite (Oxisol) from Ratnagiri, Maharashtra, an alluvium (Haplaquent) from Delhi, a Tarai soil (Haplaquoll) from Paderi, Uttar Pradesh and a medium black clay loam (Pellustert) from Trombay, Maharashtra.

Physico-chemical characteristics of these soils were determined as follows and are reported in Table 1. pH of the soils was determined in 1:2.5 soil: water suspension using a glass electrode pH meter with calomel reference electrode as described by Jackson [11]. Moisture equivalent was determined by the suction method of Bouyoucos [2]. The electric conductivity of soil suspension was determined according to the method described by Jackson [11]. The organic carbon was determined after oxidation by chromic acid with sulfuric acid (Walkley-Black method) as described by Jackson [11]. Extractable phosphorus was determined using the 0.5N sodium bicarbonate (pH 8.5) extractant as described by Olsen et al. [19]. Exchangeable potassium was determined by the flame emission spectrophotometer after extraction with ammonium acetate as described by Jackson [11]. Total nitrogen was analysed according to the method of Kjeldahl given by Steyermark [24].

Table 1. Soil characteristics

Soil	pH (1:2.5)	Moisture equivalent (%)	Electrical conductivity (mmhos/cm)	Org. C (%)	Av. P (ppm)	Av. K (ppm)	Total N (%)	Cation exchange capacity (meq %)	Ex. Ca (meq %)	Ex. Mg (meq %)	Biological activity (mg CO <sub>2</sub> / 100 g)
Rhodustalf (Red sandy loam)	5.5	22.93	0.12	0.66	0.31	51.34		5.04	1.02	0.61	7.61
Raigarh Oxisol (Laterite)	6.1	33.29	0.28	0.90	4.24	136.16	0.086	19.00	3.57	1.93	13.94
Ratnagiri Haplaquoll (Tarai soil)	7.5	25.13	1.10	1.63	7.37	82.55	0.090	23.74	8.66	4.11	14.43
Paderi Haplaquent (Alluvium)	7.7	23.00	0.27	0.74	10.80	138.35	0.071	27.56	10.70	3.24	11.45
Delhi Pellustert (Medium black clay loam), Trombay.	8.0	44.79	0.43	0.67	4.51	118.26	0.045	40.50	19.53	18.40	18.84

Cation exchange capacity of soils was determined using sodium acetate extractant as described by Jackson [11]. Exchangeable calcium and magnesium were determined using sodium nitrate extractant as described by Cheng and Bray [3]. Biological activity of soils was measured by determining the  $\text{CO}_2$  evolved per day from 100 g of moist soil according to the procedure of Sutton and Larson [26].

Two methods developed by Lindsay et al. [15] and Hinman et al. [8] were used for the formation of reaction products with TPP in these soils.

#### *A. Reaction products formed with saturated solutions of TPP in soils*

The saturated solution of TPP was prepared by shaking excess compound in water at  $24 \pm 1^\circ\text{C}$  for two days [15]. The pH of the saturated solution was 5.70 and phosphorus and ammonium concentrations were 8.23 and 12.33 moles/litre, respectively.

A method similar to that of Lindsay et al. [15] was employed to obtain the reaction products of pyrophosphate salts when added in solution to soil. Saturated solutions (150 ml) were allowed to react with 300 g of air-dried soil ( $-20$  mesh) for  $\frac{1}{2}$  hour and twenty four hours, respectively, at room temperature ( $24 \pm 1^\circ\text{C}$ ). Subsequently, the mixture was filtered on a Buchner funnel using suction. The filtrates, after addition of four drops of saturated phenol for avoiding the bacterial growth, were stored in flasks and incubated for 15 days, three months and one year; the only variation was that the longest incubation period of one year was omitted for the one day reaction time. At the end of the incubation periods, the precipitate formed was removed from the flask, washed with distilled water and dried with acetone. The pH of the filtrates was measured immediately after filtration to observe the changes occurring owing to precipitation.

