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Evaluation of the Feasibility of Struvite Precipitation from Domestic Wastewater as an Alternative Phosphorus Fertilizer Resource

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This Master's Project

Evaluation of the Feasibility of Struvite Precipitated from Domestic Wastewater as an Alternative Phosphorus Fertilizer Resource

by

Amanda R. Bird

is submitted in partial fulfillment of the requirements

for the degree of:

Master of Science

in

Environmental Management

at the

University of San Francisco

Submitted:

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Amanda R. Bird Date

Received:

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Cindy Lowney, Ph.D. Date

Abstract

Finite phosphate rock ore reserves are estimated to be exhausted in 100 to 150 years. Phosphate rock ore is the single global source material for phosphorus fertilizer production. Once these reserves are gone, agricultural production will be negatively impacted. There are currently no alternative phosphorus resources. However, phosphorus concentrations present in human excrement traveling through domestic wastewater treatment facilities is being disposed of directly to the environment, often resulting in pollution problems. Recovering phosphorus from wastewater with struvite precipitation systems at wastewater treatment plants can alleviate future phosphorus scarcities. Evaluation of phosphorus recovery through struvite precipitation at wastewater treatment plants and a determination of the ability for the recovered material to serve as an adequate phosphate rock ore substitute are discussed in the following paper.

Acknowledgements

I would like to thank my family for their support while conducting this research. I would also like to thank Eric Wahlberg, P.E., Ph.D., Bonnie McInerney, M.S., and Cindy Lowney, Ph.D. for their guidance and assistance with my research.

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Introduction

Phosphorus is an important limiting growth nutrient, essential for the development of life on the planet, and particularly important to food production. Biologically, phosphorus assists with energy transport between cells; without phosphorus life cannot exist (Smil 2000). A phosphorus deficiency results in stunted growth of plants, animals, humans and bacteria (Keyzer 2010). Phosphorus is obtained from mineral rock sources via strip mining operations or natural weathering (Ragnarsdottir et al. 2011). The majority of raw non-renewable phosphate rock mineral used to create phosphorus is located in large reserves in Morocco, China and the United States (Rhodes 2013). These reserves are estimated to be exhausted within the next 100-150 years (Rhodes 2013; Keyzer 2010; Shu et al. 2006). As phosphorus resources become increasingly scarce in the natural environment, its' cost will increase dramatically; there are currently no synthetic or chemical substitutes for phosphorus (Childers et al. 2011). The majority of mined phosphate rock is processed into phosphorus fertilizer for global food production. Without fertilizer derived from phosphate rock we could not supply enough food for our current (or future) population.

Prior to the Sanitation Revolution of the 19th and 20th centuries, organic phosphorus was returned to agricultural fields in the form of manure, both human and animal. This old system of direct application of human wastes to agricultural fields perpetuated a circular organic phosphorus cycle. The Sanitation Revolution introduced centralized wastewater treatment systems as a way to prevent disease outbreak from human wastes in expanding and increasingly dense urban areas, turning the circular phosphorus cycle into a linear system. In this new system, phosphorus rich effluent from wastewater plants discharged directly into aquatic ecosystems, bypassing land application entirely. Shortly after the Sanitation Revolution, the Green Revolution industrialized agriculture with the use of artificial nitrogen and inorganic phosphate rock fertilizers, dramatically increasing food production. The main technological advancement of the Green Revolution was the development of nitrogen fixation methods from inert materials naturally present in the atmosphere (Gorman 2013).

Prior to the development of the Haber-Bosch nitrogen synthesizing process of 1913, nitrogen was removed from soils during crop harvests and was returned to the soil by nitrogen fixing plants. Farmers rotated crops in their fields to maintain adequate nitrogen levels or intermingled nitrogen-fixing plants with their crops (Gorman 2013). The bacteriological process of returning nitrogen to soils is slow, inconvenient, and limited food production capacities since a single crop could not be grown year after year. Artificial nitrogen creation promoted exponential increase in food, because nitrogen inputs were no longer restricted. However, healthy plant development requires elemental inputs of nitrogen (N), potassium (K) and phosphorus (P) (Keyzer 2010). Nitrogen encourages plant biomass growth, phosphorus aids in root and flower development while potassium is important for overall plant health. High nitrogen fertilizer inputs stimulate fast plant growth but ultimately leave the plant weak and susceptible to disease, because other nutrients are deficient. A balance of NPK nutrient inputs is important for overall healthy plant development, whichever nutrient is present among NPK in the smallest quantity limits the development of the plant and is hence the limiting growth nutrient (Thomas 1929). As nitrogen production increased with the Green Revolution, inputs of potassium and phosphorus were also increased to keep pace. The Haber-Bosch process created a large source of manufactured nitrogen; however inorganic phosphate rock sources remained the only source of phosphorus fertilizers (Ashley et al. 2011; Childers et al. 2011). The combination of the Sanitation Revolution and Green Revolution resulted in the present-day situation of a human-altered linear phosphorus cycle and an associated rapid depletion of natural phosphate rock (Ashley et al. 2011).

The lack of alternative sources for phosphate rock inputs in agriculture production limits the earth's carrying capacity by restricting food production. Without phosphorus fertilizer alternatives we face dwindling reserves of phosphate rock. Recycling phosphorus from waste streams is a possible alternative source for phosphorus fertilizers. Struvite precipitation, an emerging technology in domestic wastewater treatment, is a potential source for recycling and resource recovery (Cordell et al. 2009). Struvite precipitation recovers phosphorus from anaerobic digester supernatants and solids dewatering reject waters at wastewater treatment facilities, producing slow-release phosphorus fertilizer pellets for use in agriculture (Rahman et al. 2014). This process not only recycles phosphorus, reducing our reliance upon limited non-renewable phosphate rock reserves, it also reduces the amount of phosphorus that would otherwise be released into aquatic ecosystems via wastewater treatment system discharges. Phosphorus rich effluent from wastewater treatment facilities contributes to eutrophication and harmful algal blooms that currently threaten our aquatic environments.

This Master's Project aims to determine the feasibility of utilizing struvite precipitation to recycle phosphorus from domestic wastewater to be used as a sustainable alternative resource for phosphorus fertilizer production.

Phosphorus Overview

History of Phosphorus

Discovery

German alchemist Henning Brandt first discovered the mineral in 1669 during his search for the elusive Philosopher's Stone, a substance that was rumored to turn all metals to gold and produce the elixir of life to support human immortality (Ashley et al. 2011). Brandt was able to isolate phosphorus, at the time an unknown substance, through the distillation of large quantities of human urine. The discovery of phosphorus was announced in 1695, and after subsequent scientists successfully repeated Brandt's experiments, the element was fully recognized in 1795 (Ashley et al. 2011).

Beneficial Uses

Phosphorus had initially been used for various medicinal purposes in the 18th century. However, it was soon discovered that this element was well suited for match head production, due to its flammable reactivity with oxygen. White phosphorus is highly reactive, has the propensity to instantly combust when exposed to oxygen, and upon ignition it produces a toxic gas (Ashley et al. 2011). Due to the minerals' explosive properties it's utility expanded to militarization. Phosphorus was engineered into incendiary devices, smoke screens tracer bullets, and nerve gas introduced during World War II (Ashley et al. 2011; Rhodes 2013).

Prior to Brandt's discovery human civilizations had been utilizing phosphorus in agriculture for thousands of years. Farmers intuitively understood the link between crop production and phosphorus, even when they were unaware of the element itself. Evidence of farms found in archeological excavations, from early Chinese civilizations 5000 years ago to the Roman Empires, demonstrate humans recycling phosphorus by applying animal and human wastes to agricultural fields for increased food production (Ashley et al. 2011). Agricultural production began simply. Crops yielded food; soils provided nutrients required for plant to grow. Phosphorus is absorbed by crops during plant development and is permanently removed from soils during crop harvesting. After years of food production, natural soil phosphorus levels began to decrease. To sustain food production farmers began augmenting low soil phosphorus levels with animal and human waste. With population increases in urban areas during the 18th and 19th centuries, existing levels of food production became inadequate to supply demands. Agriculture was pushed away from cities, and it became arduous to continue the tradition of transporting human wastes to fields. Because farmers could not longer obtain traditional phosphorus supplies, the agriculture industry turned to an alternative source of phosphorus: guano. Guano is composed of bird droppings that have compounded over millions of years, it is found in islands off the Peruvian coast and in the South Pacific (Cordell et al. 2009). However, these sources were consumed by the end of the 19th century resulting in another phosphorus crisis.

In 1840, German chemist Justus Von Liebig identified the relationship between plant growth and phosphorus. Liebig's Mineral Theory, now referred to as Liebig's Law, scientifically explains the environmental nutrient (i.e. nitrogen, phosphorus and potassium) exchange and recycling between living and decomposing organisms (Cordell et al. 2009). Liebig determined that absorption rates of these important macronutrients must occur in balanced quantities in order for plants to reach their maximum growth capacity. In the case of these important macronutrients (i.e., nitrogen, phosphorus and potassium) a deficiency of any one component within soils result in stunted plant development (Thomas 1929). Phosphorus, nitrogen and potassium were recognized as essential nutrients for food production, in response to Liebig's work; nitrogen could be manufactured but phosphorus must be mined.

Processing inorganic phosphate rock sources to mineral phosphorus fertilizer began in the late 19th century. The product was an ordinary superphosphate (OSP), containing greater concentrations of phosphorus than manure (Cordell et al. 2009). Figure 1 illustrates the boom in phosphate rock fertilizer production upon the understanding of its importance for agricultural production. Manures have been used as phosphorus fertilizer throughout human civilization; human excreta have also been utilized, but on such a small scale that it is minimal in terms of total fertilizer use. Shown in Figure 1 are the small amounts of guano used from 1820 to the 1930s with use tapering off as supplies were depleted. Phosphate rock use increases after 1945, the time of the Green Revolution, since then phosphate rock has been the preferred phosphorus material for agriculture fertilizer production.

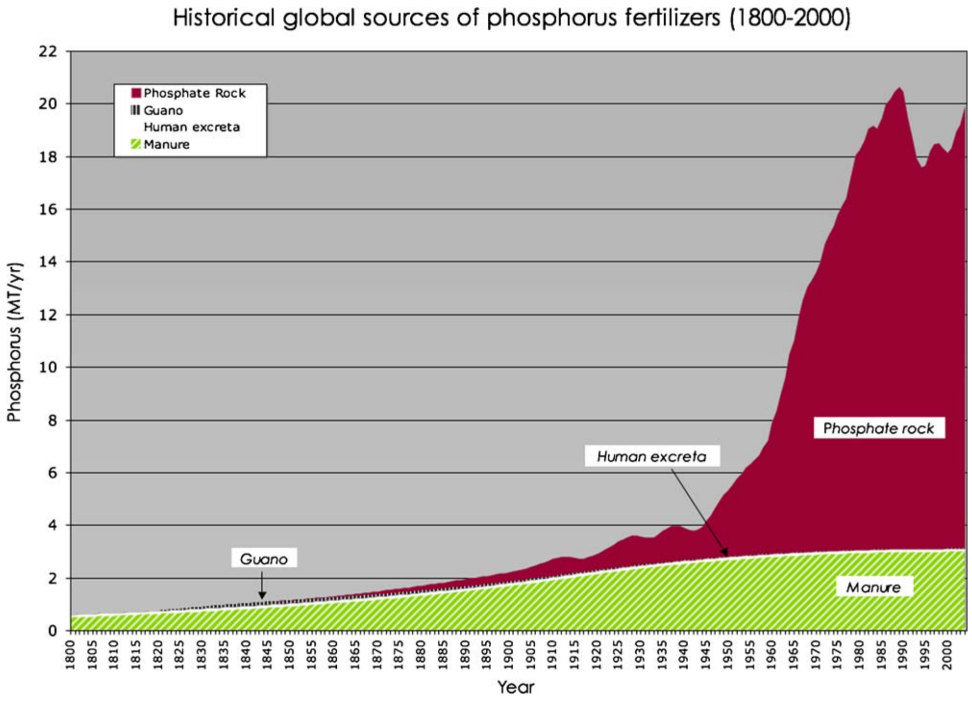


FIGURE 1. HISTORICAL GLOBAL PHOSPHORUS USE BASED ON RESOURCE TYPE FROM 1800 TO 2000, TAKEN FROM (Cordell et al. 2009).

