

Phosphate Rocks!

INTRODUCTION

On approximately two thirds of the world's arable land, phosphorus is a plant growth limiting nutrient (Lambers et al., 2013). Agriculture utilizes roughly 80% of the mined phosphate rock as fertilizer, with the remaining 20% being utilized in products such animal feed supplements, food preservatives, pesticides, fungicides, herbicides, water treatments, cosmetics, and metallurgy (Sattari, 2012). Currently we derive approximately 63% of our phosphorus fertilizer from phosphate rock, with the remainder being derived from animal manure, sewage sludge, and guano (Rittman, 2011). Phosphate rock reserves are finite, which leads to a predicament: we will run out of phosphate rock eventually. The concept, stressed by peak resource theory, is that once global reserves are depleted by half, economic factors will drive resource prices high and unattainable by many (Cordell and White, 2013). Phosphorus does not have a substitute in biomass production. Unlike energy resources, we cannot look to other resources to mitigate our dependency upon phosphate rock (Gilbert, 2009). Phosphorus has potential to be recycled (Rittman, 2011). On a large scale, if agriculture gears itself to derive phosphorus fertilizer from recycled phosphorus we can avoid phosphorus resource scarcity.

BACKGROUND

Low levels of phosphorus in soils results in phosphorus deficiencies in crops which will grow poorly and can be diagnosed by observing leaves turning a blue-green color. Farmers apply phosphorus fertilizers to agricultural soils to mitigate crop growth limitation by phosphorus.

Known global phosphate rock reserves are concentrated in just a handful of countries. Phosphate rock reserves that contain at least 8.5×10^{13} tons of phosphate rock are located in Morocco, China, Algeria, Syria, Jordan, South Africa, the United States and Russia (Jasinski, 2013). Morocco contains approximately 75% of the world's know phosphate rock reserves at 3.3×10^{15} tons of phosphate rock (Jasinski, 2013).

World Phosphate Rock Reserves 65,000 million tonnes*

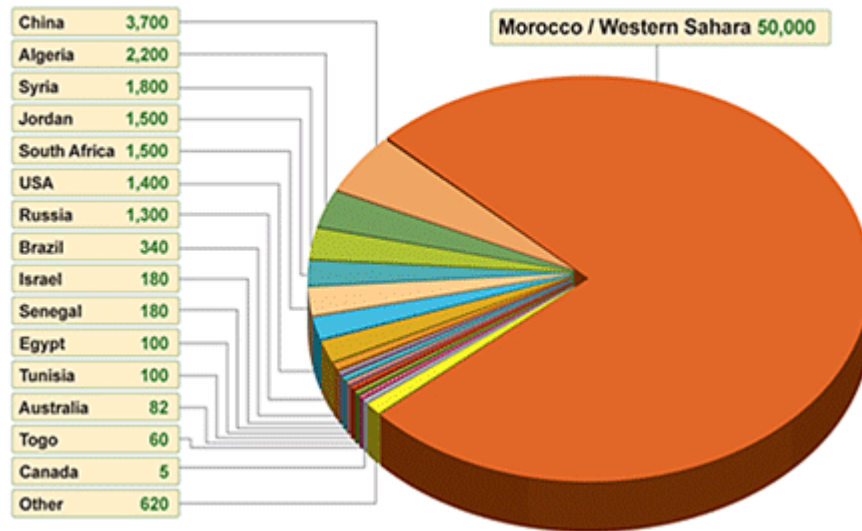


Figure 1: World Phosphate Rock Reserves
Citation: (Cordell and White, 2013)

Phosphate rock is mined, transported, and then processed. Large surface mines are the conventional method of extraction. Transportation of mined phosphate rock is usually carried by train or cargo ship. Large industrial facilities process the phosphate rock into phosphorus fertilizer (IPNI, 2010).

To process phosphate rock to phosphorus fertilizer, manufacturers initially remove large impurities through a benefaction process which separates soil particles, organic matter, carbonates, and iron oxides from phosphate rock. This is followed by a washing and screening process that removes oversized materials and fines from the ideal sized phosphate rock. Phosphate rock must then be converted to phosphoric acid through a chemical process. The

chemical process requires gypsum and yields phosphogypsum, an unusable waste product, and phosphoric acid. Phosphoric acid can then be altered with ammonium to form phosphorus fertilizer in the form of granules or a liquid solution (IPNI, 2010). A flow chart demonstrating the large steps in the chemical process to yield phosphorus fertilizer from phosphate rock can be seen in figure 2.

