

Sources of Phosphorus for Plants: Past, Present, and Future

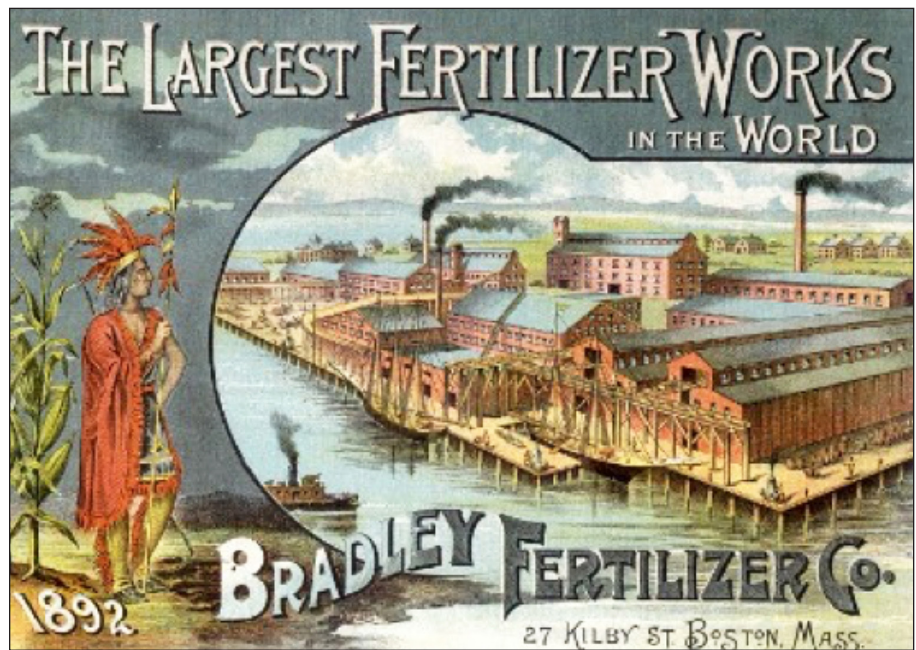
By Robert Mikkelsen

When humans first transitioned from hunting and foraging to farming, soil P depletion began as crops were harvested and removed from their fields. Early farmers learned to enrich soils with animal manure or adopt shifting cultivation. However, as cities developed, nutrients were systematically withdrawn from the field and concentrated near the city.

Plant nutrient depletion and agricultural sustainability has been addressed in various ways by different civilizations. Newman (1997) describes how P depletion as a result of crop production was handled in the U.S. Prairie (by exploiting P from organic matter mineralization), on a typical medieval English Farm with declining wheat production (running a P deficit of 0.7 to 0.9 kg P/ha/yr), for Egyptian fields which remained in P balance from annual flood water, and in Northern China, where P deficits occurred even with the traditional spreading of human excreta (with the accompanying fecal-borne diseases).

Slash and burn agriculture was commonly employed to clear land and enrich the soil with nutrients from the residual ash. One study reported that forest ash contained 11 kg P/ha and 27 kg N/ha after burning, of which more than half was blown from the field in wind (Giardina et al., 2000). Additionally, in medium to high-intensity fires, heat-induced reactions can increase P sorption by soil minerals, leading to reduced P recovery by crops. During the U.S. colonial period, slash and burn techniques forced inland migration from the Atlantic Coast as agricultural fields were successively exhausted of their nutrients with no means of restoring the fertility. When added to soil, the liming effect from ash and the input of mineral P and K made it a good amendment for growing a N-fixing crop.

In the early 1800's, it was discovered that P is beneficial for plant growth. As the value of "pounded" bones was recognized as a P source, the demand grew quickly in the early 19th century. Unprocessed bones (hydroxyapatite; $\text{Ca}_5\text{F}(\text{PO}_4)_3\text{OH}$) were crushed and applied to the soil at a rate of 1 t/A or more. In England, the demand for bones outstripped the domestic supply and by 1815, bones were imported from the Continent, reaching a maximum of 30,000 t/yr (Nelson, 1990). This led the famous plant nutritionist Justus von Leibig to complain:



“England is robbing all other countries for their fertility. Already in her eagerness for bones, she has turned up the great battlefields of Liepsic, and Waterloo, and of Crimea: already from the catacombs of Sicily she has carried away the skeletons of many successive generations. Annually she removes from the shores of other countries to her own the manerial equivalent of three million and a half men.... Like a vampire she hangs from the neck of Europe” (Liebig).

