ORTHOPHOSPHATE VS. POLYPHOSPHATE

Summary: Nearly 40 years of research present strong evidence of the rapidity of phosphate hydrolysis. Whether hydrolysis is complete in a few days or weeks, the process is fast enough to supply plants and roots with sufficient orthophosphate.

Phosphorus is required for life. It is the main component of adenosine triphosphate (ATP)—the compound essential for energy transfer. It is part of a myriad of functions. Plants are generally thought to consume only the phosphate in the ortho form. Why then are our modern-day high polyphosphate fertilizers effective in overcoming soil phosphorus (P) deficiencies when they contain large portions of their phosphate in the condensed forms—principally pyrophosphate and tri-polyphosphate? It's a question we get asked more and more, especially with the increased interest in the use of in-furrow starter fertilizers.

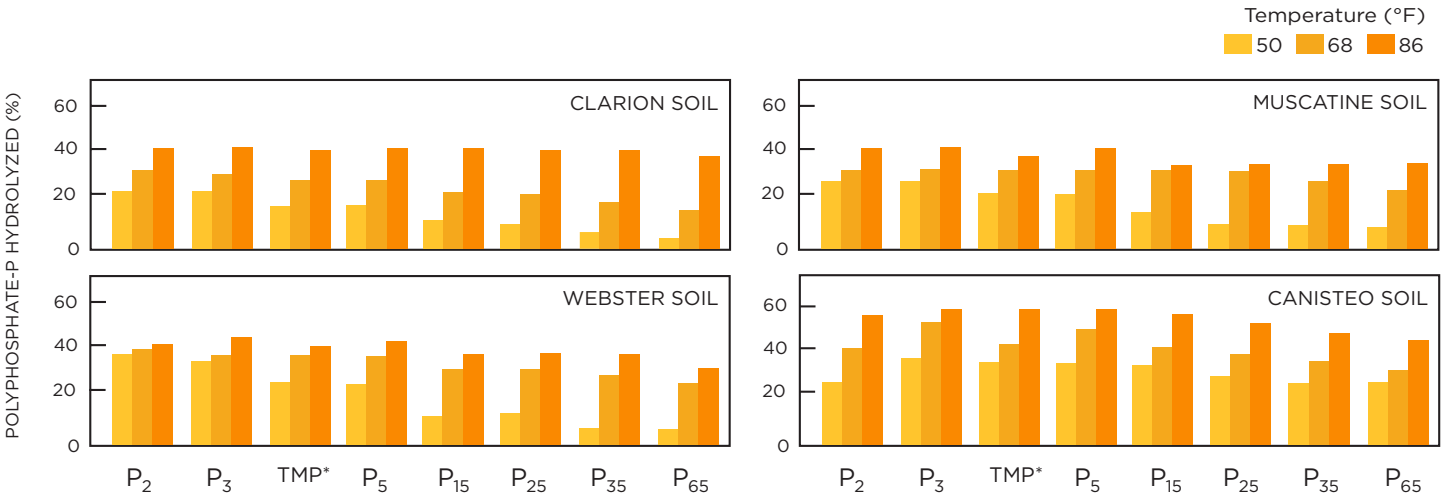
Liquid fertilizer began its growth with orthophosphates. Early in the sixties, the Tennessee Valley Authority (TVA) researched methods to make a more concentrated liquid phosphate. Growers appreciated many of the benefits of liquid fertilizers, but there was a desire to provide more plant food per gallon of fertilizer. TVA found that removing bound water from phosphoric acid boosted the phosphate content from 54% to 70%. This 30% increase reduced freight costs and made a whole new series of products possible. Super acid was born. Reacting super acid with ammonia under controlled conditions resulted in highly concentrated, easy to handle, neutralized liquid ammonium polyphosphates (APP). The polyphosphates (PP) sequestered magnesium, iron, and aluminum, which pose problems in orthophosphates. These new phosphates could accept non-chelated zinc.

