Phosphorus: Past History and Contributions to the Global Food Supply

By Terry L. Roberts

In 1669, the German alchemist Hennig Brandt accidently discovered P while searching for the 'philosopher's stone', a legendary alchemical substance capable of transmuting lower value base metals into gold (Krafft, 1969). Brandt's experiments, involving the distillation of human urine with pieces of silver, produced a white, waxy substance that glowed in the dark. He named the substance 'cold fire', which was later changed to 'phosphorus', meaning light bearer.

In 1776, P was recognized as the 13th element in the history of the discovery of elements (Emsley, 2000). In its elemental form, white P is highly reactive and is not found in nature. Exposed to air, it is flammable, can spontaneously combust, and is poisonous in low doses. Because of its life-destroying properties when used in military applications (e.g., bombs, nerve gas), it became known as the 'devil's element.'

For a century, urine was the only source of P until it was found in bones by two Swedish scientists, Ghan and Scheele, in 1770 (Wisniak, 2005). In the years following, manufacturing processes were developed for commercial P production. Bone ash was reacted with sulfuric acid to produce calcium phosphate [$Ca(H_2PO_4)_2$]. In 1831, Heinrich Kohler patented a method for acidulating bones with sulfuric acid in Austria and in 1835, James Murray, an Irish medical doctor referred to 'superphosphate of lime" in lectures and was issued patents in Ireland, Scotland, and England covering the acidulation of bones in 1842. Later P was found to be a principal constituent of certain igneous and sedimentary rocks.

About the same time, Justus von Liebig referenced mixing sulfuric acid with finely ground bones to make the bones more effective in supplying P to plants. In his 1840, and subsequent editions of *Organic Chemistry in Its Application to Agriculture and Physiology*, he recommended:

"… pour over the bones, in a state of fine powder, half their weight in sulfuric acid diluted with three or four parts water, and after they have digested for some time, to add one hundred parts of water, and sprinkle this mixture over the field before the plow … Experiments have shown that neither corn, nor kitchen-garden plants, suffer injurious effects in consequence, but that on the contrary they thrive with much more vigor" (Liebig, 1840).

Leibig, in addition to suggesting that bones be treated with acid, greatly influenced the thinking on plant nutrition and fertilizers. His theories stimulated research by others.

John Bennett Lawes used bone dust on his estate near Harpenden, England to fertilize turnips in 1836-1838, but with little effect (Nelson, 1990). He then started a series of small-scale pot experiments in 1839 with bones and mineral phosphates acidulated with sulfuric and other acids, and in 1840-1841 moved his trials to the field, which led to the granting of his famous superphosphate patent in 1842. In 1846, Lawes purchased Murray's patent, to avoid any questions of priority that might arise and 1848 he amended his patent to remove all references to bone and bone products, confining it to 'apatite and phosphorite, and other substances containing phosphoric acid.'

Lawes began manufacturing and selling superphosphate of lime in 1843 and that marked the beginning of the world's phosphate fertilizer industry. Within a decade, superphosphate was being produced by 14 firms in England and quickly spread to other parts of the world. (Russel and Williams, 1977). As bones became in short supply, producers in England switched to coprolites, a hard nodule found just above the clay layer in some nearby soils. Later apatite was imported from Norway and rock phosphate from France

The development of single superphosphate (SSP) by Lawes marked the beginning of world's phosphate fertilizer industry.

SUMMARY
Since its early rudimentary forms, phosphate fertilizer has developed in step with our understanding of successful food production systems. Recognized as essential to life, the responsible use P in agriculture remains key to food security.

KEYWORDS:
phosphate; fertilizer history; broadbalk experiment; sustainable yields

ABBREVIATIONS AND NOTES:
P = phosphorus; N = nitrogen

https://doi.org/10.24047/BC10316

from www.era.rothamsted.ac.uk, Rothamsted Research Ltd.

Site of the Broadbalk Experiment in Rothamsted, England, started by John Bennett Lawes in 1843.

and Belgium. Rock phosphate was discovered in the U.S. in 1867, and soon after in many other countries throughout the world.

Single superphosphate, with a relatively low P content (~20% P_2O_5), dominated P fertilizers for more than 100 years. Small amounts of concentrated superphosphate (44 to 48% P_2O_5), i.e. triple superphosphate (TSP) were produced in Germany in the early 1870s (Leikham and Achorn, 2005). However, as its production was dependent on phosphoric acid ... it wasn't until the 1950s that TSP became an important phosphate fertilizer with the development of the first phosphoric acid plant (Robinson, 1980). The introduction of TSP began the era of 'high analysis' phosphate fertilizers and established the phosphate industry near deposits of rock phosphate (Leikham and Achorn, 2005). Production of TSP peaked in the 1980s, but has since been replaced by ammonium phosphates. When synthetic ammonia became commercially available, its use to ammoniate superphosphate grew rapidly. Production of different grades of ammonium phosphate have been available since at the early 1910s, but it wasn't until the 1960s that ammonium phosphate production became commonplace.