The identification of the reaction products was made by means of chemical analysis, X-ray diffraction technique and infra-red spectroscopy. Calcium and magnesium after removing iron, aluminium and phosphorus were estimated according to the method of Cheng and Bray [3], potassium by flame photometry and ammonium by Kjeldahl's method. Aluminium was estimated using aluminon and iron using orthophenanthroline by the method of Fortune and Mellon [6] as modified by Lindsay and Stephenson [16]. The diffraction patterns were obtained from Philips PW 1031 wide angle goniometer tracings with a Geiger counter X-ray diffractometer,  $\text{CuK}\alpha$  radiation,  $\lambda = 1.5405 \text{ \AA}$ , scanning rate  $0.5^\circ/2/\text{min}$ . Intensities were measured as peak heights above background and expressed as per cent of the strongest line. The "d" spacings of the X-ray diffraction patterns of reaction products were compared with those of standard compounds as listed by Lehr et al. [13]. The presence of a particular compound in the reaction product is indicated by a minimum of six to seven "d" spacings corresponding to within  $\pm 0.05 \text{ \AA}$  of the values for the standard. Similar technique for identification of reaction products of pyrophosphates and orthophosphates in soils have been

used by several authors [15, 23, 27, 29]. For infra-red spectroscopy (I.R.), the infra-red absorption spectra of samples with KBr phase were obtained on Perkin-Elmer infra-red spectrophotometer model 1378. The wave number ( $\text{cm}^{-1}$ ) of the peaks in the spectra of reaction products were compared with those of standard compounds as listed by Lehr et al. [13]. The presence of a minimum of six to seven peaks in the I.R. spectrum of the reaction product with values within  $\pm 0.05 \text{ cm}^{-1}$  of those of the standard compounds was the basis for identification. Similar technique has been used in earlier studies on reaction products of orthophosphates in soils [20, 29].

### *B. Reaction products formed on application of TPP to soil*

These studies were conducted with TPP in the same soils as those employed in studies on the formation of reaction products with saturated solutions of the compound. The procedure of Hinman et al. [8] modified in respect of quantity of phosphorus compound used for placement and duration of the incubation period was adopted. 2.25 g of the compound (TTP) was placed in a small depression (2.5 cm dia.) at the centre of the soil contained in a plastic cylinder (6.5 cm dia., 5 cm height and having a capacity of about 200 g soil) with a fine mesh nylon base. The soil surface was covered with plastic sheet having holes for exchange of air. The moisture content in the soil columns was maintained by placing the plastic cylinder with its perforated base in a glass petridish to which water was added; this procedure permitted constant wetting of the soil column. The soil was then incubated for six weeks. At the end of incubation period, the soil was airdried and the reaction products formed at the site of fertilizer placement and at a distance of 0.5 cm from the placement site were recovered and finely ground for X-ray analysis from which the identification of reaction products was carried out.

The "d" spacings for the reaction product samples and for controls (without added phosphorus) were determined. Spacings that occurred in the treated soil, and not found in the controls were taken to be those of reaction product.

## **Results and discussion**

### *A. Reaction products formed with saturated solutions of TPP in soils*

Six reaction products namely, calcium diammonium pyrophosphate monohydrate – CDP [ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ], magnesium diammonium pyrophosphate tetrahydrate – MDP [ $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  (monoclinic)], ammonium ferric aluminium pyrophosphate [ $\text{NH}_4\text{Fe}_{0.67}\text{Al}_{0.33}\text{P}_2\text{O}_7$ ], ferric ammonium pyrophosphate ( $\text{FeNH}_4\text{P}_2\text{O}_7$ ), calcium tetraammonium dihydrogen pyrophosphate [ $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$ ] tricalcium tetraammonium hexahydrogen pyrophosphate trihydrate [ $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4 \cdot 3\text{H}_2\text{O}$ ] were identified by X-ray diffraction and IR techniques. The relative amounts of the reaction products formed in each soil are reported in Tables 2 and 3.