Phosphate rock mining for fertilizer production increased by a factor of ten from 1954 to 2012 to match increases in global food demands for the growing world population. World population growth, shown in Figure 2, illustrates the dramatic increase of world human populations from 3.02 billion in 1960 to a projected height of 7.5 billion people in 2020. In the early 1990's grain demand dropped resulting in a corresponding drop of phosphate fertilizer use and phosphate rock production (USEPA; Van Kauwenbergh 2010). Between 1990 and 2010 phosphate rock production decreased with reserve estimates ranging between 11,000 and 18,000 metric tons. In 2011 the USGS revised its phosphate rock reserve estimations by a factor of four in response to the 2010 International Fertilizer Development Center's (IFDC) adjusted world reserve estimates (Rhodes 2013). Estimated reserves present in Morocco and Western Sahara were increased by a factor of nine and provided increases in global reserve estimates, values that were again increased in 2012 by 6,000 metric tons (Rhodes 2013). Phosphate rock production levels reflect increases in world-estimated reserves by increasing production rates from 2010 to 2012, illustrated in Figure 2.

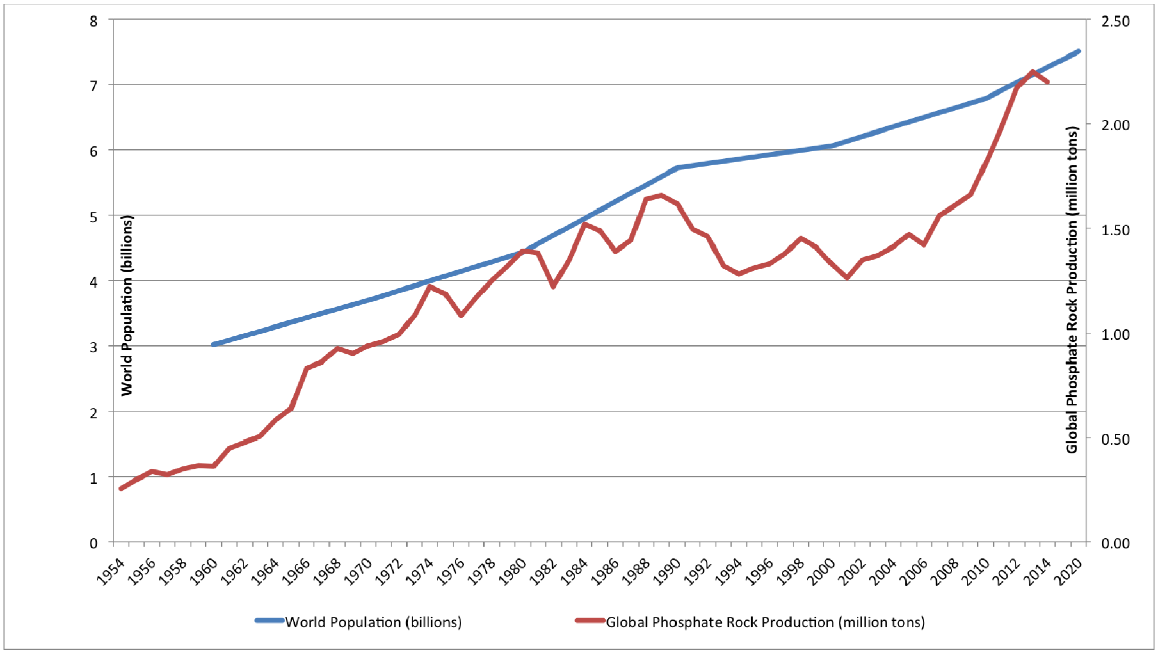


FIGURE 2. GLOBAL PHOSPHATE ROCK PRODUCTION INCREASES IN RELATION TO WORLD POPULATION RISES FROM 1954 TO TODAY, DATA SOURCED FROM (United Nations 1999; Jasinski 1999, 2001, 2003, 2005, 2009, 2011, 2013; Rabchevsky 1997; Llewellyn 1993; Stowasser and Lewis 1971; Stowasser 1973, 1975, 1977, 1980,1985, 1989, 1991; Sweeney 1969; Lewis and Tucker 1961; Lewis 1963, 1965, 1967; Tucker and Ruhlman 1953, 1955, 1957, 1959).

Human populations levels have rapidly increased since the Industrial Revolution and Green Revolutions in the beginning of the 20th century. Comparing the similar growth rates of phosphate rock production and human population levels implies that phosphate rock production, linked to the Green Revolution, is an important component that has lead to human populations reaching these unprecedented levels (Ashley et al. 2011; Childers et al. 2011).

Phosphorus Cycle

Natural Biochemical Cycle

Plants can only utilize phosphorus in inorganic form, as a phosphate molecule (PO_4) (USEPA 2012; Rhodes 2013). Organic phosphorus is an inorganic phosphorus compound combined with a carbon-based molecule (USEPA 2012; Rhodes 2013). Both inorganic and organic phosphorus exist in particulate and dissolved forms in aquatic environments. Aquatic plants absorb the soluble inorganic material while marine fauna consume the organic forms as well as aquatic plants to obtain phosphorus nutrients to facilitate growth. As plants and animals die, the phosphorus present in their tissues returns to sediments or soils in organic form where bacterial processes convert the organic phosphorus into inorganic phosphorus minerals (USEPA 2012). Phosphorus is geologically bound in rock as an inorganic mineral and released naturally through chemical weatherization from wind and rain erosion. Wind and rain transport dissolved and particulate, inorganic and organic phosphorus to waterways and oceans. Particulate inorganic and organic phosphorus settle and become sediments whereas dissolved inorganic and organic phosphorus are consumed by marine flora and fauna or are transported downstream (Rhodes 2013; USEPA 2012). Oceanic inorganic phosphorus sediments are pushed to the Earth's surface via tectonic uplift, with the result that inorganic mineralized phosphorus is bound in rock once again. A schematic representation of the phosphorus cycle is shown below, in Figure 3. The timescale of the phosphorus cycle transitioning between land and oceans is 10^7 to 10^8 years, much longer than the timescale of human life (Smil 2000). Mineralized inorganic phosphorus found on the Earth's surface today was formed 10 to 15 million years ago (Cordell et al. 2009). Superimposed on the global phosphorus cycle are numerous phosphorus cycles on smaller time scales. On landmasses with freshwater systems not leading directly to the oceans, inorganic and organic phosphorus are transferred in smaller closed loop systems, operating on a shorter timescale of one month to one year, a timescale easily observable from human perspective. On land, inorganic mineral phosphorus from the soil is absorbed by plants and is used for biomass development; organic phosphorus is returned to the soil through decomposition of dead plants, and by microorganisms, shown in Figure 3 (USEPA 2012). Through natural chemical processing, decomposed matter is converted into an inorganic mineralized form that is once again available for plant uptake.

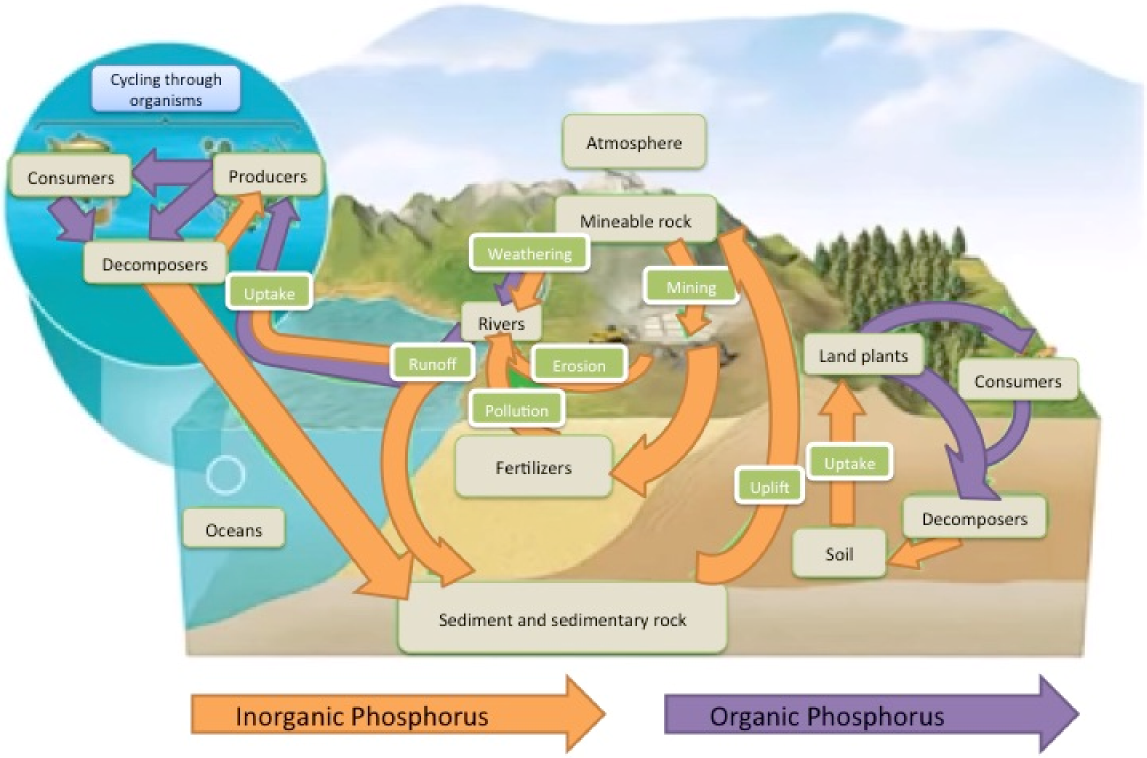


FIGURE 3. GLOBAL PHOSPHORUS CYCLE WITH ORANGE ARROWS REPRESENTING INORGANIC PHOSPHATES AND PURPLE ARROWS REPRESENTING ORGANIC PHOSPHATES, ADAPTED FROM SCHEMATIC IN (Post 2013).

Prior to urbanization, human populations facilitated the local phosphorus cycle to aid in food production. The relationship of humans, farming, human waste recycling, and phosphorus is shown in Figure 4. Inorganic phosphorus in soil feed plants for biomass development; plants decompose and return organic phosphorus to the soils where decomposers convert the material into inorganic phosphorus. Humans recycled their own organic phosphorus rich waste, as well as the waste from domesticated livestock directly onto their fields, boosting phosphorus levels within the soil and increasing vegetable food production.