Lawes experimenting with fertilizer materials led to his establishment of the Rothamsted Experimental Station on his estate in 1843 (Rothamsted Research, 2018). However, with no formal training in chemistry or other sciences he appointed Joseph Henry Gilbert, a chemist who had briefly studied under Liebig, as his scientific collaborator. Lawes and Gilbert worked together for nearly 60 years. They planted the first of the classical Rothamsted long-term experiments on the Broadbalk field in 1843 and during the next 13 years established nine long-term experiments. The objective was to measure the effects of inorganic fertilizers on crop yields. Inorganic fertilizers were compared to farmyard manure tested alone and in various combinations. Single superphosphate was tested in all of the studies. Growing the same crop on the same land, year after year was a feature of many of the studies.

Rothamsted has become home to the oldest, longest-running trials on fertilizer in the world. One of the most important early results from the experiments was that crops do not respond to N when there is too little plant-available P in the soil (Johnson and Poulton, 2018). We have learned much about plant-available P, P fixation, residual P, and the response of crops to P fertilization from these long-term trials.

Rothamsted's Broadbalk experiment has grown winter

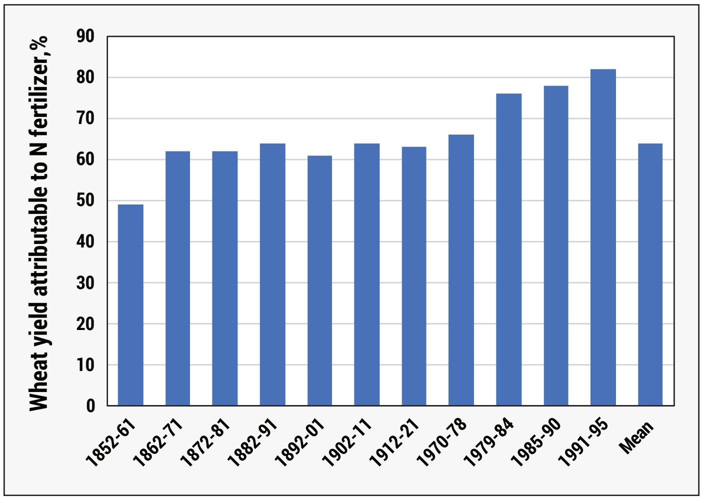

Figure 1. Winter wheat grain yield from NPK compared with P+K applied alone in the Broadbalk experiment at Rothamsted, England. Years between 1921 and 1969 are not shown because part of the experiment was fallowed for weed control (Adapted from Stewart et al., 2005).

wheat continuously since 1843. Application of N fertilizer, with P and K has been responsible for up to 82% of wheat yield compared to P and K applied alone, with an overall average of 64% (**Figure 1**). Between 1970 to 1995, with high-yielding varieties of winter wheat receiving 95 kg N/ha, omitting P decreased yields by an average of 44% (Stewart et al., 2005).

Nitrogen provides the basis for animal and human protein and is essential for crops to achieve optimum yields. About half the world's population is supported by N fertilizer (Erisman et al., 2008), but N is not used efficiently or effectively without P. Examples of the positive interaction between N and P on wheat yield and nitrogen use efficiency (NUE) from Australia, Canada, United States, and the United Kingdom have been recently reviewed by Duncan et al. (2018). They reported on data from 11 studies showing grain yields ranging from 1,000 to 3,590 kg/ha without fertilizer, 1,100 to 4,015 when N was applied alone, and 2,610 to 6,270 kg/ha when N and P were applied together (**Figure 2**). The additional yield from the P ranged from 142 to 3,205 kg/ha. Applying P with N, increased NUE in 9 of the 11 studies, resulting in increases ranging from 2.1 to 31.2 kg additional grain/kg N applied compared to N applied alone. Phosphorus is a crucial for balanced plant nutrition.