SOIL REACTIONS

There is a normal hydrolysis of concentrated APP that is strongly temperature-related. Many know first hand the problem of hydrolysis that occurs if APP is left to "cook" all summer in a tank. Poly content is reduced, and sequestered metals may fall out, leaving residue in the tank (and cloudy product). And, once the polys are hydrolyzed, the product may not be able to sequester added micronutrients such as zinc. Diluted APP solutions may hydrolyze to orthophosphate but water dilution does not appear to accelerate the normal hydrolysis process.

Adding APP to soil is quite a different matter. Research studies examining the conversion of condensed phosphates to orthophosphate report half-lives of less than one day to as long as 100 days. A half-life is the time it takes to convert half of the polyphosphate to orthophosphate. Some conditions that influence conversion rate are temperature, pH, aerobic status, biological activity, and minerals. Liquid polyphosphate converts more quickly than dry. Water-soluble polys convert quicker than acid-soluble polys. Researchers have had to take extra care with soil sample storage since polyphosphates convert more rapidly in field-moist soils than air-dried.

FIGURE 1. HYDROLYSIS RATE DIFFERENCES IN FOUR SOILS AT THREE TEMPERATURE REGIMES



*Trimetaphosphate

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SODIUM PHOSPHATE RESEARCH

Sutton and Larsen (1964) studied the hydrolysis rate of radioisotope-labeled sodium pyrophosphate in pot and water cultures. They surmised that hydrolysis to orthophosphate was largely enzymatic and reported half-lives ranged from 4 to 100 days with the average being 18. Rates were higher at higher soil pH values. Hydrolysis proceeded more quickly with higher biological activity (as measured by CO_2 evolution). Pyrophosphate was not converted rapidly in the water culture, and plants absorbed 2.4 times more orthophosphate. Subsequently, Sutton, et al. (1966) found that pyrophosphatase level, CO_2 evolution, temperature, and uptake were loosely correlated. Low temperatures restricted hydrolysis and therefore P uptake in barley. Gilliam and Sample (1968) studied hydrolysis rates in soils with different chemical properties to assess the relative importance of chemical and biological influences. They found a significant chemical contribution to hydrolysis rate. All the observed changes could not be attributed solely to biological factors. Coarse-textured soils appeared to hydrolyze PP faster than fine. Hons et al. (1986) also found texture to significantly interact with other factors to influence rate. Significant interactions expressed were: texture x organic matter content, texture x pH, texture x time, organic matter x time, pH x soil moisture, pH x time, and temperature x time.

Dick and Tabatabai (1986) demonstrated hydrolysis rate differences in four soils at three temperature regimes (Figure 1). Rates were lower at 50°F than at 68°F or 86°F. The amount of P hydrolyzed in the three acid soils (Clarion, Webster, Muscatine) decreased with increasing chain length, although there were no significant differences between pyro (P_2) and tri-polyphosphate (P_3).

Chang and Racz (1977) quantified temperature effects on sodium pyrophosphate hydrolysis (Figure 2). Rates increased linearly and increased about two-to-three fold from 68°F to 95°F. Tri-polyphosphate hydrolysis was greater than pyrophosphate, and both rates were higher in the non-calcareous soil. About 40-70% of the phosphate hydrolyzed in 120 hours at 68°F, whereas about 80-95% hydrolyzed in 120 hours at 95°F.

Minerals may also affect hydrolysis rate. Dick and Tabatabai (1987) showed Ca^{2+}, pH, and non-buffered phosphatase activity to be positively correlated with hydrolysis rate, while percentage of clay, extractable Al^{3+}, and water soluble Mg^{2+} were negatively correlated.

APP

The most commonly applied polyphosphate is ammonium polyphosphate. There are likely only subtle differences between ammonium and sodium phosphate reactions in soils (Mnkeni and Mackenzi, 1987). Hashimoto et al. (1969) reported that APP hydrolysis increased with greater microbial activity and indicated that the catalytic influence of soil minerals was less with higher APP concentrations. Sample et al. (1979) reported that diammonium phosphate (DAP), triammonium pyrophosphate (TPP), and APP fertilizer additions behave essentially as salts. The NH^{4+} moved along with the phosphate ions in the form of salt diffusion. High concentrations caused the NH4+ to displace calcium on the exchange complex. Displaced calcium precipitated phosphates. Ortho and polyphosphates influenced soil aluminum (Al) and calcium (Ca) by releasing into soil solution and subsequent reprecipitation. Both elements appeared to be reprecipitated in place with added DAP. Sequestration by TPP and APP moved the cations slightly before complex ion reactions caused precipitation back to insoluble forms. Virtually all movement was in the ortho form (Sample et al., 1979), probably due to the high hydrolysis rate. Hydrolysis was occurring faster than diffusion through the soil column. They calculated hydrolysis half-lives for the first two weeks as 8.8 days and for the second two weeks as 15.6 days.

