Ammonium polyphosphates which contain triammonium pyrophosphate - TPP \((\text{NH}_4)_3\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}\) and tetraammonium pyrophosphate - TAPP \((\text{NH}_4)_4\text{P}_2\text{O}_7\) as the principal non-orthophosphate constituents are of special interest as potential phosphate fertilizer materials for crops on Indian soils in view of their high phosphorus and nitrogen content, marked degree of water solubility, and sequestering action with micro-nutrients. These high analysis polyphosphates are of advantage in our country where handling, transport and storage costs amount to a substantial fraction (up to 40 - 45 per cent) of the cost of the fertilizer to the farmer. Since plants absorb their requirements of phosphorus from soils principally in the orthophosphate form, it is essential to determine the rates of hydrolytic degradation of the ammonium pyrophosphates to orthophosphate in major Indian soil types. Water-soluble phosphorus fertilizers, when applied to soils, undergo rapid transformation to compounds which persist over extended periods and form the principal source of phosphorus for plants. Hence, the knowledge of different reaction products formed with the ammonium pyrophosphate compounds in major Indian soil types is of vital importance in relation to the efficiency of ammonium polyphosphates as fertilizer materials. Further, it is well established that plant roots growing in soil take up phosphorus present in their vicinity and it is, therefore, necessary to assess the mobility pattern and adsorption of the pyrophosphates in Indian soils.

Intensive research has been undertaken in recent years to evaluate the agronomic efficiency of ammonium pyrophosphates, their hydrolysis and mobility in soils, and reactions with soil constituents. However, these studies are limited to some soils of North America (U.S.A. and
Canada) and U.K. and no comparable data are available for Indian soil types. Ammonium orthophosphate fertilizers - mono- and diammonium orthophosphates (MAP, DAP), are currently produced and extensively used as phosphatic fertilizers in Indian agriculture. Studies on the mobility, transformation and reaction products of ammonium orthophosphates in principal Indian soil types are required to permit valid comparisons of the behaviour of ammonium ortho- and pyrophosphates in Indian soils.

The present investigation was, therefore, undertaken through controlled studies to elucidate the chemical aspects of rates of hydrolytic degradation of TPP and TAPP in arable and non-arable (flooded) soils, representative of the major Indian soil types; to examine the mobility pattern and adsorption behaviour of ammonium ortho- and pyrophosphates in contrasting soils; to isolate and identify the reaction products formed with ammonium ortho- and pyrophosphates in major Indian soils; and, to evaluate the efficiency of the principal reaction products of ammonium ortho- and pyrophosphates formed in these soils as sources of phosphorus for plants.

The soils used for these studies were a red sandy loam (Rhodustalf), an acidic coastal alluvium (Haplaquent), a medium black clay loam (Pellustert), a deep black clay loam (Pellustert), two different alluviums (Haplaquents) and a laterite (Oxisol), which are representative of major soil types which occur extensively in India. The physico-chemical properties of these soils, namely, pH, moisture equivalent, total soluble salts, free CaCO₃, cation exchange capacity, exchangeable calcium and magnesium, available phosphorus and potassium,
The rates of hydrolytic degradation of TPP and TAPP in six soils of varying pH under arable soil conditions and in two contrasting soils under non-arable regimes were determined in the laboratory over periods ranging from 0 to 24 days at 24 ± 1°C. The rates of hydrolysis of both pyrophosphates follow first order kinetics. The kinetic rate constants (k) for hydrolytic degradation of TPP in upland soils range from $1.14 \times 10^{-3}$ h$^{-1}$ to $3.22 \times 10^{-3}$ h$^{-1}$ and the corresponding half-lives ($T_{1/2}$) for the orthophosphate formation range from 25.25 to 9.00 days. The k-values for TAPP vary from $1.27 \times 10^{-3}$ h$^{-1}$ to $3.51 \times 10^{-3}$ h$^{-1}$ and values of $T_{1/2}$ range from 22.80 to 9.23 days. The observed rates of hydrolysis of TAPP were marginally higher than those of TPP. The rates of hydrolytic degradation of both pyrophosphates were lower in acidic coastal alluvium, red sandy loam and laterite than those obtained in neutral and alkaline soils of alluviums (Paderi and Delhi) and medium black clay loam. This indicates that the extent of hydrolytic degradation of pyrophosphates was generally greater in soils having higher organic carbon content, biological activity, cation exchange capacity and pH.

