Advanced phosphorous fertilizers: Are polyphosphates worth it?

If you look into mineral phosphate fertilizers, most of them are of the orthophosphate variety, where phosphorous is present in the form of PO_4^{-3} anions with varying degrees of hydrogen additions depending on the charge balance of the salts. However, there are several different varieties of phosphorous that can be used to fertilize crops. Since the 1970s, polyphosphates have been researched and sold by several different fertilizer companies as a "better way" to fertilize crops. In this post I am going to talk about what polyphosphates are, what the differences with regular orthophosphate fertilizers are, and whether it is worth it or not to replace your current phosphorous fertilization for a regime including or consisting exclusively of these polyphosphates.

Chemical structure of ammonium polyphosphate

Traditional fertilizers like Mono Potassium Phosphate, MKP (KH_2PO_4) will contain phosphorous in a chemical state that is readily available to plants. The HPO_4^{-2} and $H_2PO_4^-$ that are generated from this salt in water at a pH between 6-7 are favorably and effectively taken up by plants under normal conditions. However, upon significant presence of calcium/magnesium minerals or high pH levels, it is common for a lot of the phosphorous to become trapped in the form of insoluble phosphates. These calcium and magnesium phosphates will be unavailable to plants and the soil will quickly become P limited, making P fertilization difficult due to the eagerness with which the soil chemistry can sequester the

added phosphate.

Polyphosphates like ammonium polyphosphate (APP), where the phosphorous is not present as single phosphate anions but as a complex P polymer, can overcome some of the above problems as their tendency to form insoluble salts with cations is suppressed and their solubility is significantly higher. Their use in calcium-rich soils has been proven experimentally multiple times, the following reference provides an example of this (1). However, is there any benefit provided beyond their superiority in this type of high pH and high Ca conditions?

The chemical properties of APP have been extensively studied and we know that many of their benefits in comparison with orthophosphate (OP) salts are eliminated by a simple move towards acidic pH (2,3). Field experiences have shown that when the soil conditions are not this bad, the differences between APP and OP are expected to be low (4,5). Under normal pH and ion-concentration conditions, APP seems to provide very similar results to normal sources of phosphate, as it will tend to hydrolyze and form these phosphates with time anyway. This effect can be especially dramatic in more acidic media, where the decomposition of these phosphates can be quite rapid (6).