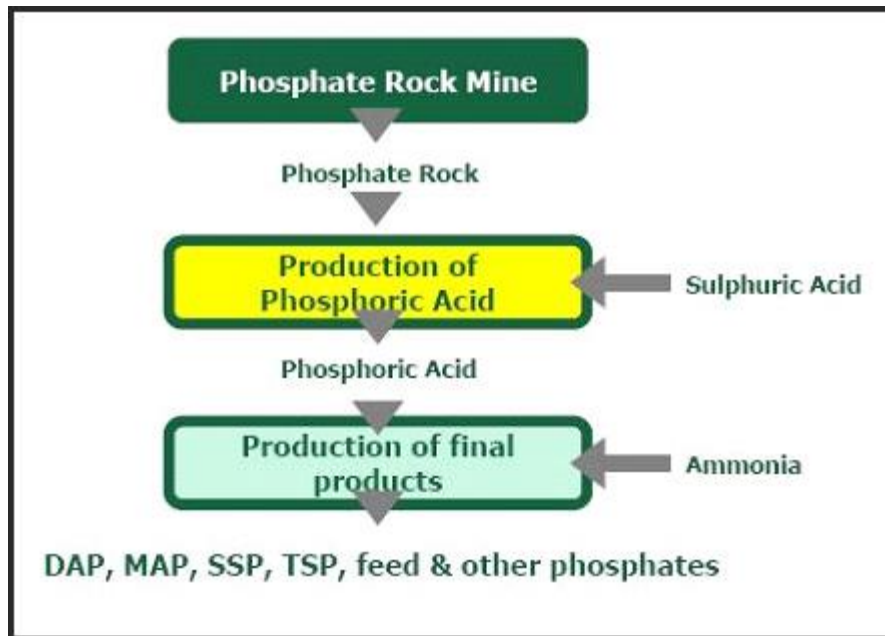


Figure 2: Phosphate Chemical Process Flow Chart
Citation: (Sunkar, 2007)

PREDICTIONS

Peak resource theory applied to phosphate rock reserves is known as peak phosphorus. Peak phosphorus is inevitable assuming continued consumption of phosphate rock (Cordell and White, 2013). It is heavily debated in the literature as to when peak phosphorus will occur. Some authors argue that we will reach peak phosphorus by 2035 (Cordell and White, 2011) while others predict that we will reach peak phosphorus by 2100 (Sattari et al., 2012). In contrast, Scholz and Wellmer contest that we will have viable phosphate reserves for the next four hundred years (Scholz and Wellmer, 2013). Factors contribute to the wide range of predicted values of when peak phosphorus will occur, such as mathematical models,

assumptions of variables, national governments changing their reported volume of reserves, private enterprise retaining data, no international organization in charge of global phosphate reserves, unknown technological advances in mining technology, and lack of thorough exploration.