The K-values for TPP in the two contrasting soils, namely, acidic coastal alluvium and medium black clay loam, under flooded conditions, range from $1.67 \times 10^{-3}$ h$^{-1}$ to $3.17 \times 10^{-3}$ h$^{-1}$ with corresponding half-lives ranging from 17.27 to 9.30 days whereas the K-values for TAPP range from $1.55 \times 10^{-3}$ h$^{-1}$ to $3.12 \times 10^{-3}$ h$^{-1}$ with corresponding $T_{1/2}$ ranging from 18.60 to 9.26 days. The rates of hydrolysis of both pyrophosphates were higher in medium black clay loam than those in
acidic coastal alluvium. The rates of hydrolysis of both pyrophosphates in these soils were enhanced under the flooded regime as compared to the rates at field capacity moisture status. Under flooded soil regime, the rate of hydrolysis of TPP was slightly higher than that of TAPP.

The present findings clearly suggest that in the 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, 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.

The studies on the mobility and adsorption behaviour of MAP, TPP and TAPP were carried out in red sandy loam, laterite, medium black clay loam and deep black clay loam soils. The movement of phosphates was studied in these soils under conditions approximately those prevailing under assured irrigation. In addition, the mobility of these phosphates was evaluated in two contrasting soils, namely, laterite and medium black clay loam soils under conditions where anion movement was likely to be predominantly by diffusion process. The results indicated that the pyrophosphates as well as the orthophosphate were totally immobilized in the soil layer to which they were applied under conditions of continuous replenishment of moisture in the laterite, medium and deep
black clay loam soils. In the red loam about 10 per cent of the orthophosphate and 5–8 per cent of the pyrophosphates were transported down from the site of application. No detectable quantities of either the pyrophosphate or the orthophosphate moved out of the fertilized layer in all soils examined under conditions of diffusion.

The adsorption behaviour of MAP, TPP and TAPP in the red sandy loam, laterite, medium black clay loam and deep black clay loam soils followed the Langmuir equation. Since the Langmuir plots of the ortho- and pyrophosphates in the case of two soils, namely, medium and deep black clay loam soils indicated a slight degree of curvature at higher equilibrium phosphate concentrations, the experimental data were also fitted into a modified Langmuir equation which incorporates a square root term to account for the above mentioned deviation from the conventional Langmuir equation. Data on the adsorption maxima computed according to the Langmuir equation for the ortho- and pyrophosphates in these four soils showed that the adsorption maxima are higher for the pyrophosphates than for the orthophosphate. The adsorption maxima derived by the modified Langmuir equation which includes a square-root term also indicated higher values for the pyrophosphates.

The present findings on the adsorption behaviour and mobility of MAP, TPP and TAPP suggest that although differences exist between the adsorption characteristics of the pyro- and orthophosphates in the soils examined, these are not reflected in the relative mobility of the phosphates largely because of rapid hydrolysis of the pyrophosphates in these soils especially in the zone immediately below the surface layers to which the pyrophosphates were applied.
Studies on the reaction products formed with MAP and DAP fertilizers in six major Indian soils were carried out in the following three Parts:

(a) Isolation and identification of reaction products formed with saturated solutions of MAP and DAP in soils.

(b) Identification of reaction products formed on application of MAP and DAP compounds to soils in situ.

(c) Evaluation of the efficiency of orthophosphate reaction products compared to MAP as sources of phosphorus for maize plants.

For the isolation and identification of reaction products, the saturated solutions of MAP and DAP were allowed to react with air-dried soils, and the soluble phases separated from the soils were incubated for varying durations of 15 days, 3 months and one year. The precipitates formed were separated, dried at room temperature (24 ± 1°C) and identified with the help of X-ray diffraction technique, infrared spectroscopy and chemical analysis. With MAP, five different reaction products, namely, ammonium taraakite, potassium taraakite, brushite, metastrengite and zinc ammonium phosphate (hexagonal) were identified from the six soils. The predominant reaction product from red, laterite and two alluvial soils was ammonium taraakite accompanied by trace amount of potassium taraakite and small amount of metastrengite. Brushite was the principal reaction product in the medium black clay loam and alluvial (Paderi) soils; trace to small amounts of metastrengite were also observed in these soils. Zinc ammonium phosphate (hexagonal)
was observed in the acidic and alluvial soils with increased reaction time of one year. In the present investigation, no transformation of the two predominant reaction products, namely, ammonium taranakite and brushite was observed up to one year of incubation period of the soil-fertilizer solution extracts.