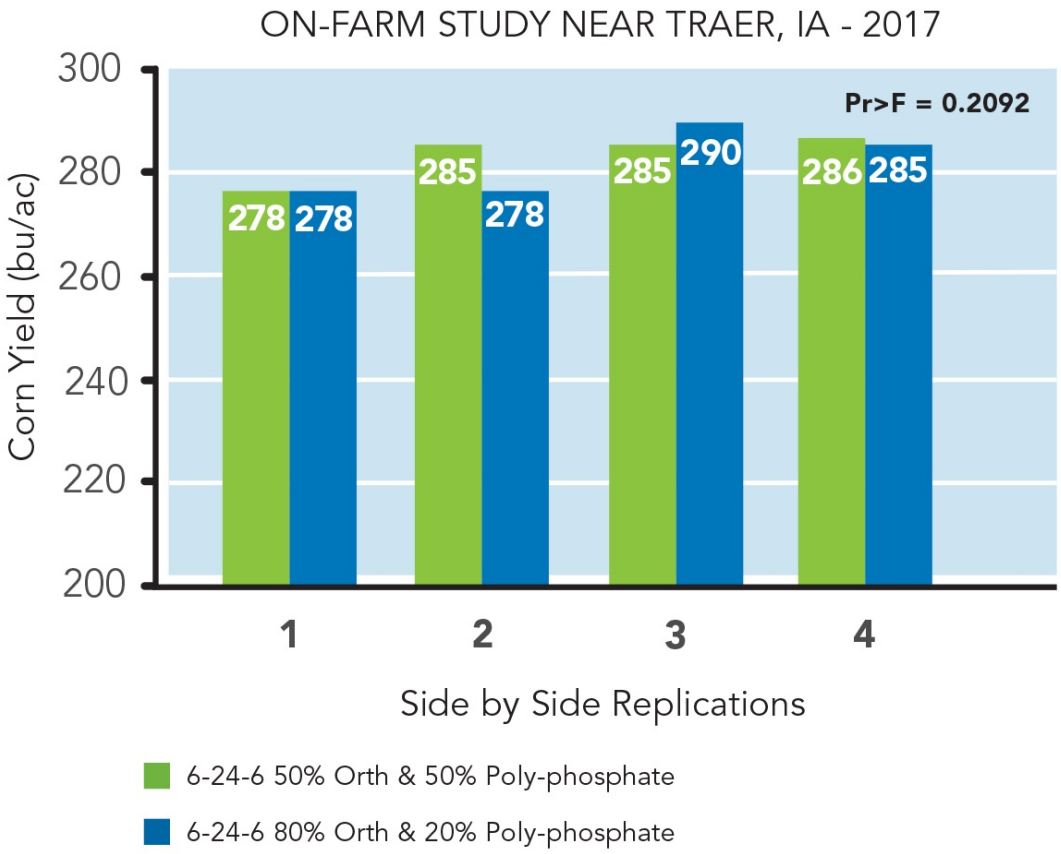


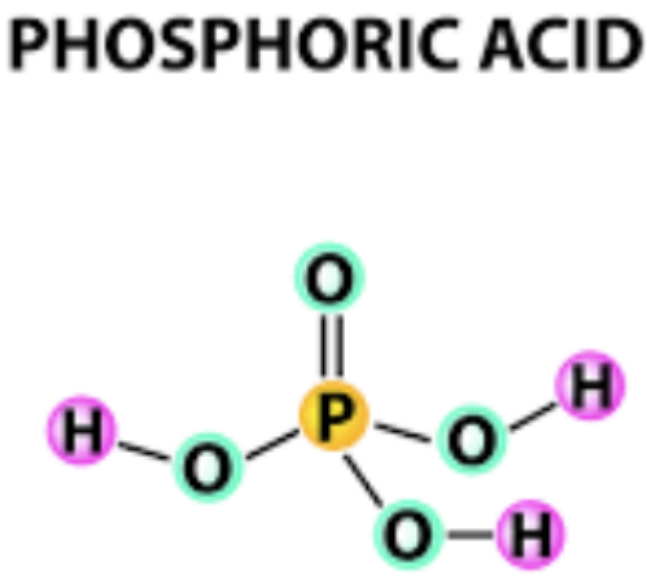
Figure 2. 4 *side-by-side comparisons of corn yield from two 6-24-6 starter fertilizers that contained either 50% ortho & 50% poly-phosphate or 80% ortho and 20% poly-phosphate.*

If soil conditions are not unfavorable, poly and ortho phosphates will give the same result. Taken from this study.

To sum things up, under normal conditions, polyphosphate is no better than your normal sources of phosphorous. If you are running a hydroponic setup within a normal pH range and nutrient concentrations, polyphosphates are just a more expensive way to add phosphorous to your system, they will likely provide no added benefit in terms of yields or crop health compared to using regular phosphate fertilizers. However, if you are growing your crops in a Ca-rich soil that is particularly high pH, where P sequestration due to precipitation is a substantial issue, then polyphosphates offer an alternative method of fertilization that is likely to increase yields against normal orthophosphate fertilizers.

How much Phosphorous are you adding to your solution to adjust pH?

Phosphoric acid is one of the most commonly used pH down agents in hydroponics. This is because phosphoric acid is available in high purity, is easier to handle and has lower cost. However, phosphorous is a significant plant macro-nutrient as well, and substantially changing the level of available P in a nutrient solution can have negative effects on plant growth. Since many hydroponic users – especially those that use hard water sources – might be adding significant amounts of acid to correct their pH level, it is important to estimate how much phosphorous you're contributing to your solution by adjusting pH and whether this means you also need to adjust your formulation to use less P within it.



Schematic representation of a phosphoric acid molecule.

Phosphoric acid is generally available in concentrations from

30 to 80%, most hydroponic users will use pH-down solutions that are in the 35-45% range, which are prepared to be concentrated enough to last a significant amount of time while diluted enough to allow for easier handling and to be less corrosive. You can use the equation given above to calculate the P contribution in ppm from a given addition of phosphoric acid (you can look up the density for a given concentration using this table). Adding 1mL/gal of 45% phosphoric acid will contribute around ~48 ppm of P to your nutrient solution. This is a very large amount of P considering that the normal range for flowering plants is between 30-60 ppm.

Having an excess of P can be very problematic as phosphorous can strongly antagonize certain nutrients, especially if the pH of the solution drifts up as the plants are fed. At P concentrations exceeding 120 ppm, this element can start to antagonize elements like Fe, Ca and Zn very strongly, preventing their absorption and leading to plant issues. Furthermore, excess of P can often cause problems with P absorption itself – as it can become locked up inside the plant as Fe or Ca salts – which can lead to P deficiency-like symptoms. The most tricky thing about P toxicity issues is that they do not show as certain characteristic symptoms, but mostly as deficiencies for other nutrients or even P itself. The exact symptoms will depend on the VPD and particular environmental conditions as these play an important role in Ca absorption as well.