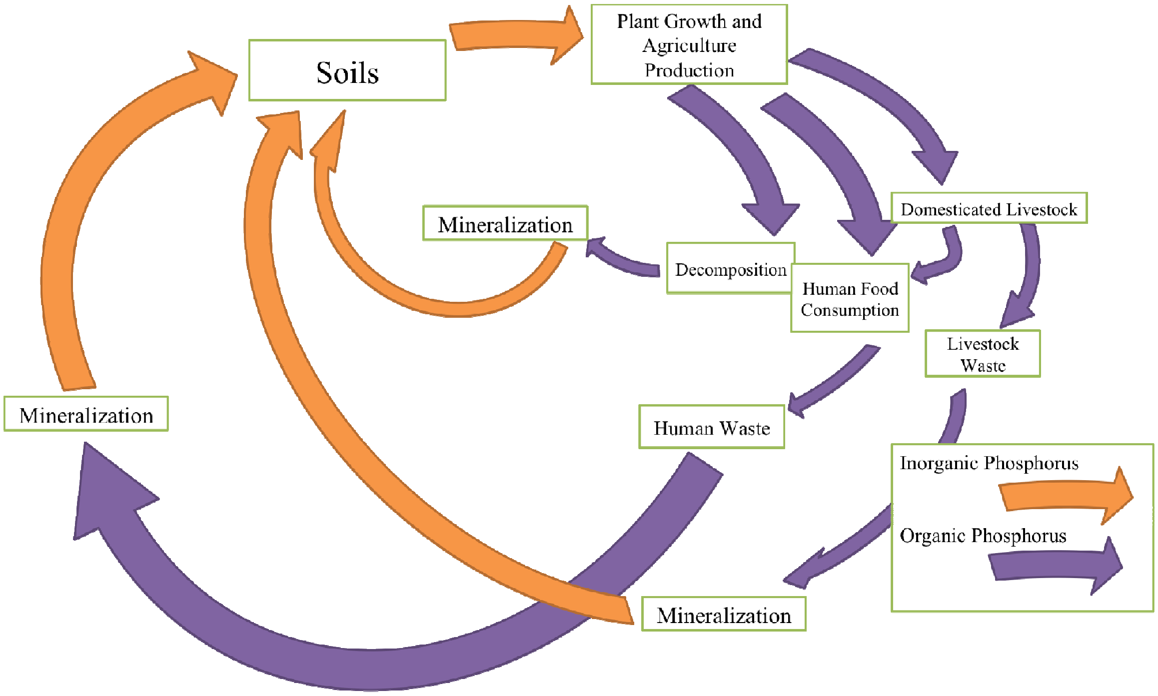


FIGURE 4. PHOSPHORUS CYCLE ON LAND WITH HUMAN ACTIVITY AND MANURE SOIL AUGMENTATION PRACTICES.

Sanitation Revolution

Before the development of large cities, human waste was disposed of by direct application onto agricultural fields or by dumping into the nearest waterway. By the 18th century populations had increased and decentralized sewage disposal systems evolved into localized cesspools, usually located within residential basements. Teams of "night soil" men were employed to empty these cesspools and transfer the phosphorus-rich materials to nearby agricultural fields (Ashley et al. 2011). As city populations increased, decentralized cesspool systems regularly exceeded their capacities, resulting in raw human sewage spilling out of basements into backyards and down roadways. During this era the flushing toilet was invented, patented, popularized and yet only exacerbated the refuse problem; this new system used water to move sewage through pipes, increasing the volumes of sewage flowing into already overloaded cesspool systems (Ashley et al. 2011). Disease outbreaks, such as typhoid and cholera, took place throughout urbanized areas; humans and vermin frequently came into direct contact with sewage from overflowing cesspools and aided in the spread of these contagious diseases. One of the more famous outbreak events, documented by British Dr. John Snow in 1850s London and commonly referred to as the Broad Street Pump epidemic, spread cholera among 500 people within 10 days. In this situation a single cesspool, from a household with a sickly occupant, overflowed and contaminated a drinking water pump at the street corner of Broad and Cambridge in an affluent neighborhood (Ball 2008). Using his own innovative disease investigation technique, Snow traced the origins of the disease back to the contaminated drinking water pump. Snow's work with the cholera outbreak directly connected epidemic diseases in urbanized areas with human sewage contaminating drinking water supplies. Because of his discoveries, centralized wastewater treatment systems became the new, safer method for managing human wastes in urbanized areas.

Centralized wastewater systems developed in the mid-1800s consisted of a series of sewer pipes that collected food, soiled water, and human wastes and transported it to a single treatment facility on the outskirts of town to prevent human exposure to untreated sewage, and to halt the associated spread of diseases. This network of pipes vastly improved public health; however, it re-routed phosphorus-rich human wastes that would have otherwise been collected for deposition on agriculture fields to treatment at centralized facilities and disposed of it to nearby waterways (Cordell et al. 2011). These first generation centralized wastewater treatment systems were specifically designed to protect human health. The impact of such facilities on the phosphorus cycle was not considered.

Green Revolution

The Industrial Revolution of the 1900's optimized manufacturing processes for the mass-production of goods. After World War II, many military munitions manufacturing facilities were converted to mineral phosphate fertilizer production for worldwide agricultural use; military combustion products and phosphate fertilizer are both sourced from phosphate rock (Keyzer 2010). The high phosphorus concentrations in the new fertilizers, sourced from inorganic phosphate mineral rock, increased agricultural production; however, their use also decreased the use of manure fertilizers. Once production of inorganic phosphate fertilizer began, demand quickly increased as shown in Figure 5 around 1945. The drop in fertilizer consumption in the early 1990s was caused by the global drop in grain demand, resulting in reduced crop production and therefore less use of phosphate rock fertilizers (USEPA; Van Kauwenbergh 2010).

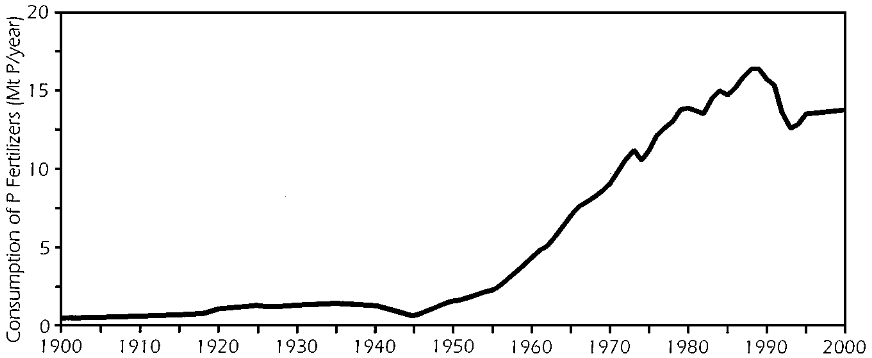


FIGURE 5. CONSUMPTION RATES OF INORGANIC PHOSPHORIC FERTILIZER FROM 1900 TO 2000, TAKEN FROM (Smil 2000)

Resulting from the Green Revolution, agricultural production was able to meet food demands of an increasing human population as well as reduce global numbers of undernourished (Cordell et al. 2009). Agriculture production was no longer dependent on manure fertilizer. Instead, all necessary phosphorus was sourced from ancient mineral deposits in the form of mineral phosphate fertilizers.

Current Issues

Although the Green Revolution fed the growing populace, it transformed the issues of providing adequate global food supplies to issues of compounding environmental degradation. The Sanitation and Green Revolutions combined to produce a net benefit for the human population, but not for the planet. Naik and Stenstrom's (2012) comparison of disease mortality and access to centralized wastewater treatment systems across 39 countries demonstrated the benefits of centralized wastewater treatment facilities. The study was based on comparisons of access to wastewater treatment, incidences of disease mortality, and improvement of the overall health of communities (Naik and Stenstrom 2012). Naik and Stenstrom concluded that waterborne pathogenic disease outbreaks are dramatically reduced by centralized wastewater treatment facilities. While these centralized wastewater treatment facilities did solve important health problems for cities, their disposal practices of treated sewage to surface waters caused environmental pollution and damaged ecosystems.

Consequences of engineering advancements of the Sanitation and Green Revolutions are becoming apparent. Treated sewage effluent is rich in phosphorus, when this effluent reaches waterways it diminishes water quality, due to eutrophication processes (Puchongkawarin et al. 2014; Smil 2000; Díaz and Rosenberg 2011; Childers et al. 2011). Sourcing phosphate fertilizers for agricultural production through phosphate rock mining also harms the environment, strip mining practices destroy entire ecosystems and toxic mine wastes contaminate the environment (Ragnarsdottir et al. 2011; Fuleihan 2012; Cordell et al. 2009). Phosphogypsum, a phosphate rock mine waste, contains a variety of elements including chromium, copper, cadmium, zinc, zirconium, lead, cobalt, rubidium, tin, barium, thorium, strontium, and uranium, making it a radioactive material. Phosphogypsum recyclability and reuse is regulated due to its radioactivity and must be disposed of following particular hazardous materials procedures (USEPA 2015). Any reuse of the material is prohibited until it is no longer radioactive or until the radioactive materials have been removed (Keyzer 2010).

The Green Revolution has caused preferential inorganic mineral phosphate fertilizer use over manure recycling and is stripping the world of its few mineral phosphate rock reserves, creating a dependence for agriculture production (Ashley et al. 2011). The new, human altered, phosphorus cycle is predominantly linear with minor phosphorus recycling through beneficial reuse of animal wastes, shown in Figure 6. Modern wastewater treatment plants are not usually designed to remove phosphorus. Some facilities are capable of removing phosphorus with microorganisms; these systems convert it to a solid form, and dispose of this solid phosphorus-rich material into landfills. The two grams of phosphorus excreted by each person daily travels straight through wastewater treatment facilities directly into the environment (Rhodes 2013). Of the organic phosphorus material entering wastewater treatment plants 10% exits the facility with the treated waters to be disposed of in surface waters, and the remaining 90% leaves the treatment process bound to solid material that is disposed of at landfills (Petzet and Cornel 2011; Dana Cordell and White 2013). The disposal of phosphorus-rich solid materials in landfills permanently removes large amounts of phosphorus available in the environment for plant growth and human use.