Summary

Phosphorus is the basis for all life on earth. It is the sixth most abundant element in living organisms, is a necessary constituent of DNA and our genetic code and provides the energy for all metabolic processes. Phosphorus is essential to global food security. The production of food, feed, fiber, and energy supporting population growth would not be possible without P. However, P lost from agriculture can cause problems with water quality resulting in eutrophication, and the raw material for making P fertilizer, rock phosphate, is

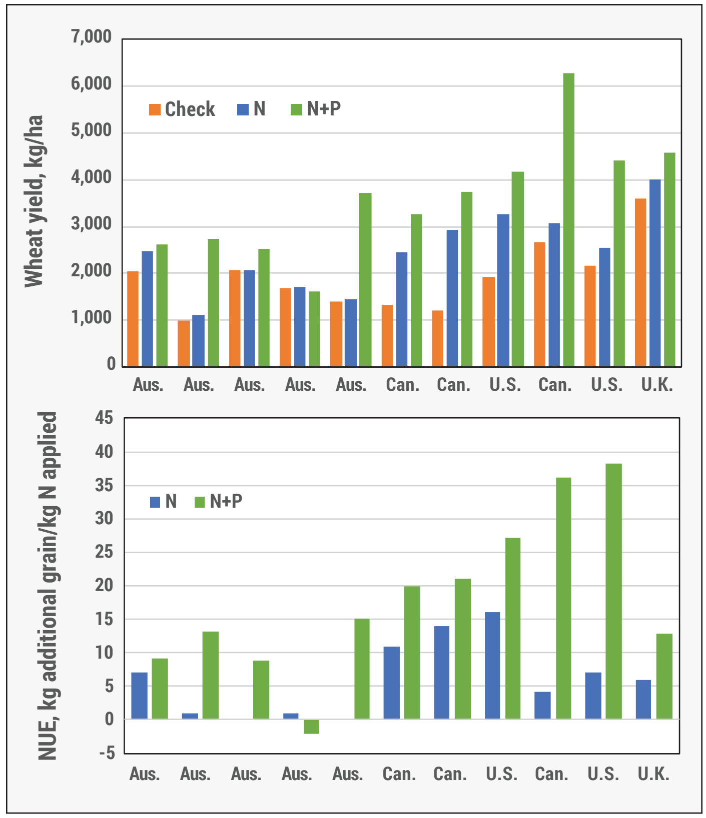

Figure 2. Summary of results from studies in Australia, Canada, U.S. and U.K. investigating the effect of N and N+P on wheat yield (top) and NUE (kg additional grain/kg N applied) (bottom) (Adapted from Duncan et al., 2018).

a non-renewable resource. While the world is in no danger of running out of rock phosphate in the foreseeable future, it behooves us to use this valuable resource as efficiently as possible (Scholz et al., 2014). Nutrient management within a 4R framework—application of the right source of plant nutrient, applied at the right rate, at the time, and in the right place—is the foundation of efficient P use. **BC**

Dr. Roberts is President of the International Plant Nutrition Institute (IPNI), based in Peachtree Corners, GA, USA. e-mail: troberts@ipni.net

References

Duncan, E.G. et al. 2018. Field Crops Res. 226: 56-65.
Emsley, J. 2000. The 13th element: the sordid tale of murder, fire and phosphorus. John Wiley & Sons, New York. p. 327
Krafft, F. 1969. Angew. Chem. Internat. Edit. 8: 660-671.
Nelson, L.B. 1990. History of the U.S. Fertilizer Industry. J.H. Parker (ed). Tennessee Valley Authority. Muscle Shoals, Alabama. p. 522
Leibig, J. 1840. Organic Chemistry in its Application to Agriculture and Physiology. L. Playfair (ed). Taylor and Walton. London. p. 387
Leikam, D.F. and F.P. Achorn. 2005. Ch. 2 *In* J.T. Sims and A.N Sharply (eds). Phosphorus: Agriculture and the Environment. Published by ASA/CSSA/SSSA. Madison, WI. p. 23-50.
Johnston, A.E. and P.R. Poulton. 2018. European J. Soil Sci. 69: 113-125.
Robinson, N. 1980. Ch. 6 *In* F.E. Khasawneh et al. (eds). The Role of Phosphorus in Agriculture. ASA/CSSA/SSSA. Madison, WI. p. 151-193.
Rothamsted Research. 2018. The history of Rothamsted research. https://www.rothamsted.ac.uk/history-and-heritage
Russel, D.A. and G.G. Williams. 1977. Soil Sci. Soc. Am. J. 41: 260-264.
Scholz. R.W. et al. Ch. 1 *In* Sustainable Phosphorus Management. A Global Transdisciplinary Roadmap. Springer Dordrecht Heidelberg New York London. p. 1-113.
Stewart, W.M. et al. 2005. Agron. J. 97: 1-6.
Wisniak, J. 2005. Indian J. Chem. Tech. 12: 108-122.