The observation that not all bones were equally effective as a plant nutrient source led to experimentation to acidify the bones before adding them to soil. One early innovator, John Lawes applied raw bone to his farm fields without

SUMMARY

The phosphate fertilizer industry developed in the 19th century to provide farmers with plant nutrients that are efficient to manufacture, affordable for farmers, and agronomically effective. Continued advances in chemistry and engineering have led to a variety of commercial products that are now widely used to restore degraded soils and replace this essential nutrient that is continually removed from fields in harvested crops.

KEYWORDS:

fertilizer production; phosphate fertilizer development

ABBREVIATIONS AND NOTES:

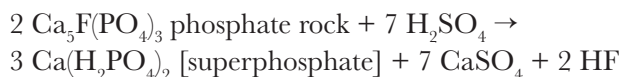
P = phosphorus; N = nitrogen; K = potassium; S = sulfur; Ca = calcium

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Large pile of bison skulls that will be ground into fertilizer in the U.S. around 1870 (left). Advertisement for Bradley Fertilizer Co. in 1881 (inset).

seeing any additional crop growth. This led him to experiment with treating bones with sulfuric acid, which proved to be very effective. In 1842 he was granted a patent for “superphosphate of lime”, composed of calcium hydrogen phosphate and calcium sulfate. The manufacturing of superphosphate quickly spread around the world and marked the beginning of the modern fertilizer industry.



The manufacturing of superphosphate consisted of placing ground bones into a pit and then stirring in sulfuric acid as the mixture solidified for several hours. The solid paste was then allowed to mature in a curing pile for a few weeks until it was ready to be broken apart with picks, crushed, screened, and bagged. The lumpy texture could make it difficult to spread uniformly in the field. This simple process also encouraged farmers to make their own superphosphate for on-farm and local use (New England Farmer: July 1869).

The name “superphosphate” is thought to have first appeared in a pamphlet by Joseph Graham who explained how “phosphate of lime (as it exists in bone) is totally insoluble in water...when deprived of a portion of the lime constituting its base, (it is) reduced into a state of superphosphate, becomes soluble...” (Cooper and Davis, 2004). The “super” likely refers to its superiority over ground untreated animal bones. In addition to

making fertilizer, much of the bone-derived P was calcined and reduced in a furnace to elemental P for use in making matches.



Mining guano off the Peruvian coast (about 1860).



Phosphate rock mining operation in North Carolina, USA.

The eventual shortage of bones led to the exploration of other potential P sources. Guano, which had accumulated from dried bird manure in large quantities in the arid islands off the coast of Peru and in the South Pacific, became an important source of P fertilizer between 1840 and 1870. However, the most nutrient-rich guano deposits (typically 4 to 5% P) were quickly depleted and its use declined in the latter half of the 19th century as low-grade mineral deposits were discovered around the world.

When Peruvian guano first became available in the U.S., it quickly began to substitute for bulky, locally derived recycled organic materials and led to the development of the commercial fertilizer industry in the U.S. Not surprisingly, the major U.S. meat processing companies and slaughterhouses were also major fertilizer manufacturers, distributing both N and P-based products for crop production.