Three different compounds, namely, calcium diammonium dihydrogen orthophosphate monohydrate (CDGP), newberyite and meta-strengite were identified as reaction products of DAP in the six soils up to the incubation period of one year. CDGP was the predominant reaction product obtained in the precipitated reaction products of laterite, acidic coastal alluvial, alluvial and medium black clay loam soils. Moderate quantities of newberyite were observed in acidic coastal alluvial, alluvial and medium black clay loam soils and trace amounts of metastrengite were present in all soils. In red soil, no precipitates of reaction products could be recovered for the incubation periods of 15 days and 3 months of half-an-hour reaction time. This could be attributed to the rapid transformation of soluble reaction products to solid phases in this soil.

To confirm the findings described in Part (a) and study to the extent possible the reaction of ammonium phosphate fertilizers with Indian soils in situ, solid MAP and DAP fertilizers were band-placed in soils, the soils maintained at field capacity moisture status for a 6-week period, and the soil-fertilizer system was sampled at the site of fertilizer placement as well as up to a distance of 0.5 cm from the placement site. The samples were assayed through X-ray diffraction
technique. The reaction products obtained with MAP and DAP fertilizer compounds when applied as a band to soils were, in general, identical with the predominant products formed by reaction of saturated solutions of these fertilizers with soils discussed earlier. While abundant quantities of ammonium tatanakite were formed by reaction of saturated solution of MAP with red, laterite and alluvial soils, trace to small quantities of this product were obtained when fertilizer was band-placed in these soils. Further, other reaction products, namely, potassium tatanakite, ferric phosphate (metastaenite) and zinc ammonium phosphate which were present in trace to small amounts in the case of reaction of saturated solution of MAP in soils could not be detected when MAP was applied as a band. In the case of band-applied DAP, COOP was identified as the predominant reaction product similar to the situation when the saturated solution of this fertilizer was reacted with soils. Besides, basic aluminium phosphate \( \left[ \text{NH}_4\text{Al}_2(\text{PO}_4)_2\text{OH}.2\text{H}_2\text{O} \right] \) as well as aluminium phosphate \( \left[ \text{AlPO}_4.2\text{H}_2\text{O} \right. \text{ (orthorhombic)} \) were identified as new reaction products in the red sandy loam and the alluvium (Delhi), respectively.

The five predominant reaction products obtained with MAP and DAP fertilizers in the six soils examined, namely, ammonium and potassium tatanakites, brushite, COOP and newberyte, were synthesized in the laboratory and their purity was confirmed through X-ray diffraction technique and chemical analysis. These compounds were compared with MAP as sources of phosphorus for maize plants (Zea mays L. variety Golden Benthem) grown in quartz sand culture for six weeks. The basal nutrients N and K\(_2\)O as urea and potassium sulphate, respectively, were added as basal dressing along with phosphorus sources before sowing the
seeds. The plants were harvested and data on dry matter yield, concentration of phosphorus in plants, total uptake of phosphorus by plants and relative uptake of phosphorus of every reaction products in terms of the standard fertilizer of MAP were recorded.

The results indicated that all reaction products significantly increased the dry matter yield and uptake of phosphorus over control. Further, the data show that the increase in yield of dry matter of maize plants correlated well with the increase in the plant uptake of phosphorus. The highest response in yield as well as phosphorus uptake by plants was obtained from the complete water-soluble MAP compound used as a standard followed by brushite and newberyite. Potassium taranakite showed significantly higher yield of dry matter and uptake of phosphorus than ammonium taranakite. While brushite, CDOP and newberyite were equally effective in terms of yield of dry matter, the plant uptake of phosphorus with CDOP and newberyite were significantly inferior to those with brushite. Brushite, CDOP and newberyite were superior to both taranakites as sources of phosphorus for plants. The relative plant uptake of phosphorus from the reaction products to that from MAP was computed and data indicated that brushite was the most effective source of phosphorus for plants among the reaction products considered whereas ammonium taranakite was the least efficient source. The order of effectiveness of reaction products as sources of phosphorus for plants was in the following order: MAP > brushite > newberyite > CDOP > potassium taranakite > ammonium taranakite.

Similar to the studies on reaction products of MAP and DAP in Indian soils described above, the investigations on the reaction
products formed with TPP and TAPP in the six major Indian soil types were carried out in three Parts:

(a) Isolation and identification of reaction products formed with the saturated solutions of TPP and TAPP in soils.