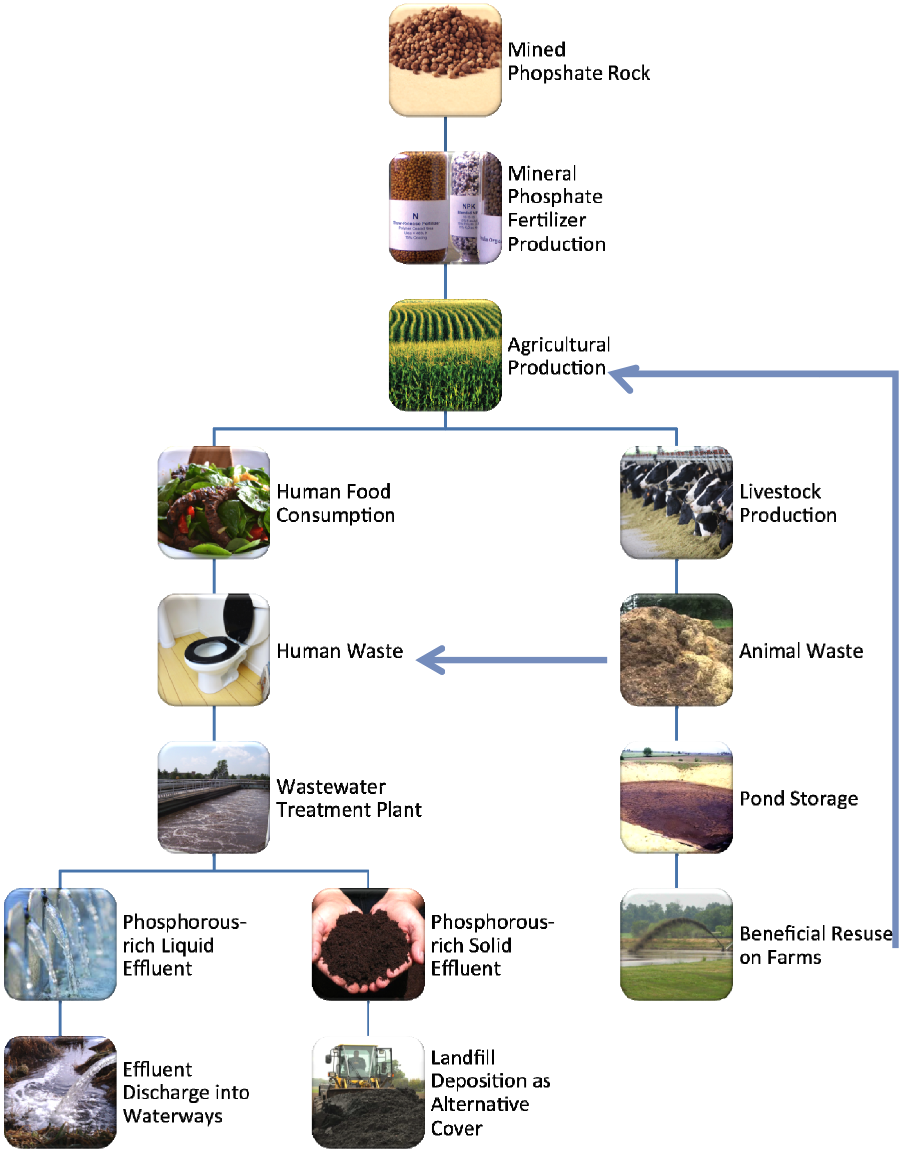


FIGURE 6. HUMAN IMPACTED PHOSPHORUS FLOW, MODERN PHOSPHORUS CYCLE.

Current methods of sewage collection and treatment have resulted in a break in the phosphorus cycle. Modern treatment facilities have solved serious public health issues, but this has been at an environmental cost. Phosphorus is no longer returned to the soil and our mineral phosphate reserves are dwindling. This altered system has transferred the human health risk to an environment risk, culminating in previously unseen aquatic environmental complications. Effluent discharges from wastewater treatment plants utilized receiving surface water systems to carry away and dilute the material, however as cities and their wastewater volumes grew receiving waterways could no longer handle the treated effluent flows. Larger treated sewage flows exceeded the nutrient carrying capacities of these waterways resulting in an overabundance of nutrients, leading to eutrophication problems. Concurrently, freshwater consumption increased with rising population levels reducing volumes of receiving waters. Receiving waters, already overloaded with nutrients from treated wastewater inputs, strained under the pressure of diluting treated wastewaters and providing drinking water (Rhodes 2013; Dubrovsky et al. 2010).

Eutrophication

When excessive inputs of phosphorus nutrients enter waterways phytoplankton populations explode. As phytomass populations exceed the carrying capacity of the waterway, by consuming all available dissolved oxygen, the organisms can no longer reproduce and die (Helmes et al. 2012; Rhodes 2013). The decomposing material creates a hypoxic environment by absorbing the remaining dissolved oxygen, effectively preventing any other plant or animal activity. This process of eutrophication changes aquatic environments; through reductions in water clarity, odor problems, reductions in fish populations and adversely impacting near coastal ecosystems (Smil 2000; Díaz and Rosenberg 2011).

Wastewater treatment facility effluent discharges to surface waters increase phosphorus loading rates to surface waters resulting in the aforementioned eutrophication problems (Seviour et al. 2003). Limiting or removing phosphorus from wastewater plant effluents is one method to reduce eutrophication problems (Lee et al. 2007). Engineering solutions have been incorporated in second-generation wastewater treatment facilities to mitigate excessive nutrient loading to receiving waters with more sophisticated and complex treatment methods: activated sludge treatment, Enhanced Biological Phosphorus Removal (EBPR), Biological Nutrient Removal (BNR), and Membrane Bioreactor (MBR) processes. These second generation facilities are designed to combat widespread stream, lake and near-coastal eutrophication issues and protect drinking water sources (Ashley et al. 2011).

Peak Phosphorus

Availability

Mineral phosphate rock mining first began in 1851 Norway; in the United States mining began in North Carolina in the late 1860s. A higher quality reserve was found and exploited in Florida 1888. This Florida reserve is now the dominant mineral phosphate rock source in the United States. Extensive reserves in Morocco and Western Sahara were discovered in 1914; phosphate rock production began in these areas 1921 (Smil 2000). Today, a total of 30 countries produce phosphate rock with the top 12 producers serving 95% of global demand, the top three producing 66%, and the United States alone serving 33% of the world's demand (Smil 2000). Active reserves are estimated to last only 100 to 150 more years (Keyzer 2010; Rhodes 2013). However, these estimates may not be accurate. Global sources are predominantly supplied from a few select large producers (e.g., China, Morocco and the United States). These large producers have the ability to manipulate their reserve estimates (Edixhoven et al. 2013). As shown in Figure 7, the distribution of the estimated 67 billion tons of global phosphate reserves are concentrated in Morocco and Western Sahara with the largest reserve cornering 74% of the market and estimated in-situ amounts of 50 billion tons, China reports reserves totaling 3.7 billion tons, and the United States estimates 1.1 billion tons.

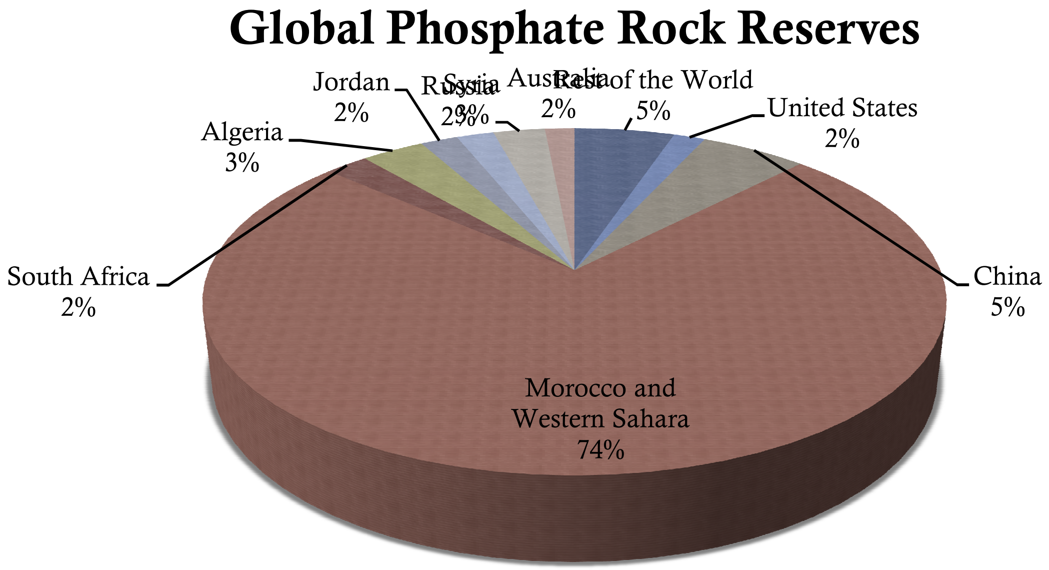


FIGURE 7. GLOBAL MINERAL PHOSPHATE ROCK RESERVES, COMPILED FROM DATA PRESENTED IN (Cooper et al. 2011; Jasinski 2015)

Despite other countries having large reserves, only the United States, Morocco and Western Sahara produce phosphate rock for global sale. China, a former global retailer, has recently placed exportation taxes of 135% on produced phosphate rock, effectively preserving all mined material for their own demands and leaving the United States and Morocco as the major suppliers for the rest of the world (Keyzer 2010; Cooper et al. 2011). United States production, largely based in Florida, has estimated the remaining reserves becoming exhausted in as little as 25 years (Childers et al. 2011).

Available phosphate rock supplies are of lower quality than previously extracted materials with lower phosphorus concentrations, more contaminants, are more difficult to extract, and are located in culturally and environmentally sensitive areas. As shown in Table 1, as of 2008, an estimated 16 billion tons of high grade phosphorus deposits remain in known reserves; 25 billion tons are low grade material; and 50 billion tons are ultra low grade material (Sverdrup and Ragnarsdottir 2011). The different grades rank phosphate rock on the amount of contaminants, phosphorus (PO_4) concentrations, and the extraction cost of the deposits. High-grade deposits have high phosphorus concentrations, are easily mined, and have low amounts of heavy metal concentrations.

High-grade phosphate rock is less costly to obtain and process. Low-grade and ultra low-grade deposits have decreased phosphorus concentrations, increased contaminant concentrations, and require increased extraction efforts and costs. The current market price of phosphate rock is high enough for extraction of low-grade phosphate rock to be competitive with high-grade sourced material, but does require higher capital investments for mining and processing. The remaining ultra low-grade sources are prohibitively expensive to recover, due primarily to their inaccessible location.

TABLE 1. ESTIMATED GLOBAL MINERAL PHOSPHATE ROCK RESERVE AMOUNTS MEASURED IN BILLIONS OF TONS, COMPILED FROM 2008 DATA PRESENTED IN (Ragnarsdottir et al. 2011)

Deposit Type	*Phosphorus Rock, (Billion Tons)*	*Accessibility*
High-grade	16	Easy to mine
Low-grade	25	Possible to extract
Ultra low-grade	50	Difficult and expensive to recover
Sum of Known Reserves	**93**	

An estimated six trillion tons of phosphate rock deposits are located on the ocean floor. These ocean reserves are difficult to extract and come with potentially high environmental risks. They are likely to be contaminated with arsenic, cadmium, chromium, mercury, lead, uranium and vanadium (Smil 2000). All of these potential contaminants are known to cause serious health hazards. Contaminant removal would be costly, require high-energy inputs, and have waste disposal issues.

Current Uses

Agricultural production has increased fourfold since the Green Revolution in the mid-1900s, resulting in a corresponding increase in global phosphorus extraction (Childers et al. 2011). United States phosphorus consumers used 28.1 million tons of fertilizer in 2014. Only 15 to 30% of phosphorus applied to a crop is absorbed by plants; large amounts of phosphorus fertilizer is wasted in agricultural runoff (Childers et al. 2011; Jasinski 2015). Excess phosphorus in agriculture runoff makes its way into aquatic environments, causing extensive eutrophication problems (Cordell et al. 2009). Nutrient runoff into the Mississippi River has contributed to eutrophication of the Gulf of Mexico and a resulting 5,052 square mile dead zone (NOAA and EPA 2014). Extraction, production and consumption of phosphorus fertilizers generate hazardous waste, carbon emissions and aquatic pollution (Ragnarsdottir et al. 2011; Childers et al. 2011; Fuleihan 2012; Cordell et al. 2011). More than 200 million tons of phosphogypsum, a phosphorus fertilizer production byproduct, is produced annually and is stored on land due to its radioactive nature, yet a few countries dispose of it directly into oceans (Fuleihan 2012; Cordell et al. 2009). Of the 200 million tons produced annually, only 15% is recycled or reused by agriculture and cement industries.