> *P contribution in ppm = (Acid concentration in % / 100) * 0.3161 * (volume of addition in mL) * (density of acid in g/mL) * 1000 / (total volume of solution in liters)*

Many growers will indiscriminately add P without considering how much was required to adjust pH, which is a bad idea due to the above reasons. A water source that is very hard might require almost 1mL/gal to fully adjust the solution to the pH range required in hydroponics, if a normal hydroponic solution

is fed – which will contain all the necessary available P (assuming the user adds very little outside of it) – then this means that the final solution might end up with P levels that will strongly antagonize several nutrients. It's therefore no wonder that many hydroponic growers in harder water areas suffer from consistent issues with Ca and Mg, many of these cases could be caused by the presence of excess P within nutrient solutions. *While many hydroponic hard-water formulations will adjust for Ca and Mg in hard water, they will generally not adjust for P as they cannot know for certain how the user will lower the pH.*

If you're a hydroponic grower using phosphoric acid, keeping track of how much P you're adding to your nutrient solution to adjust pH is going to be very important. If you're adding more than 0.25 mL/gal of 45% phosphoric acid – of course adjust accordingly for higher/lower concentrations – then you should consider adjusting your hydroponic formulation to account for this expected P addition and prevent your formulation from reaching abnormally high levels of P.

Phosphorous toxicity and concentration in higher plants

If you search the web for symptoms of nutrient toxicities you will often find clear pictures and descriptions for most elements. Feed a plant too much nitrogen and it will grow leggy and weak, with dark leaves and long stems, feed it too much boron and you will see yellowing and tissue necrosis. However you will struggle to find descriptions for toxicity

symptoms for potassium (K) or phosphorous (P). Is there really no P or K toxicity? Why are they no pictures or clear ideas of how these problems look? Today I am going to talk a bit about P toxicity and why it's so difficult to reach levels where plants react very negatively to ions from the phosphate family. *Images posted were taken from articles cited within this post.*

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You will often find websites that talk about P toxicity as saying that it is rare or that what it causes is mainly problems with other elements. In general increases in P concentration can cause problems with other elements particularly because the solubility of dihydrogen phosphate salts ($H_2PO_4^-$), salts that form with the ionic form of phosphate that's mainly present around the pH values used in hydroponics (5.5-6.5) can be very insoluble. You will struggle to find solubility values for heavy metal dihydrogen phosphates, but Fe, Zn and Cu dihydrogen phosphates can be reasonably presumed to be poorly soluble. However calcium dihydrogen phosphate has a solubility of 20g/L at 25°C and is therefore very soluble, so no problems with Ca due to having a lot of phosphorous (this salt is also known as mono calcium phosphate).

The solubility of Ca dihydrogen phosphate is in fact very important because rock phosphate – tricalcium phosphate – is one of the main sources of phosphorous in soil and it dissolves to form protonated phosphate species at the pH usually created around plant roots. This means that many plants evolved with very large occasional concentrations of dihydrogen phosphate around them and therefore they generated mechanisms to down-regulate the uptake of phosphorous from

really high concentrations.

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There is strong evidence about the above. In fact plants that evolved in phosphorous-poor soils did not evolve mechanisms for down-regulation and do exhibit P toxicity even at moderate concentrations of this element. A few plants native to Australia exhibit this behavior, you can read more about this here. Due to this fact many plants can be cultured in media that is amended with fertilizers that generate large local concentrations of phosphorous when watered without showing any strongly negative effects. Note however that plants will eliminate these down-regulation mechanisms significantly if they are in a P deficient media and if you feed them P rapidly you can cause P toxicity just because the plant couldn't react fast enough to the large increase in P concentration. See for example this study using P deficient Barley which accumulated toxic levels of P upon supplementation although this did not happen when the plants were constantly exposed to high P levels.

In hydroponics we do see excess of P manifest itself as deficiencies of other elements because of the solubility issues for heavy metal acid phosphates mentioned above. Several studies show the strong link between P concentration and the availability of some micro-elements. For example this paper shows the relationship between P and Zn and how the relationship corresponds with Zn phosphate precipitation in the roots. However if heavy metals are properly chelated we in fact don't see these problems. I have made experiments with plants – basil and mint – cultivated in 600 ppm of P where I have failed to see any significant problems although I have failed to find any papers that describe experiments under such

extreme P concentrations.

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Is more P always better then? Studies in tomatoes show better responses to salinity at higher P concentrations (for example here). Although the highest concentration tested here is 61 ppm (2mM) which is higher than but still close to what is generally used in hydroponic culture of tomato plants (30-50 ppm). Tabasco pepper has also been found to grow better under higher P concentrations (see here). A study varying P concentration in hob marjoram found lower essential oil concentrations at higher P levels, although these levels are around 60 ppm as well. Lettuce on the other hand shows increases of sesquiterpene lactones at high P levels (see here). There are a few publications about P toxicity in higher plants – notably this one about tomatoes – where problems caused by P are generally associated with the previously mentioned micronutrient issues and P concentrations in leaf tissue above 1%.

In summary P toxicity depends heavily on plant type and its ability to regulate P uptake, it is also most likely heavily dependent on micronutrient concentration and the strength and stability of the chelating agents used to prevent the precipitation of heavy metal phosphates. There are no studies I could find with P under very high concentrations (>=20mM) using chelated heavy metal sources so this is an interesting topic for research for anyone interested in exploring the limits of P uptake.