Table 2. Nature of reaction products of TPP in Indian soils

Reaction time	Rhodustalf pH 5.5			Oxisol pH 6.1		
	15D	3M	1Y	15D	3M	1Y
½ hour	N.P.	N.P.	N.P.	N.P.	N.P.	N.P.
	Ca(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O (monoclinic) FeNH <sub>4</sub> P <sub>2</sub> O <sub>7</sub> Ca(NH <sub>4</sub> ) <sub>4</sub> H <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> Ca <sub>3</sub> (NH <sub>4</sub> ) <sub>4</sub> H <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>4</sub> · 3H <sub>2</sub> O Ca(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O (monoclinic) FeNH <sub>4</sub> P <sub>2</sub> O <sub>7</sub> NH <sub>4</sub> Al <sub>0.33</sub> Fe <sub>0.67</sub> P <sub>2</sub> O <sub>7</sub>					
1 day	N.P.	N.P.	N.P.	N.P.	N.P.	++

N.P. : No precipitate formed; ++ : moderate; + : small

Table 3. Nature of reaction products of TPP in Indian soils

Reaction time	Haplaquent pH 7.7			Haplaquoll pH 7.5			Feillustert pH 8.0		
	15D	3M	1Y	15D	3M	1Y	15D	3M	1Y
½ hour	++	+++	+++	++	+++	+++	+++	++++	+++
	Ca(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O (monoclinic) FeNH <sub>4</sub> P <sub>2</sub> O <sub>7</sub> Ca(NH <sub>4</sub> ) <sub>4</sub> H <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> Ca <sub>3</sub> (NH <sub>4</sub> ) <sub>4</sub> H <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>4</sub> · 3H <sub>2</sub> O Ca(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · H <sub>2</sub> O Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 4H <sub>2</sub> O (monoclinic) FeNH <sub>4</sub> P <sub>2</sub> O <sub>7</sub> NH <sub>4</sub> Al <sub>0.33</sub> Fe <sub>0.67</sub> P <sub>2</sub> O <sub>7</sub>								
1 day	N.P.	++	++	N.P.	+	++	N.P.	N.P.	++++

++++ : Very abundant; +++ : abundant; ++ : moderate; + : small; Tr : trace

The major reaction product from the haplaquent and haplaquoll and pellustert was CDP which was accompanied by trace to abundant quantities of MDP. Trace to small quantities of ferric ammonium pyrophosphate were also present in the haplaquent, haplaquoll and the pellustert. At the longest incubation period of one year with  $\frac{1}{2}$  hour reaction time, moderate quantities of  $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$  in the haplaquent and haplaquoll soils, and moderate to abundant quantities of  $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4 \cdot 3\text{H}_2\text{O}$  in the haplaquoll and pellustert soils were obtained showing partial transformation of CDP into these products. The transformation of CDP to  $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4 \cdot 3\text{H}_2\text{O}$  occurred to the greatest extent in the alkaline pellustert soil.

The quantity of precipitates increased with the increased incubation periods. With increase of reaction time from half an hour to one day for all incubation periods, the amount of precipitate decreased. The maximum quantity of precipitate was obtained in the pellustert followed by the haplaquent and haplaquoll whereas the least amounts were recovered in the acidic rhodustalf and oxisol soils. This observation suggests that iron and aluminium released by soils had been sequestered by TPP solution, thereby preventing the formation of solid reaction products. The chemical analyses of the reaction products were carried out on those samples where adequate quantities were recovered.

The precipitates formed at different incubation times ranging from 15 days to one year showed marginally different compositions of P, Ca, Mg, Al, Fe, K and  $\text{NH}_4$  due to the effects of different incubation periods and reaction times. The chemical composition of precipitates formed at the incubation times of 15 days, three months and one year is reported in Table 4 and, for comparison, the data on theoretical composition of the various reaction products identified are tabulated in Table 5.