Supply and Demand

President Roosevelt, in the 1938 Presidential address to the US Congress, strongly emphasized the importance of phosphorous to the American people. Roosevelt expounded phosphorus is necessary to ensure the security of food production, public health, and national economic security. With the president's encouragement and technological advancements of the Green Revolution, crop production, phosphorus fertilizer use, and human population all increased by 50% in a matter of 30 years (Childers et al. 2011). Current per capita use of global phosphate rock breaks down to 20 grams per day to supply adequate dietary needs (Sverdrup and Ragnarsdottir 2011). The growth in phosphate rock production worldwide from 1978 to 2012 is shown in Figure 8. Phosphorus (PO_4) concentrations within the mined phosphate rock demonstrate a similar, slightly muted increase. Phosphorus concentrations by weight divided by the weight of mined phosphate rock represents the concentration of phosphorus present in each ton of mined phosphate rock. The percent concentration variations over the years demonstrate that while production and volumes of phosphorus (PO_4) present in the mined rock have increased, the actual concentration over time as dropped by one percent globally in the 34-year time span. Research of mined phosphate rock quality within the United States also reflects a decrease in phosphorus content, from 15% in the 1970s to less than 13% in 1996 (Rhodes 2013).

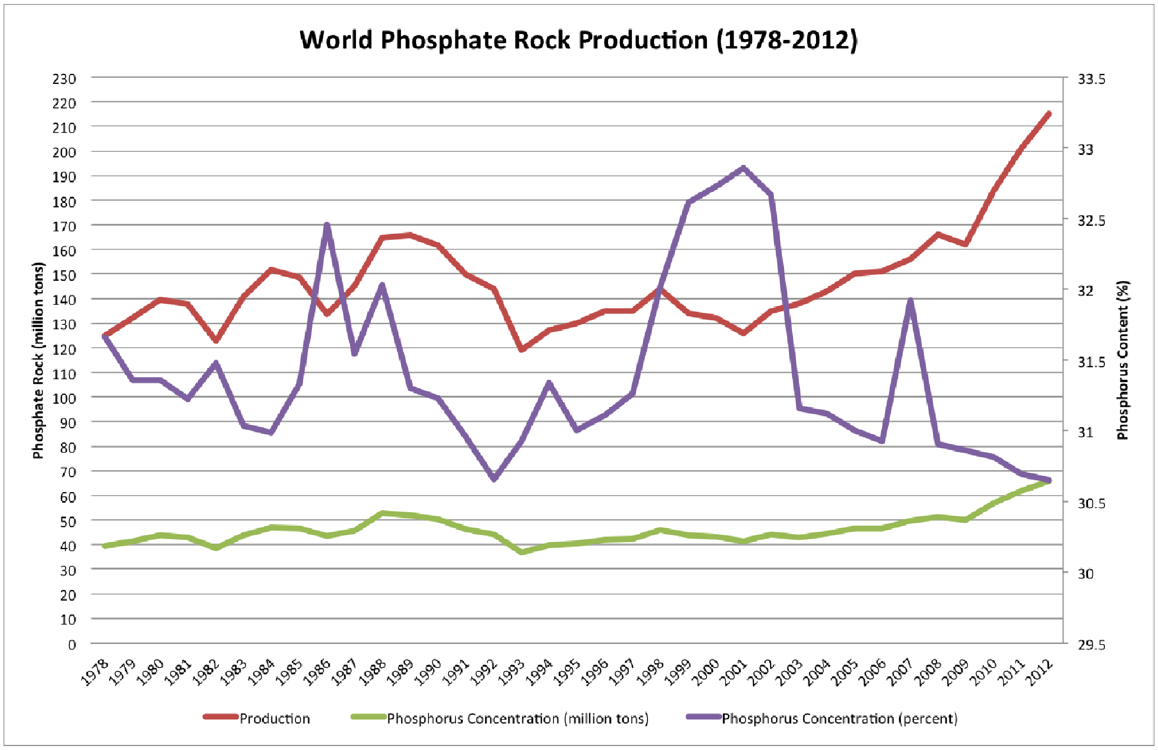


Figure 8. World production of phosphate rock from 1978 to 2012 measured in millions of tons, compiled from data presented in (Jasinski 1997, 2002, 2007, 2015; Stowasser 1987)

Phosphate rock mining operations target the most economically feasible resource first, high-grade ores that are easily accessible; with prices increasing as supplies dwindle. Extraction of low-grade phosphorus rock becomes economically viable when phosphate rock market prices increase to $800-1000 per ton, ultra low reserves are economically feasible to extract when prices increase further to $1800-2000 per ton. Continued availability and affordability of phosphorus for fertilizer, and food production, may be reaching its peak. Price increases have already caused phosphorus fertilizer to become too expensive for some countries, posing significant concerns for the health and well being of those populations. From 2007 to 2008 the price of fertilizer increased by 600%, directly influenced by increases in phosphate rock price. Rapid increases in prices and reduction in resource availability are common triggers to stimulate alternative source substitutions. However, there are currently no substitutes for phosphorus that can be produced at the scale required for current population demands (Childers et al. 2011).

Phosphorus fertilizer demand is expected to continue to increase by 2.5 to 3% per year over the next five years (Rhodes 2013). At this rate of consumption, phosphate rock reserves will only last another 100 to 150 years; this estimate includes use of all grades of phosphate rock. Consumption of only the high-grade materials would result in resource exhaustion in 50 years, followed by 75 to 100 years of extraction and production of lower quality materials with increasing levels of environmental impacts (Cooper et al. 2011).

A few countries, Morocco, China and the United States, control global phosphate rock reserves. With China's drastic reduction on exportation, only the United States and Morocco are left to meet global demand; US reserves are expected to be exhausted in as little as 30 years. Some countries have enough resources within their borders to sustain their own consumption rates; other countries (e.g. Western Europe and India) are wholly dependent upon imports from the two remaining major producers (Cordell et al. 2009). Nearly 220 million tons of phosphate rock is produced and traded globally each year (Jasinski 2015).

Drivers of Phosphorus Recovery

Pollution Prevention

Since the 1950s about 25% of the total mined phosphate rock has been lost to landfills and water bodies, a total value of 63.5 billion megatons (Mt) permanently removed from micro-phosphorus cycle on land (Childers et al. 2011; Cordell et al. 2009). This has not only negatively impacted agriculture through permanently lost agricultural inputs; it has caused environmental damage as well. The problems of eutrophication in waterways is estimated to cost $2.2 billion in annual economic losses due to degraded environmental services (e.g. drinking water quality and recreation) (Childers et al. 2011; Dodds et al. 2009). Eutrophic waters emanate foul odors, introduce harmful toxins to surface waters, and cause an unappetizing taste resulting in decreased water quality, and human and animal health. Fish kills stemming from decreased dissolved oxygen levels and presence of toxins in eutrophic waters decreases biodiversity as well as halt commercial and recreational fishing. Reduced water clarity and odor problems from eutrophic algal blooms decrease property values in the surrounding area (Dodds et al. 2009).

Processing and refining mined phosphate rock into usable fertilizers adds to fossil-fuel energy consumption, carbon dioxide emission rates, and hazardous by-product problems (Cordell et al. 2009). Strip mining procedures use large amounts of fossil-fuel energy, resulting in large carbon dioxide emissions that are linked to global climate changes. Mining creates hazardous waste materials and destroys pristine land. Closing the phosphorus cycle will help restore our natural environment. The initial capital investments required for phosphorus recycling would be miniscule compared to the estimated economic savings associated with recovering damaged environmental services (Childers et al. 2011).

Agriculture Fertilizer Security

Today's agricultural production is entirely dependent on phosphorus fertilizer inputs. The agriculture industry would decline in productivity without phosphate rock fertilizers; experience a reduction in crop yield resulting in decreasing revenues. Research and development into phosphorus recovery and recycling offers a potential solution. Phosphorus resource recovery would reduce humanities' dependence upon finite phosphate rock resources and ensure food security (Ashley et al. 2011). Elevation in cost of phosphorus fertilizer reduces the ability for farmers to purchase fertilizer, creating a negative cycle. Small farmers do not have the income to purchase increasingly expensive fertilizers, yet without the fertilizer inputs crop yields drop further and reduce small farmers' income. Development of phosphorus recovery systems for local communities can prevent the negative downward spiral of small farmers, stop rising phosphate rock fertilizer prices, increase local economies, food security and community health (Cordell et al. 2009; Cordell et al. 2011).

Phosphorus and Domestic Wastewater

Phosphorus in Wastewater

For every one million people, five tons of phosphorus is delivered to wastewater treatment facilities (Rhodes 2013). Traditional wastewater treatment processes do not remove phosphorus; concentrations of total phosphorus in treatment plant effluents range from 10 to 25 mg/L (Rhodes 2013). Phosphorus leaving the facility is either dissolved in effluent waters or bound to sediments and treated with solid materials (Puchongkawarin et al. 2014; Rhodes 2013). Phosphorus in wastewater comes from detergents, food additives, food wastes and human excreta, amounting to roughly two grams of total phosphorus per capita a day (Verstraete et al. 2009; Rahman et al. 2014; Cornel and Schaum 2009; Rhodes 2013).

Traditional wastewater treatment facilities are designed to remove suspended solids, nitrogen, and organic material and yet are unable to remove enough phosphorus from influent sewage water to ensure environmental protection during effluent discharges. Phosphorus enters and exits wastewater treatment plants with 100% of the material entering into the environment. Phosphorus flows through traditional wastewater treatment systems appears in Figure 9; 10% of phosphorus leaves with treated water into the aquatic environment; 90% of phosphorus attaches to solids within the system, and leaves through biosolid production, as beneficial soil amendments or as landfill disposal (Petzet and Cornel 2011; Cordell and White 2013).

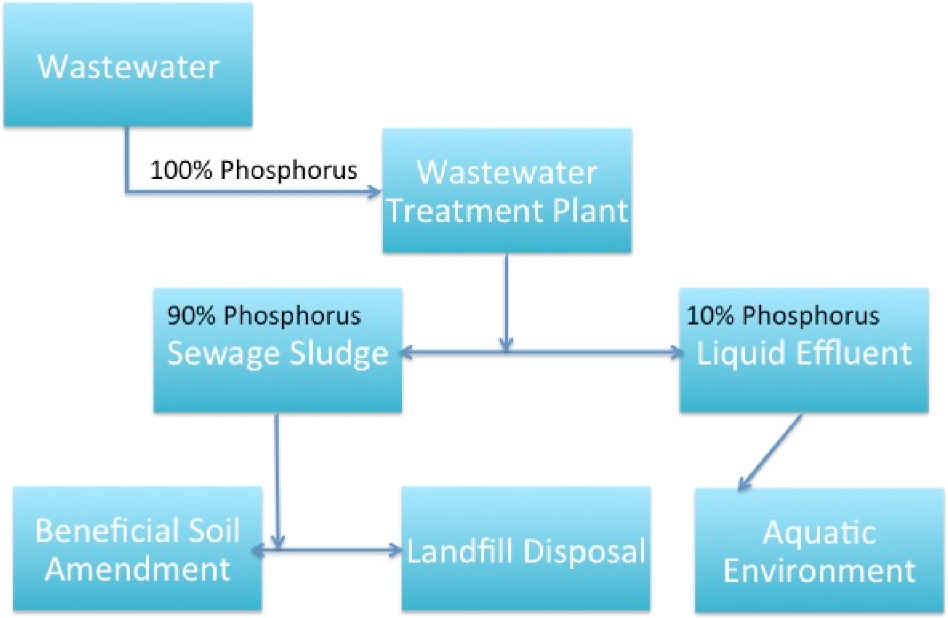


FIGURE 9. FLOW CHART OF PHOSPHORUS THROUGH A WASTEWATER TREATMENT PLANT UTILIZING CHEMICAL PRECIPITATION REMOVAL TECHNIQUES, ADAPTED FROM AN EXAMPLE PRESENTED IN (Petzet and Cornel 2011).