(b) Identification of reaction products formed on application of TPP and TAPP compounds to soils in situ.

(c) Evaluation of the efficiency of pyrophosphate reaction products compared to MAP as sources of phosphorus for maize plants.

Experimental techniques similar to those described earlier under the studies on MAP and DAP were employed for the formation of reaction products of TPP and TAPP with the six soil types. The results indicated that six reaction products, namely, calcium diammmonium pyrophosphate monohydrate (CDP), magnesium diammmonium pyrophosphate tetrahydrate (monoclinic) (MDP), ammonium ferric aluminium pyrophosphate, ferric ammonium pyrophosphate, calcium tetraammonium dihydrogen pyrophosphate and tricalcium tetraammonium hexahydrogen pyrophosphate trihydrate were identified with TPP in the six soils examined by X-ray diffraction technique, infrared spectroscopy and chemical analysis at different incubation times of 15 days, 3 months, and one year. The predominant reaction product from the two alluviums and the medium black clay loam soil was CDP which was accompanied by MDP. Trace to small quantities of FeNH₄PO₄ were also present in alluvial and medium black clay loam soils. Moderate quantity of Ca(NH₄)₄H₂(P₂O₇)₂ in both alluvial soils and moderate to abundant quantities of Ca₃(NH₄)₄H₆(P₂O₇)₄·3H₂O in alluvial (Paderi) and medium black clay loam soils, respectively,
were obtained only at the highest incubation period of one year with the half-an-hour reaction time, showing transformation of $\text{Ca(NH}_4\text{)}_2\text{P}_2\text{O}_7$ into these products. No predominant reaction product was observed in red and laterite soils except small quantities of $\text{FeNH}_4\text{P}_2\text{O}_7$ and $\text{NH}_4\text{Fe}_{0.67}\text{Al}_{0.33}\text{P}_2\text{O}_7$ at the incubation period of three months with one day reaction time and moderate quantity of $\text{Ca}_3(\text{NH}_4)_4\text{H}_6(\text{P}_2\text{O}_7)_4\cdot3\text{H}_2\text{O}$ in laterite soil at one year incubation period with half-an-hour reaction time. The moderate quantity of $\text{Ca(NH}_4\text{)}_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$ in acidic coastal alluvium was the only reaction product observed at the three months incubation period with the half-an-hour reaction time.

With TAPP, five reaction products identified were CDP, MDP, magnesium hexaammonium pyrophosphate hexahydrate (MHP), ferrous hexaammonium pyrophosphate hexahydrate (FHP), ferrous dihydrogen pyrophosphate. The predominant reaction product was CDP which occurred in the precipitated reaction products in all soils except red sandy loam. Moderate to small quantities of $\text{FeH}_2\text{P}_2\text{O}_7$ were observed in laterite and acidic coastal alluvium. Small to moderate quantities of this compound in alluvium (Delhi) and medium black clay loam soil, respectively, were observed at the longest incubation period of one year. Moderate quantity of $\text{Mg(NH}_4\text{)}_6(\text{P}_2\text{O}_7)_2\cdot6\text{H}_2\text{O}$ and small quantity of $\text{Fe(NH}_4\text{)}_6(\text{P}_2\text{O}_7)_2\cdot6\text{H}_2\text{O}$ existing in the precipitate of medium black clay loam soil at 15 days incubation period were not obtained in those precipitates recovered at longer incubation periods of 3 months and 1 year. This could be attributed to the transformation of $\text{Mg(NH}_4\text{)}_6(\text{P}_2\text{O}_7)_2\cdot6\text{H}_2\text{O}$ and $\text{Fe(NH}_4\text{)}_6(\text{P}_2\text{O}_7)_2\cdot6\text{H}_2\text{O}$ into stable compounds $\text{Mg(NH}_4\text{)}_2\text{P}_2\text{O}_7\cdot4\text{H}_2\text{O}$ and $\text{FeH}_2\text{P}_2\text{O}_7$, respectively.
The greatest amounts of precipitated reaction products were obtained in alkaline and neutral soils whereas the lowest amounts were formed in the acidic soils, thereby indicating that the solid phase (precipitated) reaction products formed relatively rapidly in those soils containing higher quantities of Ca and Mg cations and very slowly in soils containing principally Fe and Al cations. It is also important to note that no orthophosphate compound appeared as a reaction product in any of the precipitates due to hydrolysis of pyrophosphates up to the prolonged incubation period of one year. This may be attributed to very high concentrations of ammonium and phosphorus ions in soil-fertilizer solution extracts, inhibiting the biological activity required for the hydrolysis of pyrophosphate to orthophosphate.