Data on contents of Ca (~6 to 8 per cent),  $\text{NH}_4$  (~10 to 16 per cent) and P (~19 to 25 per cent) showed that the predominant reaction product, CDP was formed at all incubation times for the haplaquent and haplaquoll and incubation times of 15 days and 3 months for the pellustert. At one year incubation period, the slightly increased quantities of P (26 to 28 per cent) suggested the presence of  $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$  and  $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4 \cdot 3\text{H}_2\text{O}$  in the precipitates of the haplaquent, haplaquoll and pellustert soils.

The values of contents of Mg (~0.7 to 7 per cent), P (~20 to 28 per cent) and  $\text{NH}_4$  (~11 to 16 per cent) revealed the presence of MDP in trace to small quantities in precipitates of the haplaquoll, in small to moderate quantities in precipitates of the haplaquent, and in small to abundant quantities in precipitates of the pellustert for all incubation periods. The formation of MDP compound increased slowly with increased incubation times. Moderate quantities of this compound were also found in the haplaquoll (Paderi) at incubation period of three months with one day reaction time. The values of Fe content (0.1 to 1.4 per cent) and Al content (~0.1 to 0.5 per cent) in the precipitates suggested the formation of  $\text{FeNH}_4\text{P}_2\text{O}_7$  and  $\text{NH}_4\text{Fe}_{0.67}\text{Al}$

Table 4. Chemical composition of reaction products formed by TPP with soils

Soil	Reaction time	Elemental composition (%)						
		P	Ca	Mg	Al	Fe	K	NH <sub>4</sub>
		15 days incubation period						
Haplaquent	½ hour	22.62	7.90	0.70		0.32		15.88
Haplaquoll		24.81	7.84	0.70		1.40	0.84	14.66
Pellustert		20.65	8.00	3.52		0.12		11.26
		3 months incubation period						
Haplaquent	½ hour	23.55	6.20	1.44	0.32	0.18		15.46
Haplaquoll		19.70	6.20	1.44	0.33	0.37		10.65
Pellustert		21.95	7.70	6.25	0.11	0.14		12.95
Rhodustalf	1 day	25.37	1.71	0.51		0.05		
		1 year incubation period						
Oxisol	½ hour	18.38	5.00	0.43		0.56	0.28	10.11
Haplaquent		26.16	5.72	6.90	0.15	0.01	0.10	15.53
Haplaquoll		25.96	6.80	5.50	0.26	0.12		13.41
Pellustert		28.07	7.00	5.22		0.06		12.78

Table 5. Theoretical composition of some pyrophosphate compounds

Compound	Elemental composition (%)						
	P	Ca	Mg	Fe	Al	NH <sub>4</sub>	
Calcium diammonium pyrophosphate monohydrate Ca(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	19.25	12.44				11.18	
Magnesium diammonium pyrophosphate tetrahydrate Mg(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·4H <sub>2</sub> O (monoclinic)	20.24		7.94			11.80	
Calcium tetraammonium dihydrogen pyrophosphate Ca(NH <sub>4</sub> ) <sub>4</sub> H <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	26.82	8.68				15.60	
Tricalcium tetraammonium hexahydrogen pyrophosphate trihydrate Ca <sub>3</sub> (NH <sub>4</sub> ) <sub>4</sub> H <sub>6</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>4</sub> ·3H <sub>2</sub> O	26.15	12.68				7.60	
Ferric ammonium pyrophosphate FeNH <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	24.70			23.47		7.18	
Ammonium aluminium-ferric pyrophosphate NH <sub>4</sub> Al <sub>0.33</sub> Fe <sub>0.67</sub> P <sub>2</sub> O <sub>7</sub>	25.78			16.41	3.70	7.50	



$0.33\text{P}_2\text{O}_7$  in small to trace amounts in the rhodustalf and haplaquoll. In addition, trace quantity of  $\text{FeNH}_4\text{P}_2\text{O}_7$  was also present in the pellustert. Thus, the chemical data, in general, support, the conclusions drawn from X-ray and IR data.