Phosphorus rich effluents cause environmental degradation and health concerns, but can also negatively impacts the facilities themselves. Concentrations of phosphorus dissolved in wastewater reduce treatment plant operation efficiencies. Phosphorus combines with other materials present in wastewater, such as ammonia, creating a mineral buildup within piping infrastructure. This nuisance material, struvite, can only be removed with physical force, not by chemical destabilization. Without rigorous infrastructure inspection and constant removal of struvite, a wastewater treatment plant's capacity and treatment capabilities decrease (De-Bashan and Bashan 2004).

Traditional Phosphorus Removal

Wastewater is by nature heterogeneous material. This makes isolating and removing particular components difficult (Verstraete et al. 2009). Chemical sedimentation treatment process can be placed at the final stage of a wastewater treatment plant to remove organic phosphorus from the treated waters. Additions of phosphate binding chemical compounds like lime, aluminum sulfate (alum) or ferric chloride are used to remove phosphorus through chemical sedimentation. The sediment materials are transferred to the solids treatment systems within the plant to be removed with biosolid production (Elliott and Taylor 2014; Lee et al. 2007). However, biosolids with high levels of phosphorous and chemicals are becoming an environmental concern when utilized as soil amendments. The chemicals used to remove phosphorus from wastewater comprises of heavy metals and salts, materials that are prohibited for use in soil amendments (Smil 2000; De-Bashan and Bashan 2004; Koch et al. 2003; Ashley et al. 2011).

On average, a single person in the United States produces two grams of phosphorus per day. Of the 318.9 million people living in the United States, 75% are residing in homes connected to municipal sewers inputting 32 billion gallons of sewage per day into centralized wastewater treatment plants. Within this sewage influent is approximately 950 thousand pounds of phosphorus, of that roughly 850 thousand pounds leave the treatment plant through the solids removal process to be disposed in landfills or soil augmentation.

Enhanced biological phosphorus removal (EBPR) systems, developed 30 years ago, are the closest treatments for removal of phosphorus during wastewater treatment (Seviour et al. 2003). The EBPR system consists of four main treatment stages: pretreatment, primary treatment, secondary treatment, and solids handling. The initial pretreatment of raw wastewater entering a facility involves removing coarse and nonorganic material from the wastewater stream, such as rocks, eggshells, garbage and hair. Wastewaters flow to the primary treatment phase where solid material is removed through settling. Secondary treatment consists of biological treatment processes. This section of the facility houses microorganisms that are used to oxidize remaining organic material in the water and convert it to a form that is easier to remove. The process train of the plant branches into two paths after secondary treatment; one continues water treatment and the other performs solids handling and removal operations (Kerri et al. 2008).

Within an EBPR system, microorganisms in secondary treatment metabolize and store phosphorus in cellular structures, converting the soluble phosphorus into larger solids that can be removed from the liquid stream (Acelas et al. 2014). It is essential for wastewater treatment facilities to remove phosphorus from the treated waters for regulatory compliance. A balance of microorganisms to incoming sewage flows is maintained to optimize treatment processes. As the microorganism populations reach a predetermined amount, based on food-to-mass ratio calculations, they are removed or 'wasted' from the secondary treatment phase. The removed material, sludge, proceeds to the solids handling and removal stage at the facility prior to final disposal (Kerri et al. 2008).

EBPR facilities utilize anaerobic digesters to break down sludge material. In temperature controlled and oxygen deficient environments of anaerobic digesters, acid-forming bacteria consume organic material present in the sludge to produce organic acids and carbon dioxide gases. A second group of bacteria, gas formers, break down the organic acid and produce methane and carbon dioxide gases. Materials within digesters are gently mixed to provide optimal contact with bacteria. As the gentle mixing does not provide large amounts of vertical agitation, digesters stratify. The typical stratification pattern within anaerobic digesters is shown in Figure 10. Fresh sludge, pulled from the secondary treatment processes, is pumped into the bottom of digesters. In fluid zones of digesters, the upper third of the digester, bacteria consume organic materials and produce biogases. The gasses accumulate in the top dome of digesters and is either funneled to a gas-flaring device or collected for electricity generation. The upper sections of the fluid zone comprise of supernatant, a concentrated liquid that gravitationally separates from the sludge and bacteria. The supernatant is steadily pumped out and returned to the head of the wastewater treatment train to undergo treatment again. Digested sludge removed from the bottom portion of digesters is sent to dewatering systems to convert the digested sludge to biosolids before final disposal. After processing through an anaerobic digester, about 50% of the incoming organic material is been destroyed through bacterial activity (Kerri et al. 2008).

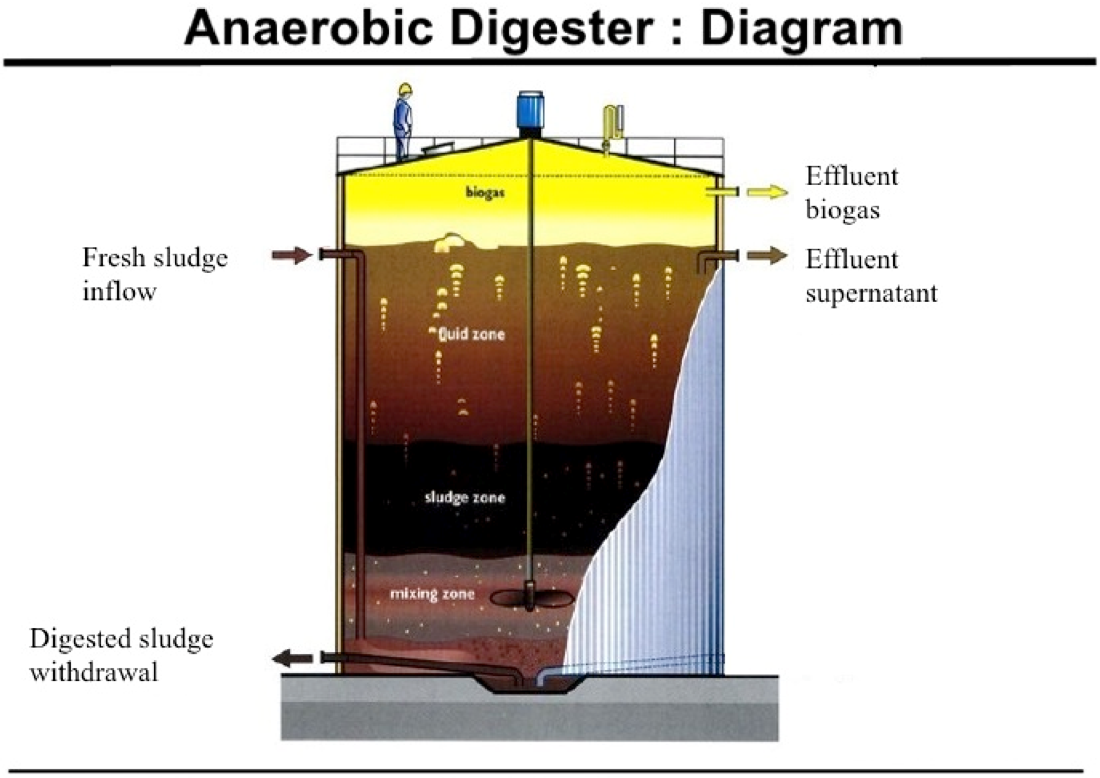


Figure 10. Diagram of a typical anaerobic digester at an EBPR wastewater treatment plant, adapted from diagram in (Abedeen 2010).

It has been found during anaerobic digester treatment about 80% of phosphorus removed earlier in secondary biological treatment is released back into a liquid form and becomes part of the supernatant (Liao et al. 2003; Munch and Barr 2001; Xavier et al. 2014; Pastor et al. 2008). The high levels of phosphorus concentrated in the small flows of supernatant from digesters, relative to average raw sewage influent flows, can cause an upset or shock to the treatment system due to nutrient overloading (Kerri et al. 2008; Acelas et al. 2014; Elliott and Taylor 2014).

Treated sludge removed from anaerobic digesters is pumped to the final stage of solids handling sludge dewatering processes. Dewatering processes feed the digested sludge through a mechanical dewatering system, either a vacuum filter, pressure filter, centrifuge, or belt filter press. These systems reduce the moisture content of digested sludge by 60 to 80%, leaving a ‘cake’ ranging from 20 to 40% solid composition (Kerri et al. 2007). This cake material is referred to as biosolids and is either beneficially reused as soil amendments in agricultural production or is deposited at landfills as alternative cover material, dependent upon chemical compositions (Cordell et al. 2011). The liquids removed during the dewatering phase are combined with the removed supernatant flows from the anaerobic digesters to form reject water that is returned to beginning of the treatment plant.

Government Regulations

Surface water pollution and increased incidents of eutrophication within national waters due to anthropogenic nutrient sources led to the formulation of the Federal Water Pollution Control Act (i.e., Clean Water Act) of 1972. Total phosphorus concentrations as low as 100 µg/L provide sufficient phosphorus to encourage eutrophication within surface waters (Rhodes 2013). The Clean Water Act set up framework to impose nutrient limits on discharged effluents from wastewater treatment plants (Smil 2000; Koch et al. 2003). Research conducted by the U.S. Geological Survey (USGS) demonstrate waterways impacted by total phosphorus pollution are often found downstream from wastewater treatment plant effluent discharge sites (Dubrovsky et al. 2010; Seviour et al. 2003). The federal government has since recommended discharges into surface waters entering lakes to not exceed 0.05 mg/L of phosphorus and 0.1 mg/L for disposal into flowing waters (Litke 1999). Starting in 2011 the EPA, under the Clean Water Act, is working with states and stakeholders to set up frameworks to monitor phosphorus levels in water and develop numeric criteria standards for water effluent discharges from industrial facilities, including wastewater treatment plants. The federal government has determined, based on the different circumstances of each state, that states should design and implement their own phosphorus nutrient limits that will suit their specific set of circumstances and desired goals to solve aquatic phosphorus pollution issues within their borders (Stoner 2011).

In 1994 the U.S. Environmental Protection Agency (EPA) conducted a State Nutrient Water Quality Standards survey to develop a report on how the Clean Water Act has altered discharge practices of wastewater treatment plants within the country. The survey concluded 21 states did not have any water quality standards for phosphorus, many rely upon narrative regulations, and 10 states have chosen to adopt EPA discharge criteria (EPA 1998). The map of the United States shown in Figure 11 is colored to indicate the number of states that have imposed phosphorus discharge limitations upon wastewater treatment facilities; darker shades of green have the highest number of limitations and white indicates no phosphorus discharge limitations. As of 1999, 19 states did not have regulated limitations; 15 states had one to ten facilities with phosphorus discharge limits; 9 states had eleven to fifty regulated facilities; 5 states had fifty-one to one hundred; and 2 states had limited more than one hundred wastewater treatment plants.