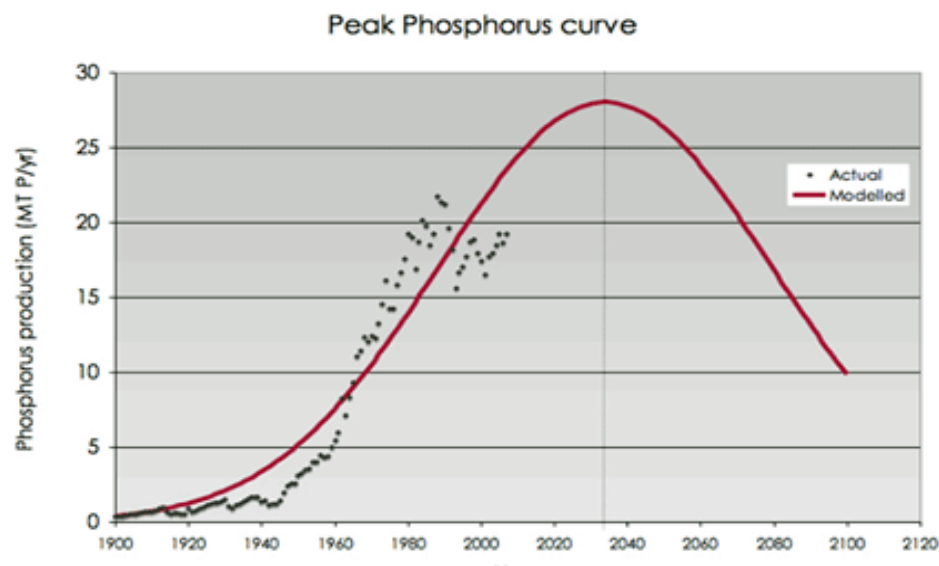
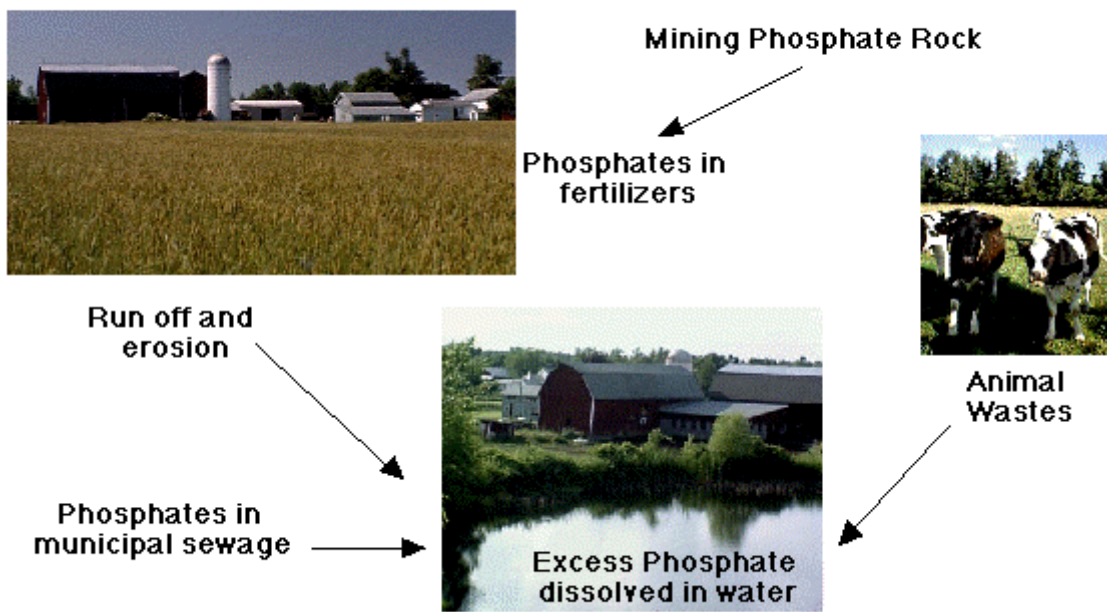


Figure 2: Peak Phosphorus Curve
Citation: (Cordell and White, 2013)

RECYCLE

There is potential for the recycling of phosphorus in our agricultural systems. Currently, we can observe phosphorus rich waste water coming off of our agricultural and developed lands. The inputs of phosphorus to water are derived from soil erosion, animal waste and human waste. Cordell calculated levels of phosphorus leaving agricultural lands as a percentage of the current volume of phosphorus fertilizer being applied in 2011 (Cordell and White, 2011). Soil erosion contributed 46% of phosphorus flow off of agricultural lands, while animal waste and human waste contains 40% and 15% respectively. Phosphorus recovery from animal waste is economically and technically viable with known technologies (Rittmann et al., 2011). Viable technologies for phosphorus recovery from soil erosion still need to be developed (Rittmann et al., 2011).

Human Influences on Phosphate Cycle



C. Ophardt c.1997

Figure 4: Human Influences on the Phosphate Cycle
Citation: (Ophardt, 1997)

Phosphorus loss due to animal waste is easily recovered due to concentrated amounts of phosphorus in a small volume of material (Rittmann et al., 2011). Animal wastes contain a lot of energy, microbes, and phosphorus. For example, pig waste runoffs coming from feedlots have a phosphorus concentration and chemical oxygen demand (COD) of 380mg P L^{-1} and $14,000\text{ COD L}^{-1}$ respectively (USDA, 1996). Anaerobic digestion of animal waste can be converted to a useful source of energy as well as releasing phosphorus from the organic waste in the form of inorganic phosphorus. That same pig waste can be converted to $1.6 \times 10^8\text{ kJ L}^{-1}$ of energy value assuming a 90% conversion (USDA, 1996). Inorganic phosphorus in a water stream coming out of an anaerobic digester must be recovered by precipitation, adsorption, ion exchange, or biological uptake. Anaerobic digestion of animal waste is a proven technology that has the opportunity to link phosphorus recovery with energy production, making it a viable option today (Rittmann et al., 2011).