In studies of reaction products formed on application of TPP and TAPP compounds to soils in situ using experimental technique similar to that employed in the studies on MAP and DAP described earlier, four reaction products, namely, CDP, MDP, ferrous hexammonium pyrophosphate-hexahydrate, and ferrous dihydrogen pyrophosphate were identified with TPP in the six soils examined. CDP was obtained in all soils except the red soil, and MDP was observed only in alluvial (Delhi) and medium black clay loam soils. The reaction products Fe(NH$_4$)$_6$(P$_2$O$_7$)$_2$.6H$_2$O and FeH$_2$P$_2$O$_7$ were identified with TPP in red soil, where FeNH$_4$P$_2$O$_7$ and NH$_4$Fe$_{0.67}$Al$_{0.33}$P$_2$O$_7$ could not be detected even though the latter compounds were identified with the reaction of saturated solution of TPP. Besides, Ca(NH$_4$)$_4$H$_2$(P$_2$O$_7$)$_2$ and Ca$_3$(NH$_4$)$_4$H$_6$(P$_2$O$_7$)$_4$•3H$_2$O obtained by reacting saturated solutions with soils were not detected when TPP was applied as a band to soils.
With TAPP, five reaction products identified were CEP, MOP, ferrous hexammonium pyrophosphate hexahydrate, ferrous dihydrogen pyrophosphate and dicalcium pyrophosphate tetrahydrate (orthorhombic). The CEP was the predominant reaction product in all soils except red sandy loam. The maximum formation of CEP and Ca\(_2\)P\(_2\)O\(_7\)\(\cdot\)4H\(_2\)O (orthorhombic) was observed in alluvium (Paderi) and medium black clay loam mainly because they contained relative higher levels of exchangeable calcium (≈9 meq to 20 meq per cent). MDP in the medium black clay loam and Fe(NH\(_4\))\(_6\) (P\(_2\)O\(_7\))\(_2\)\(\cdot\)6H\(_2\)O in red soil were identified with TAPP. Fe(NH\(_4\))\(_6\) (P\(_2\)O\(_7\))\(_2\)\(\cdot\)6H\(_2\)O in red soil and Ca\(_2\)P\(_2\)O\(_7\)\(\cdot\)4H\(_2\)O (orthorhombic) in medium black clay loam were identified as new reaction products but Mg(NH\(_4\))\(_6\) (P\(_2\)O\(_7\))\(_2\)\(\cdot\)6H\(_2\)O and Fe(NH\(_4\))\(_6\) (P\(_2\)O\(_7\))\(_2\)\(\cdot\)6H\(_2\)O which were obtained when saturated solution of the pyrophosphate was reacted with the medium black clay loam soil could not be detected when the fertilizer was band-placed in soil.

In general, the predominant reaction products formed with TPF and TAPP when these fertilizers were applied as a band to soils were similar to products obtained on reaction of saturated solutions of these pyrophosphates with soils. Besides, it is noteworthy that no orthophosphate compound appeared as a reaction product along with pyrophosphate reaction products in any soil when these fertilizers were applied as a band to soils. This finding could be attributed to the very high concentrations of ammonium and phosphorus ions at and in close proximities to the site of placement of the pyrophosphate pellets inhibiting thereby the biological activity required for the degradation of pyrophosphate to orthophosphate.
The three predominant reaction products of TPP and TAPP formed with the above soils, namely, CDP, MDP and Mg\((\text{NH}_4)_6(\text{P}_2\text{O}_7)_2\cdot6\text{H}_2\text{O}\) (MHP) were synthesised in the laboratory and their purity was confirmed through X-ray diffraction technique and chemical analysis. The efficiency of these pyrophosphate reaction products vis-a-vis MAP as sources of phosphorus for maize plants was evaluated in quartz sand culture. Experimental methods were similar to those used for the evaluation of the relative efficiency of orthophosphate reaction products of fertilizers described earlier. Results indicated that under all phosphorus treatments the increase in dry matter yield correlated well with increased uptake of phosphorus over the control. While the highest uptake of phosphorus by maize was obtained with MAP, significant increases in phosphorus uptake over control (no phosphorus) were observed with the three pyrophosphate reaction products examined. Phosphorus concentration in maize plants (mg P/g plant) was higher with CDP as compared to MDP and MHP; however, no significant differences were observed between the three reaction products in terms of yield of dry matter. The relative uptake of phosphorus from the reaction products to that of MAP revealed that CDP was the most effective source of phosphorus for maize plants within the pyrophosphate reaction products whereas MHP was the poorest source. In terms of an overall assessment, the effectiveness of these reaction products as sources of phosphorus for plants was in the following order: MAP > CDP > MDP, MHP.