Lindsay et al. [15] have reported the formation of CDP and MDP on addition of  $\text{MgCa}(\text{CO}_3)_2$  to a saturated solution of ammoniated superphosphoric acid (11-14-0 grade, containing 49 per cent of its P as orthophosphate and 42 per cent as pyrophosphate, eight per cent as tripolyphosphate and one per cent as tetrapolyphosphate). Similarly, Philen and Lehr [20] also reported the formation of MDP with 2 M TPP solution in montmorillonite and attapulgite minerals.

### *B. Reaction products formed on application of TPP to soils*

The reaction products formed with TPP when applied in solid form to soils are reported in Table 6. Four reaction products, namely, CDP as a predominant reaction product in all soils except the rhodustalf, MDP in the haplaquent and pellustert,  $\text{Fe}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeH}_2\text{P}_2\text{O}_7$  in rhodustalf were identified in soils at the placement sites as well as at distance of 0.5 cm from placement sites except  $\text{FeH}_2\text{P}_2\text{O}_7$  which was only identified at a distance of 0.5 cm from the placement site.  $\text{FeNH}_4\text{P}_2\text{O}_7$  and  $\text{NH}_4\text{Fe}_{0.67}\text{Al}_{0.33}\text{P}_2\text{O}_7$  could not be detected with band placement of TPP in the rhodustalf even though these compounds were identified with reaction of saturated solution of TPP with this soil at longer incubation periods. Besides,  $\text{Ca}(\text{NH}_4)_4\text{H}_2(\text{P}_2\text{O}_7)_2$  and  $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$  obtained on reaction of saturated solutions of TPP with the haplaquent, haplaquoll and pellustert at longer incubation period were not detected when TPP was applied as a band to soils, suggesting that the extended period of incubation of the band-placed fertilizer in soil was required for the formation of these products.

Savant and Racz [23] have reported the formation of reaction products —  $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  and CDP in lakeland soil (pH 7.9) and  $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$  in Plum Ridge soil (pH 7.8) and Newdale soil (pH 7.5) of Canada when TPP was applied as a band to these soils. No other report is available in literature on the reaction products formed when TPP was applied to soils.

While the TPP compound used in the present study contained very small amounts of orthophosphate ( $\sim 1.5\%$  of total P), the transformation products of this small orthophosphate component likely to have been formed in soils could not be detected by the X-ray diffraction and infra-red spectroscopy technique employed in the present investigation. Further, no hydrolytic degradation of the identified pyrophosphate reaction products to orthophosphate reaction products was observed even during the longest incubation period of one year when the saturated solution of TPP was reacted with soils as well as when TPP was applied as a band to soils. Similar findings have been

Table 6. Reaction products obtained for TPP when applied as a band to soils Incubation period: 6 weeks

Soil	pH (1:2.5)		Reaction products	
	Control	At placement site	0.5 cm from placement site	At placement site
Rhodustalf	5.5	6.7	6.7	$\text{Fe}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ $\text{FeH}_2\text{P}_2\text{O}_7$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (monoclinic) $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (monoclinic)
Oxisol	6.1	7.0	6.9	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$
Haplaquoll	7.5	7.3	7.3	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$
Haplaquent	7.7	6.8	6.7	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (monoclinic)
Pellustert	8.0	7.1	7.1	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (monoclinic)

reported by Lehr et al. [14], Philen and Lehr [20] and Savant and Racz [23]. Two mechanisms by which pyrophosphate prevents the formation of orthophosphate have been suggested. One is the inactivation of microbial activity, which contributes significantly to the hydrolytic degradation of pyrophosphate, by phosphate ions at concentration more than 0.2 M in pyrophosphate [7]. The other is prevention of either nucleation or crystal growth of orthophosphate salts by the pyrophosphate [12].

Current research in our laboratory is aimed at synthesis of persistent reaction products of triammonium pyrophosphate in major Indian soil types reported in the present paper, and evaluation of these reaction products as sources of phosphorus to plants grown in quartz sand culture.

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