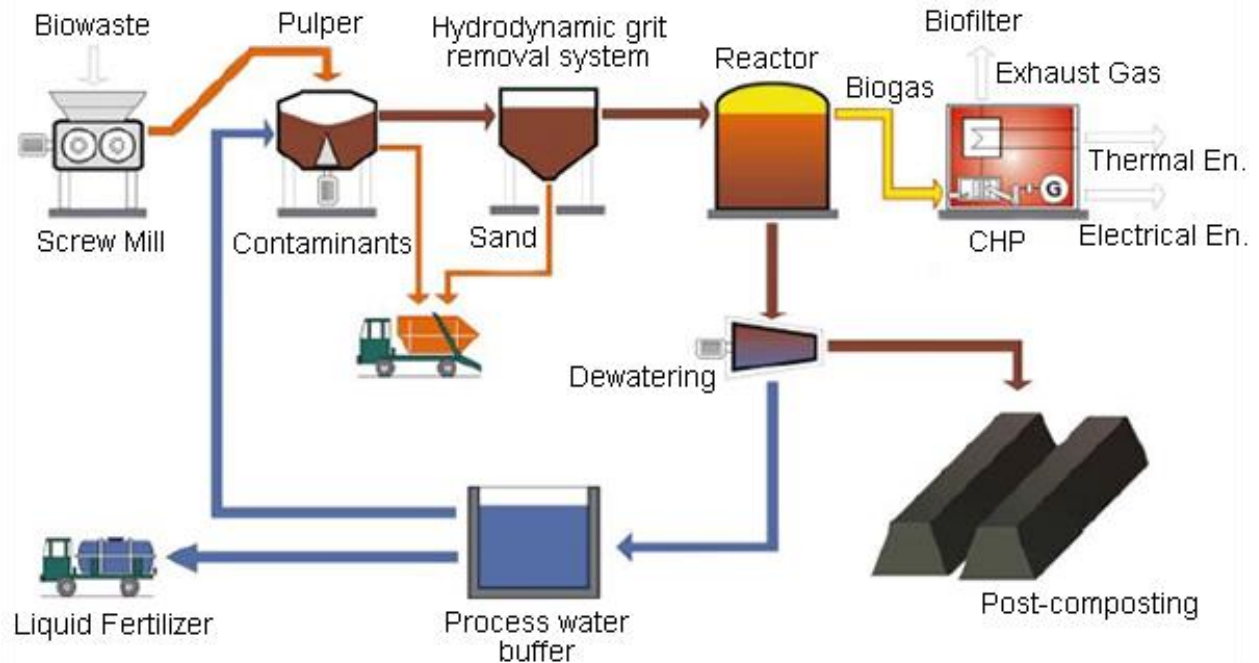


Figure 5: Anaerobic Digester Flow Chart
Citation: (Wtert, 2009)

Phosphorus loss to soil erosion is not easily recoverable as phosphorus is typically diffused into surface water during storm events. Soil erosion has many processes, including particle transfer and solution transfer. Particle transfer can be thought of as soil particles moved by fluvial mechanisms into surface water flow. In contrast, solution transfer can be thought of as chemicals dissolving into soil water and the solution transfers to surface water flow. Surface water has a variable flow rate with a low phosphorus concentration (Rittmann et al., 2011).

Currently we do not capture phosphorus loss due to soil erosion. Mechanisms of capturing phosphorus loss from soil erosion should be a priority in an effort to close the loop of the human influenced phosphorus cycle. Phosphorus from particle transfer can be associated with particulate matter that can settle out in lakes, and reservoirs. A potential location to capture of phosphorus loss due to soil erosion is in the sediment build up behind dams.