Mineral deposits of phosphate rock (apatite) were later developed and substituted for bones in the production of superphosphate. The P fertilizer industry entered the mod-

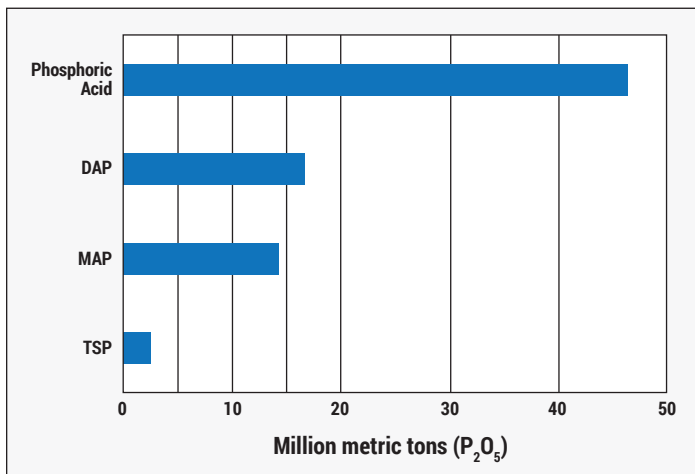
ern era as phosphate rock sources became readily available and accessible from geologic deposits around the world (e.g., England, 1847; Norway, 1851; France, 1856; USA, 1867; Tunisia, 1897, Morocco, 1921; Russia, 1930).

All common P fertilizers are now produced from phosphate rock as the starting material. Most sources of phosphate rock are too insoluble for direct use as a P source for plants. Phosphate rock from a few geologic deposits are suitable for direct application, especially if used for perennial crops growing in acidic soils, where the acidity and low Ca concentrations help speed rock dissolution and the release of P.

Superphosphate became the dominant P fertilizer in the world for over 100 years, but is no longer widely used and traded (with the notable exception of pastures in Australia and New Zealand). Other P sources remained available in limited quantities (such as manure, guano, ground phosphate rock and basic slag) and new P fertilizers were tested (such as triple superphosphate, ammoniated phosphates,

Table 1. Properties of common phosphate fertilizers.

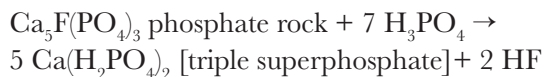
Fertilizer	Acronym	Chemical formula	Common nutrient content		Solution pH
			P	P ₂ O ₅	
Single superphosphate Ordinary superphosphate	SSP OSP	Ca(H ₂ PO ₄) ₂ + 2 CaSO ₄	7 to 9	16 to 20	<2
Triple superphosphate	TSP	Ca(H ₂ PO ₄) ₂	20	45	1 to 3
Monoammonium phosphate	MAP	NH ₄ H ₂ PO ₄	23	52	4 to 4.5
Diammonium phosphate	DAP	(NH ₄) ₂ HPO ₄	20	46	7.5 to 8
Monopotassium phosphate	MKP	KH ₂ PO ₄	23	52	4.5
Ammonium polyphosphate	APP	[NH ₄ PO ₃] _n	15 to 16	34 to 37	6
Phosphoric acid (fertilizer/merchant grade)	PA	H ₃ PO ₄	23	52 to 54	1
Superphosphoric acid (orthophosphoric and polyphosphoric acid)			28 to 33	65 to 75	1 to 1.5



World production of phosphoric acid and P fertilizers in 2017 (IFA, 2018).

nitric phosphates), but they were not commercially competitive for many years.

The additional advantage of treating the phosphate rock with phosphoric acid instead of sulfuric acid was discovered in the 1870's. This process resulted in the production of fertilizer with soluble P concentrations almost three times higher than superphosphate, named triple superphosphate (TSP). However, TSP did not gain widespread usage until much later. This new concentrated P source greatly reduced fertilizer transportation costs and the manual labor required to spread powdered P fertilizer on the field, as granulation technology did not become widespread until 1950's.



The nitrophosphate (Odda) process was developed in Norway in the late 1920's. This reaction involves mixing phosphate rock with nitric acid to produce calcium nitrate and phosphoric acid. A compound fertilizer containing both N and P (and K is frequently added) is also commonly produced from this process.

The Modern Era

In 1933, the National Fertilizer Development Center (NFDC) of the Tennessee Valley Authority (TVA) was given the mission of improving the efficiency of fertilizer manufacturing and fertilizer use on farms. This organization was pivotal in advancing global fertilizer technology and use. The majority of fertilizers produced in the world are still made with processes first developed by the TVA. The successor organization, the International Fertilizer Development Center (IFDC) still continues research and development projects on new fertilizer technology.