Venugopalan and Prasad (1989) also showed that hydrolysis rate was rapid in the beginning and slowed down with incubation time,

FIGURE 2. TEMPERATURE EFFECT ON HYDROLYSIS OF WATER-SOLUBLE SODIUM PYROPHOSPHATE AND SODIUM TRIPOLYPHOSPHATE

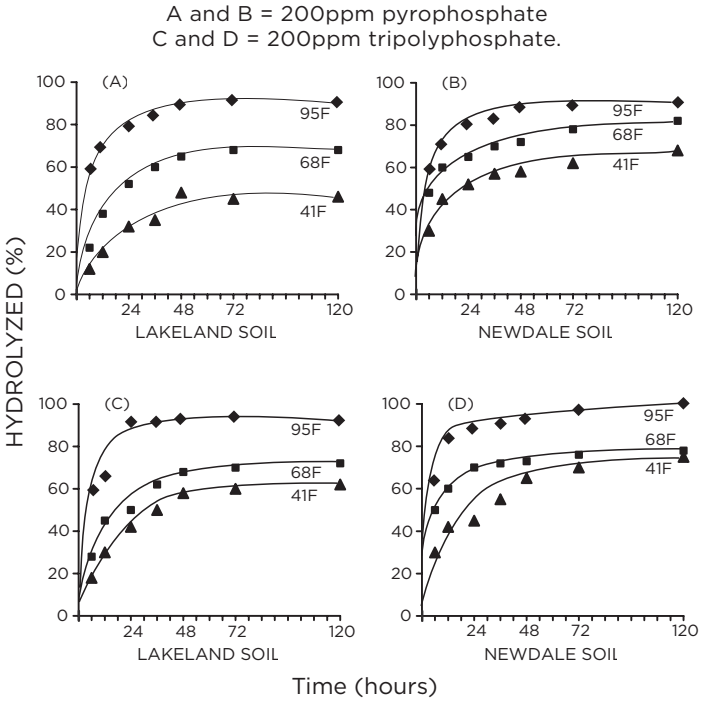

TABLE 1. HALF-LIFE VALUES (DAYS) FOR SOLID AND LIQUID APP IN DIFFERENT SOILS UNDER AEROBIC AND ANAEROBIC CONDITIONS

	Solid APP		Liquid APP	
	Aerobic	Anaerobic	Aerobic	Anaerobic
Alluvial	27.0	9.2	8.7	2.0
Sodic	15.0	7.0	5.4	1.8
Laterite	12.5	3.9	5.2	1.6

regardless of soil type. They further demonstrated that liquid APP hydrolyzed faster than solid APP, and that anaerobic conditions (caused by subsequent flooding) accelerated hydrolysis (Table 1).

PLANT UPTAKE

Plant available phosphate is mainly controlled by hydrolysis reactions because most P is taken up as orthophosphate. Small amounts may be used as pyrophosphate. Dick and Tabatabai (1986) found that hydrolysis rates were faster in non-sterile solutions, presumably because corn roots exude enzymes which facilitate the conversion to orthophosphate. Gilliam (1970) reached similar conclusions in experiments using ^{32}P. He concluded that ortho and pyrophosphate were equally effective in supplying P to P-deficient wheat, corn, and barley. P-deficient roots absorbed the pyrophosphate ion per se and also rapidly hydrolyzed the PP. Nearly 55% of the P was present in the ortho form after 24 hours. P-deficient wheat roots had 1.6 times as much pyrophosphatase activity as non-deficient roots.

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