In the Mississippi River, dissolved phosphorus concentration increased by over 50% between the years of 1993 and 2003, which correlated with an increase in agricultural

applications of phosphorus fertilizers (USGS, 2007). Since phosphorus was dissolved in solution it is unlikely to will not settle out behind dams. Properly measuring and applying phosphorus fertilizer where it is needed in the field should reduce phosphorus loss due to solution transfer.

Phosphorus loss in human wastewater is easily recovered due to concentrated amounts of phosphorus in a small volume of material. Wastewater treatment professionals have been working for decades on phosphorus capture technologies. The primary objective to capture phosphorus from human waste was to prevent eutrophication potential (Rittmann et al., 2011). By taking these technologies one step further the agricultural sector can utilize the captured phosphorus to derive phosphorus fertilizers (Golbert, 2009).

Enhanced biological phosphorus removal (EBPR), a technology currently being applied to human wastewater treatment facilitates, utilizes heterotrophic bacteria known as polyphosphate accumulating organisms (PAOs) (Rittmann et al., 2011). In general, bacteria contain about 1-2% of their biomass as phosphorus in cellular components, such as DNA and phospholipid bi layers. PAOs have the ability to store phosphorus in polyphosphate inclusions in their cell, which increases the proportion of phosphorus in the bacteria to 5-7% (Rittmann et al., 2011). The microbe *Accumulibacter phosphatis* has been identified as the primary PAO responsible for EBPR (Wylie, 2007). To utilize finished PAOs, growers apply them directly to the field as a slow release fertilizer. In order to produce a fast acting fertilizer, chemical engineers need to figure out a process to derive inorganic phosphorus from organic forms existing in PAOs (Rittmann et al., 2011).

In the pipes of wastewater facilities a pesky precipitate, that has been known to clog up the works, is part of the phosphorus recycling solution. Struvite is a precipitate that contains magnesium ammonium and phosphate. Starting in 2000, Don Mavinic, a civil engineer at the University of British Columbia, was working on a way to remove struvite; he analyzed the precipitate and found that it contained phosphorus, magnesium, and ammonium. He

developed a method to remove struvite and has marketed it as a green fertilizer. Fertilizer producers and consumers must be aware of potential high levels of both zinc and copper in Struvite (Suzuki, 2006). Struvite harvesting has already been applied to anaerobic sludge digestion of both humans and animals. There is a struvite recovering system at the Portland waste water treatment plant, which has proven that this technology can work (Gilbert, 2009).

BREEDING AND CROP SELECTION

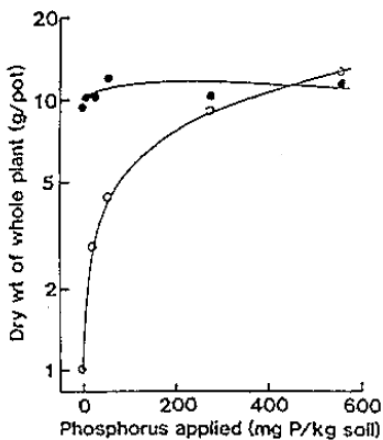
Although plant breeding cannot fertilize soils with phosphorus, it can increase the amount of available phosphorus to crops. Crop breeders tend to focus on the above ground biomass of plants for which they are selecting. If breeders want to prepare crops for phosphorus scarce soils, they should also pay attention to the below ground biomass of the plant.

Phosphorus is one of the most difficult nutrients for plants to acquire. In soil, phosphorus may be present in relatively large amounts but much of it is unavailable to the plant due to the low solubility of phosphates of iron, aluminum, and calcium. These factors lead to soil solution concentrations of 10 μm or less and very low mobility (Smith et al., 2011). Due to phosphorus having a low mobility and the large demand by the plant for phosphorus a phosphorus depletion zone becomes present in the rhizosphere. Plants have evolved a few strategies to handle the phosphorus depletion zone.

Phosphorus growth efficiency is an important trait to select for in plants to perform better in low phosphorus soils. Phosphorus efficient plants are defined as plant which could produce higher yields per unit of nutrient absorbed compared with other plants grown under similar conditions (Wang et al., 2010). Phosphorus efficiency can be increased by changes in root morphology, mycorrhizal symbiosis, enhancements in internal phosphatase activity, and the secretion of organic acids into the rhizosphere (Koide, 1999).