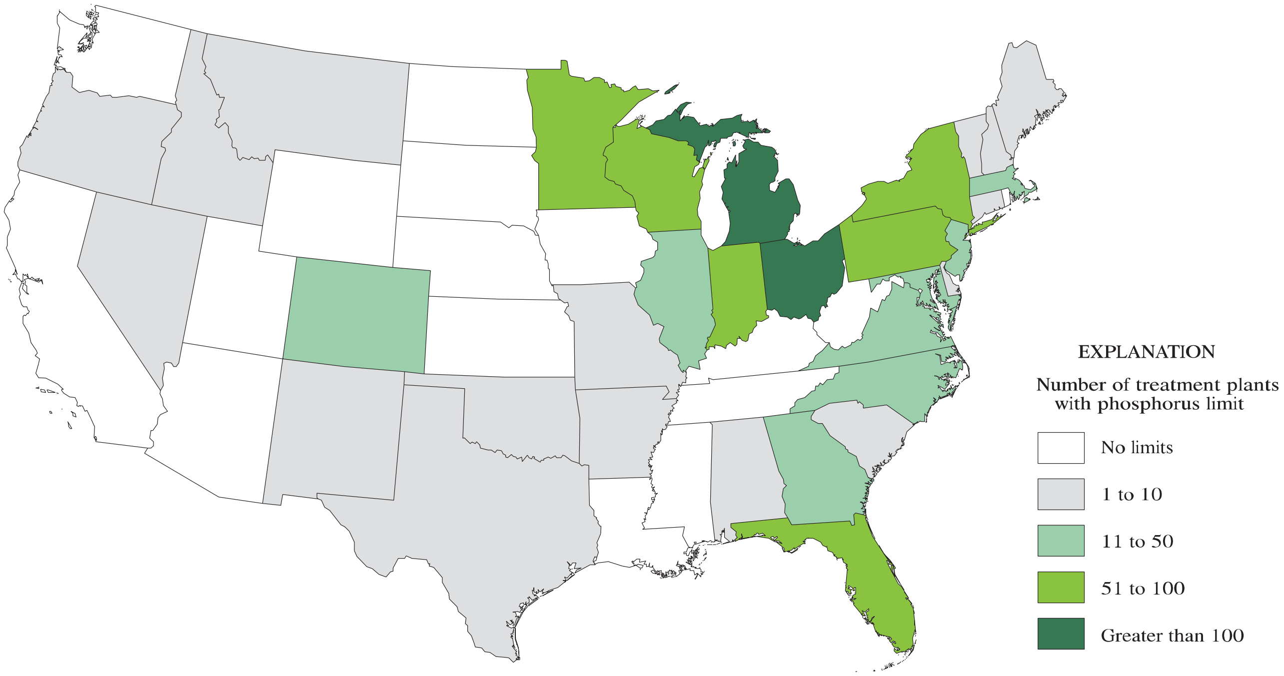


FIGURE 11. NUMBER OF WASTEWATER TREATMENT PLANTS WITH PHOSPHORUS LIMITS AS OF 1999. ALASKA AND HAWAII DO NOT HAVE ANY IMPOSED LIMITATIONS, GRAPHIC TAKEN FROM (Litke 1999).

Through the Clean Water Act, the EPA issues permits for wastewater treatment facilities to operate. Every wastewater plant operating within the United States must have an active, EPA issued National Pollutant Discharge Elimination System (NPDES) permit. An NPDES is a point-source control measure used to protect the national waters of the United States by regulating quantities of pollutants discharged from water and wastewater treatment facilities. Shown in Table 2, the EPA permitted 15,558 wastewater treatment facilities for NPDES permits in 2014. This value is not indicative of the number of facilities currently in operation but instead tells the number of new facilities and renewed permits. Of the permits issued in 2014 2,942 facilities were required to monitor effluent discharges for phosphorus and 1,796 wastewater treatment facilities had permits with defined phosphorus limitations.

TABLE 2. NPDES PERMITS FROM THE FEDERAL GOVERNMENT IN 2014 FOR WASTEWATER TREATMENT FACILITIES RELATING TO PHOSPHORUS DISCHARGES, RAW DATA OBTAINED FROM (EPA 2014)

NPDES Permits	*Number of facilities*
Permitted	15,558
Permitted with Permit Data	4,738
Reported with Phosphorus Monitoring Requirements	2,942
Permitted with Phosphorus Monitoring Requirements and Defined Effluent Limits	1,796

Data presented in Table 3 show the breakdown of how much phosphorus was actually discharged from permitted facilities in 2014. The average reported discharge amount present in effluent water was 238 mg/L, with a total average of 18,729 pounds throughout reporting facilities and a combined discharge total for all facilities being almost 89 million pounds. A few facilities reported extreme phosphorus discharges reported of 4,493,211mg/L and volumes in excess of 4 million pounds.

TABLE 3. AVERAGE REPORTED PHOSPHORUS DISCHARGES FROM NPDES PERMITTED WASTEWATER TREATMENT PLANTS THROUGHOUT THE COUNTRY IN 2014, RAW DATA OBTAINED FROM (EPA 2014).

Reported Phosphorus Discharges in 2014	*Average throughout reporting facilities*	*Maximum reported*
Phosphorus Concentration (mg/L)	238	4,493,211
Amount Discharged (lbs)	18,729	4,209,340
Total Discharges (lbs)	**88,735,637**	

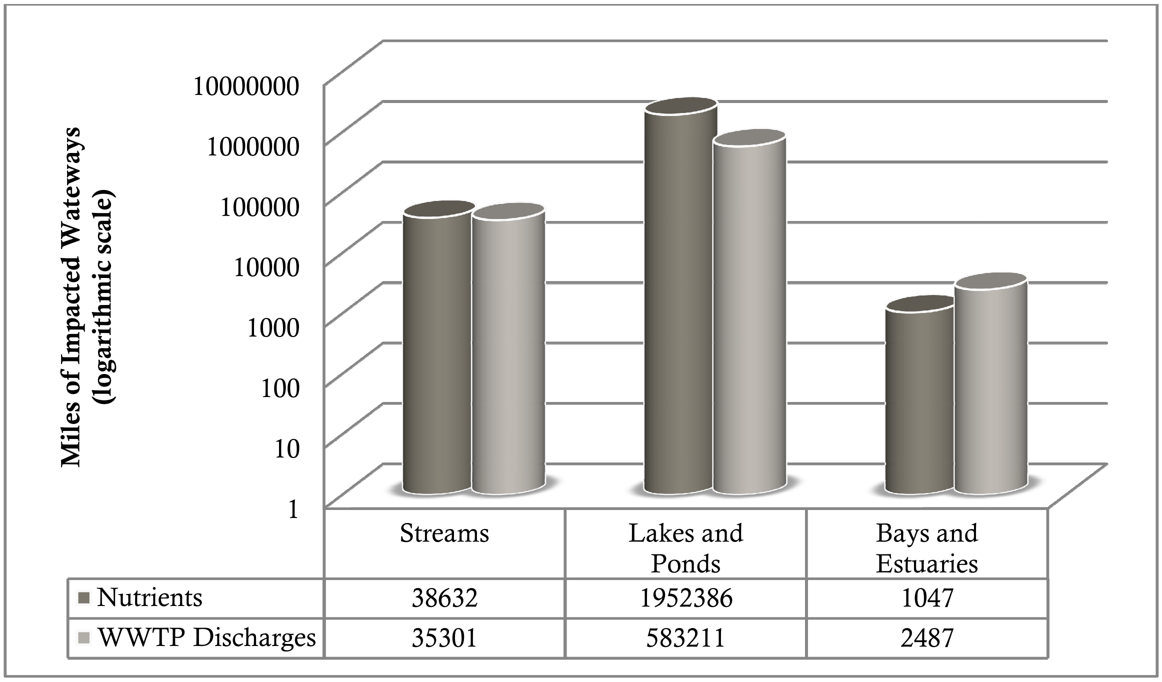
Recommended aqueous effluent discharge limitations have had a significant impact upon wastewater treatment plant biosolid management programs (Elliott and Taylor 2014). These restrictions have caused facilities to switch from disposing phosphorus in effluent waters to a solid phosphorus disposal method included with biosolids treatments. Incorporating chemical precipitation has had the intended result of reduced effluent aqueous phosphorus discharges into the environment, but has unintentionally resulted in biosolids with high phosphorus concentrations along with elevated metal salt levels (Elliott and Taylor 2014; Seviour et al. 2003). Concerns have been raised about phosphorus leaching from biosolids produced by facilities employing chemical precipitation techniques (Elliott et al. 2005; Elliott et al. 2002(1); Elliott et al. 2002). If regulations are created restricting beneficial reuse of these biosolids as soil amendments, a new issue arises of proper disposal of this material. Phosphorus level standards for animal manures applied to agricultural fields already exist. Currently, nutrient standards are under review to create new regional numerical limits for phosphorus levels in biosolids based upon protecting ecoregions (Litke 1999).

Importance of Phosphorus Removal

Environmental Impacts

Eutrophic waters caused by nutrient overloading from wastewater effluent discharges reduces water clarity and threatens the beneficial reuse of the waters (Smil 2000; Dodds et al. 2009). These negatively impacted aquatic environments often result in fish kills and changes in specie diversity (Smil 2000; Dodds et al. 2009). In near coastal ocean environments, high concentrations of phosphorus also prevent the development of corals (Smil 2000). High phosphorus concentrations in treated effluents from wastewater facilities pose greater threats to aquatic environments than total phosphorus runoffs from agriculture fields from phosphate rock fertilizer application (Millier and Hooda 2011; Howell 2010). Studies in the United Kingdom define healthy levels of phosphorus in rivers to be between 0.002 mg/L and 0.1 mg/L. These same studies repeatedly measured levels of 0.14 to 0.35 mg/L downstream of wastewater treatment discharge points (Howell 2010). Wastewater treatment plant effluents are clearly a large part of phosphorus pollution problems in waterways (Seviour et al. 2003).

The 1999 National Water-Resources Investigation Report conducted by USGS found wastewater treatment plants discharge a total of 260,000 metric tons of phosphorus into aquatic environments annually (Litke 1999). The bar graph shown in Figure 12 demonstrates the extent of phosphorus impacts on aquatic environments in the United States, measured in 2004. In streams, 38,632 miles were adversely impacted by high nutrient loadings and 35,301 miles were impaired because of wastewater treatment plant discharges. Lakes and ponds had negative impacts caused by nutrient loading rates along 1,952,386 miles and 583,211 miles of impairment linked directly to wastewater plant discharges. Bays and estuaries were impacted to a smaller extent with 1,047 miles impaired by nutrient loadings from agricultural runoff and 2,487 miles impaired from wastewater treatment plant discharges.



	Streams	Lakes and Ponds	Bays and Estuaries
■ Nutrients	38632	1952386	1047
■ WWTP Discharges	35301	583211	2487

FIGURE 12. MILES OF IMPAIRED WATERWAYS CAUSED BY NUTRIENTS (NITROGEN AND PHOSPHORUS) AND WASTEWATER TREATMENT PLANT EFFLUENT DISCHARGES, RAW DATA MEASURED IN 2004 FROM (EPA 2009).

Struvite Precipitation in Wastewater Treatment

Process Overview

Struvite Formation within Wastewater Treatment Plants

Reject water flows in EBPR systems, accounting for only two percent of facility influent flows, have high concentrations of ammonia and phosphorus. This is caused by the bacteriological treatment occurring within anaerobic digesters, with phosphorus concentrations raging from 260 to 500 mg/L (Elliott and Taylor 2014; Yang et al. 2009). These nutrients recirculate within wastewater treatment systems and are removed at slow rates, each time the reject water undergoes phosphorus removal in secondary EBPR systems it is re-released to liquid form during anaerobic digestion (Munch and Barr 2001; Forrest et al. 2008).