The quartz sand culture experiments on evaluation of the principal reaction products of mono- and diammonium orthophosphates and tri- and tetraammonium pyrophosphates as sources of phosphorus for
plants vis-a-vis monosodium orthophosphate taken as the standard were conducted simultaneously under identical experimental conditions. It was, therefore, of interest to examine the comparative efficiency of ortho- and pyrophosphate reaction products to supply phosphorus to plants. The data indicated that the overall effectiveness of the different reaction products of ammonium ortho- and pyrophosphate fertilizers formed in the major Indian soil types studied in the present investigation to supply phosphorus to plants was in the following order: Brushite $\gg$ CDP $\gg$ newberyite $\geq$ MDP $\geq$ CDCP $\geq$ MHP $>$ potassium taranakite $>$ ammonium taranakite.

It is noteworthy that the major reaction products, brushite, newberyite and CDCP from orthophosphates (MAP and DAP) and CDP and MDP from pyrophosphates (TPP and TAPP) formed in soils having pH range from slightly acidic to alkaline showed nearly equal efficiency as sources of phosphorus for plants. The potassium and ammonium taranakites which are the predominant reaction products of MAP with acidic red, laterite and acidic coastal alluvial soils are clearly inferior to the reaction products of DAP in these acidic soils as well as inferior to the reaction products of pyrophosphates in the neutral alluviums and alkaline black clay loam soil. An interesting observation is the nearly equal efficiency of CDP, the major reaction product of the tetraammonium pyrophosphate in the laterite and acidic coastal alluvium and CDCP which is the corresponding reaction product of DAP in these soils. In the absence of the formation of significant quantities of reaction products of TPP in the acidic red, laterite and coastal alluvial soils, valid comparison of their effectiveness vis-a-vis the taranakites formed with MAP in these
soils to supply phosphorus to plants were not attempted in the present investigation.

The foregoing results on the relative efficiency of the predominant reaction products of the ammonium ortho- and pyrophosphate compounds in specific Indian soil types provide new evidence to support the findings of the earlier greenhouse and microplot experiments conducted at this laboratory on the agronomic evaluation of the ammonium ortho- and pyrophosphates which have indicated that the new high analysis ammonium polyphosphate fertilizers containing the tri- and tetraammonium pyrophosphates are equal or slightly superior to the conventional ammonium orthophosphate fertilizers for cereal crops in the majority of Indian soil types. Thus, the results of the present investigations underline the considerable potential of the new high analysis ammonium polyphosphate fertilizers in Indian agriculture.

The techniques used in the present investigation to isolate and identify the predominant reaction products of ammonium ortho- and pyrophosphate fertilizers in major Indian soils through reaction of saturated solutions of these water-soluble phosphates with soil and their reaction with soil in situ through placement of the solid fertilizer in soil would simulate the chemical reactions occurring in the proximity of band-placed ammonium ortho- and pyrophosphate granules in soils. By comparison, the technique employed in the present studies on hydrolysis of ammonium pyrophosphate to orthophosphate forms in Indian soils and the data on the rate constants of hydrolytic degradation of the pyrophosphates and half-lives for orthophosphate formation would be relevant to the situation where these fertilizers are uniformly incorporated in and intimately
mixed with the soil. These data also serve to indicate the influence of the chemical and biological properties of different Indian soils on the hydrolytic degradation of the pyrophosphates.

As indicated above, when the ammonium pyrophosphates are applied through band placement to the Indian soil types examined the pyrophosphates undergo rapid transformation to relatively complex reaction products identified in the present investigation. In this situation, the rate constants of hydrolytic degradation of these complex pyrophosphate reaction products and the corresponding half-lives for orthophosphate formation would not be identical to those for the original ammonium pyrophosphates. Further, quantitative studies on the hydrolytic degradation of the principal reaction products of ammonium pyrophosphates in contrasting soil types are, therefore, planned as follow-up work of the present investigation.