The most common strategy observed worldwide is the formation of arbuscular mycorrhizal (AM) symbiosis. Approximately 80% of terrestrial plant species are capable of forming AM symbiosis, which is a result of over 450 million years of coevolution between fungi and plant root (Smith et al., 2011). The major advantage to the plant from AM symbiosis regarding phosphorus nutrition is the fungi's ability to increase the effective absorptive surface area of the root system by ten to a thousand fold (Smith et al, 2011). AM fungi can scavenge phosphorus from large volumes of soil and rapidly transfer that phosphorus back to the cortical cells of the plant root. Through this action AM symbiosis can explore soil beyond the rhizosphere and increasing the depletion zone from the rhizosphere to the larger volume mycorrhizosphere.

The phosphorus response curve for mycorrhizal citrus plants compared to non-mycorrhizal citrus plants is demonstrated in figure 6. Phosphorus is utilized most efficiently in low phosphorus levels with mycorrhizal plants. On a global scale, if our crops are utilizing mycorrhizal symbiosis in low to medium phosphorus fertilization regimes compared to high phosphorus fertilization regimes there is an observable phosphorus savings due to the increased efficiency.



Phosphorus response curve for citrus (1), ● = mycorrhizal plants, ○ = nonmycorrhizal plants

Figure 6: Phosphorus Response Curve for Citrus
Citation: (Parke and Kaeppler, 2000)

Selecting for the formation of AM symbiosis in crop plants can contribute towards increasing phosphorus growth efficiency in crops (Smith et al., 2011) Crops and cultivars within those species can differ largely from one another in their ability to respond to mycorrhizal colonization (Parke and Kaeppler, 2000). Mycorrhizal symbiosis is deterred by highly fertile soils, in which most cultivates are selected. Without paying attention to mycorrhizae under high fertilization, breeders can select for the absence of AM forming alleles and lose the benefits of mycorrhizal symbiosis (Parke and Kaeppler, 2000).

The actions of agriculturists in the field can affect AM symbiosis and root colonization (Dalpé and Monreal, 2004). Tillage practices reduce AM potential by disturbing the existing hyphal networks. High levels of phosphorus fertilization have been demonstrated to inhibit mycorrhizal efficiencies in soybean (Dalpé and Monreal, 2004). By cropping a non-mycorrhizal host in a previous year it delays mycorrhizal development in the following mycorrhizal host crop. Liming has demonstrated to increase mycorrhizal colonization of barley roots (Dalpé and Monreal, 2004). Once growers grasp the concept of growing and working with mycorrhizae they will increase their AM potential in the field.

Cluster roots are root structures found in lupines. Cluster roots release of phosphate-mobilizing organic acids. While some lupines do not form cluster roots, they are still capable of exuding large amounts of phosphate-mobilizing organic acids which make poorly available phosphorus more available. The ability of exuding large amounts organic acids can be added to other plants through genetic modification which would allow plants to perform better on phosphorus deficient lands (Lambers et al., 2013).

CONCLUSION

Phosphate rock reserves are finite and no substitute exists for phosphorus in biological processes. Assuming that the Hubbert peak resource theory regarding finite resources holds true, a peak phosphorus event is inevitable. The timing of this event is in debate with the

earliest estimates only two decades away. No matter when peak phosphorus is scheduled to occur, agriculturalists and fertilizer manufacturers should change their view of a linear flow, based on phosphate rock availability, to viewing phosphorus as a cyclical flow.

Current phosphorus losses off agricultural lands are in the form of soil erosion, animal waste and human waste. Anaerobic digestion of animal waste is a proven technology that can be used today to capture phosphorus, and generate energy in this perceived waste stream. Enhanced biological phosphorus removal, a technology utilized in human waste water treatment facilities, holds promise to capture phosphorus from various waste streams.

Another strategy, to content with reduced phosphorus availability, is to breed for phosphorus efficiency in crop plants. This will increase crop performance in low phosphorus soils. Selecting crop plants for their ability to form AM symbiosis is easily implemented into an existing breeding program and the benefits, in regards to global phosphate rock consumption, are worth the investment.

As agriculturalists enjoy phosphorus affluence at the moment but we cannot disregard the challenges ahead. Society must utilize this time to generate and implement solutions to linear phosphorus flow to steer clear of peak phosphorus.

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