Diammonium phosphate (DAP) became the dominant P fertilizer following the introduction of the TVA process in the early 1960's where phosphoric acid is reacted with ammonia, using a pipe-cross reactor. TVA also introduced processes for manufacturing nitric phosphate, solid ammo-

nium polyphosphate, and urea phosphate. The popular fluid ammonium polyphosphate became widespread after TVA introduced a method for combining superphosphoric acid (a mixture of phosphoric acid and polyphosphoric acid), with ammonia in the T-pipe reactor. The polyphosphate in superphosphoric acid keeps metal impurities from precipitating from solution.

As fertigation becomes more common, introducing soluble P fertilizer into irrigation systems requires careful management to prevent precipitation with constituents in the water that can lead to fouling and plugging of the irrigation system (Mikkelsen, 1989). A variety of excellent water-soluble P sources can be used for fertigating crops (such as monopotassium phosphate or urea phosphate), but close attention to the system chemistry is required.

The most common P fertilizers in the world are currently DAP, monoammonium phosphate (MAP), and TSP. A large amount of P is traded as phosphoric acid, of which 80 to 85% is used in the production various P fertilizers.

The current global outlook is for steadily declining positive growth rates for P fertilizer. However, this global average masks specific regional trends such as the slowing P demand in China and increasing demand for P fertilizer in Africa (IFA, 2018).

The Future

Phosphorus fertilizers have achieved farmer acceptance by being: 1) efficient to manufacture, 2) affordable, and 3) agronomically effective. New P fertilizer materials will additionally need to satisfy various environmental criteria (such as during mining and reclamation, manufacturing, and field use), social demands (such as energy consumption, greenhouse gas production, phosphogypsum management), and consumer expectations (such as minimizing trace elements in fertilizer, using sustainable mining practices, minimizing water quality impacts). These new considerations place additional constraints on the development of new fertilizer products.

Improved recovery of P that is directly consumed in human food and in animal feed will certainly gain more importance as P recycling from various waste streams is emphasized. Future efforts to more effectively reuse and recycle P derived from waste streams will likely include:

- 1. Manure-based fertilizers and composts:** Phosphorus may be separated by solid-liquid processing and the products may be further concentrated by drying, composting, fortifying, or pelletizing.
- 2. Combustion products and ash from manures and sludges:** Incineration at 800 to 900°C concentrates the mineral fraction without cause significant P volatilization losses. Heating P-containing waste products to higher temperatures will vaporize ele-

mental P which can be condensed and oxidized to phosphoric acid.

3. Extract P from organic waste streams: A variety of useful P fertilizers can be produced from various waste products, including struvite and calcium phosphate minerals such as brushite and hydroxyapatite.

Additional work has recently focused on the behavior of organic P materials in the soil, and manageable factors that control the value of these P sources for plant nutrition. The use of microbial inoculants and biofertilizers is under investigation to improve fertilizer P recovery by plant roots. While recent attention has focused on root-fungi interactions for enhancing P uptake, other plant-growth promoting organisms may significantly contribute to P solubility and rhizosphere activity.

Rapid advances in the field of material sciences also offer new matrices and delivery mechanisms for supplying P to crops. Many new approaches have been suggested, but the economic barrier has so far prevented widespread adoption of new P fertilizer technologies.

Conclusion

The development of the modern P fertilizer industry has provided farmers with easy and safe access to effective and affordable crop nutrients. These products replace P that is removed from the field during harvest and enhance the fertility of nutrient-depleted soils. The commonly used P

fertilizers have their origins in chemistry and processes that are well established.

Emerging insights into material science and engineering may provide breakthroughs in innovative P fertilizer sources. Closer integration of new fertilizer products and root biology may also improve recovery of applied P. The development of innovative P fertilizers that sustain agricultural productivity and minimize off-site environmental impacts would make a significant contribution for agricultural science. **BC**

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