Struvite (magnesium ammonium phosphate, $MgNH_4PO_4$), is a white crystalline mineral compound which forms under conditions of elemental supersaturation within liquid. This is common in reject waters of wastewater treatment plants (Doyle et al. 2003; Rahaman et al. 2014; Acelas et al. 2014; Korchef et al. 2011; Bergmans et al. 2014). When magnesium (Mg^{2+}), ammonium (NH^{4+}) and phosphate ($PO^{3-}{}_4$) concentrations exceed solubility levels, supersaturation occurs and minerals combine and precipitate into solid form (Wu and Bishop 2004). The reject water removal system, by design, constricts flows resulting in partial pressure reduction that removes dissolved carbon dioxide and results in an increase in pH (Battistoni et al. 1997; Fattah et al. 2010; Barak and Stafford 2006). Increased pH levels in reject waters provide optimal conditions for struvite precipitation (Wu and Bishop 2004; Barak and Stafford 2006). Zones of increased agitation, such as in pipe bends or pump impellers, also provide opportune conditions for natural struvite formation (Xavier et al. 2014). The chemical conditions for struvite precipitation at varying levels of water pH are shown in Figure 13. The solubility of struvite is pH dependent, remaining in liquid form at low pH levels and precipitating into solid forms at high pH levels (Wu and Bishop 2004).

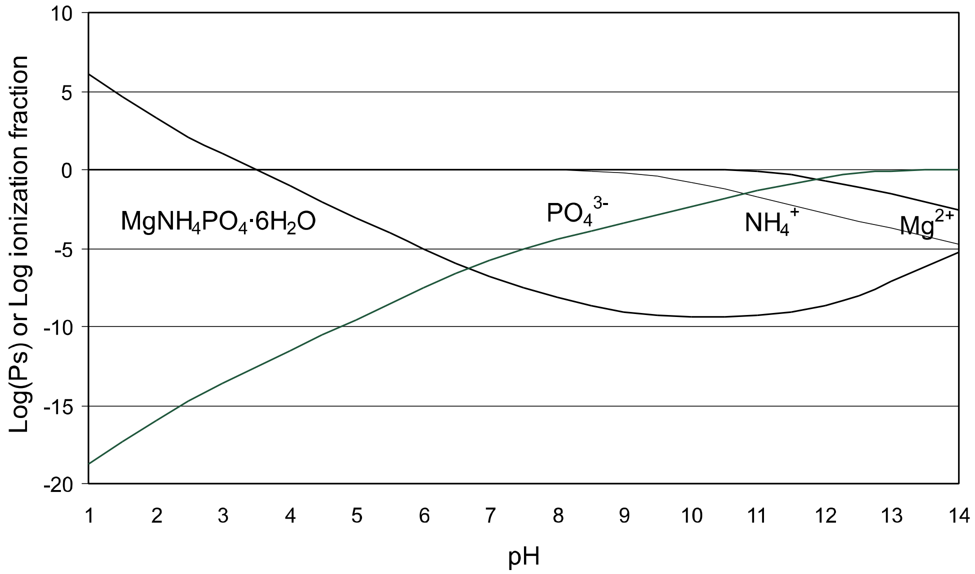


FIGURE 13. SOLUBILITY CONDITIONS FOR STRUVITE DEPENDENT UPON CONCENTRATIONS OF MAGNESIUM, AMMONIUM, PHOSPHATE AND PH LEVELS, TAKEN FROM (Wu and Bishop 2004).

Wastewater pH levels typically range from 6.0 to 8.0 and struvite precipitates around pH 12.6, as shown in the following speciation equations:

$$[1] NH^{4+} \Leftrightarrow NH_3(aq) + H^3 : 9.3 pH$$
$$[2] H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+ : 2.1 pH$$
$$[3] H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H^+ : 7.2 pH$$
$$[4] HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H^+ : 12.3 pH$$
$$[5] MgOH^+ \Leftrightarrow Mg^{2+} + OH^- : 2.56 pH$$
$$[6] MgNH_4PO_4 \cdot 6H_2O \Leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O : 12.6 pH$$

EQUATION 1. STRUVITE SPECIATION EQUATIONS ADAPTED FROM EQUATIONS PRESENTED IN (Wu and Bishop 2004).

Lowering the partial pressure of aqueous reject waters, during passage through pipe bends, pump impellers and screens, from 0.5 atm to 0.05 atm results in a release of dissolved carbon dioxide and consequently increases pH levels from 7.0 to 8.0 increasing the chance of struvite precipitation (Fattah et al. 2010).

Reject water piping systems are a source of constant maintenance problems for treatment facilities due to struvite scaling. Struvite deposits are characteristically cement-like and removal of the material from wastewater treatment plant infrastructure is costly, laborious and disrupts treatment efforts. Struvite scaling results in operational inefficiencies, reduced flow capacities in piping and is very difficult to remove (Forrest et al. 2008; Doyle et al. 2003). Current methods of removal include acid washing, use of expensive glass-lined pipes and removal with chisels (Forrest et al. 2008; Doyle et al. 2003). However, these solutions are only temporary and benefits are quickly nullified as struvite deposition continues to develop and disrupt facility operations.

Struvite scale inside the digester sludge pipeline at the Hyperion Wastewater Treatment Plant in Los Angeles caused a pipe diameter reduction of 50% after only one year of operation (Jaffer et al. 2002). Optimal physical and chemical conditions for struvite precipitation in reject water-piping systems from solids dewatering processes and anaerobic digesters often result in large precipitated struvite volumes that completely close pipes within a matter of months, as experienced at the Penggol Pigwaste Plant in Singapore (Mohajit et al. 1989). The Sacramento Regional Wastewater Treatment Plant in California had to replace 3.5 miles of pipe after failed struvite scaling removal attempts (Doyle et al. 2003)

Phosphorus Recovery and Recycling Through Struvite Precipitation

Struvite is 9.8% magnesium, 7.3% ammonium, 38.8% phosphate, and 44.1% water and other organic compounds (Mohajit et al. 1989). Research has demonstrated struvite can be recovered at rates of 80 to 90% from reject waters through struvite precipitation processes (Shu et al. 2006; Geerts et al. 2015; Xavier et al. 2014; Korchef et al. 2011; Forrest et al. 2008; Petzet and Cornel 2011; Chanan et al. 2013). Total phosphorus recovery efficiency rates of these systems range anywhere from 50 to 80% and also reduce ammonia concentrations by 29% (Shu et al. 2006; Xavier et al. 2014). Processing reject waters through struvite precipitation systems reduces nutrient impacts upon wastewater treatment plants from reject water addition to influent flows, reduces struvite scaling issues in infrastructure and allows precipitation to occur in a controlled environment (Xavier et al. 2014; Bergmans et al. 2014).

Struvite precipitation processes involve a struvite crystallizer reactor. The diagram in Figure 14 illustrates how these reactors operate in reverse gravitational flows by pumping reject waters from anaerobic digesters and solids dewatering machinery into the bottom of a struvite crystallizer reactor (Cullen et al. 2013; Britton et al. 2005; Fattah et al. 2010; Rahaman et al. 2014). The upward flow through increasingly larger reactor chambers allows struvite crystals to separate by density and size. The smallest particles (prills) remain in the uppermost reactor until enough minerals accumulate, increasing the size and density to drop the prill down into the smaller reactor chamber below. From the top down, each reactor zone has a reduced liquid detention time. The largest diameter zone at the top of the structure has the smallest struvite particles with the longest detention time to allow for crystal growth (Cullen et al. 2013). The largest prills present in the lowest and smallest reactor chamber are removed, dried and bagged.

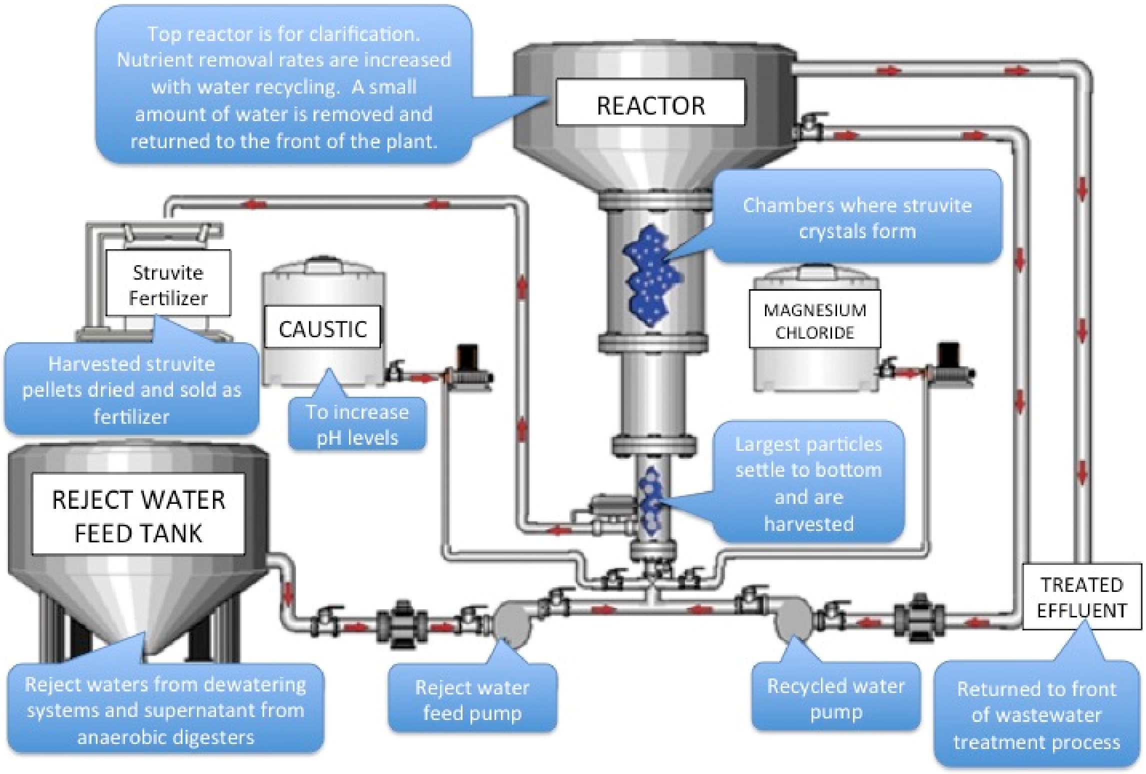


FIGURE 14. STRUVITE CRYSTALLIZER PROCESS DIAGRAM, ADAPTED FROM SCHEMATIC PRESENTED IN (Hanzen and Sawyer 2010).

Precipitation of struvite requires a molar ratio of 1:1:1 of magnesium, ammonium and phosphate. Reject waters provide adequate amounts of ammonium and phosphate, but are low in magnesium concentrations. Therefore, magnesium additions are necessary for struvite crystal formation (Chanan et al. 2013; Bergmans et al. 2014; Xavier et al.

2014; Munch and Barr 2001; Acelas et al. 2014). As mentioned earlier and shown in Figure 13 and Equation 1, struvite precipitates at higher pH levels. Supernatants and reject water pH levels are often too low for struvite formation; therefore pH levels must be raised (Barak and Stafford 2006; Bergmans et al. 2014; Rahaman et al. 2014). Within a crystallizer reactor pH levels are increased with additions of caustic chemicals, often in the form of sodium hydroxide (Britton et al. 2005; Bergmans et al. 2014; Rahaman et al. 2014; Xavier et al. 2014).

Systems in Operation

Pilot-Scale Studies

Lulu Island Wastewater Treatment Plant

Pilot-scale studies have demonstrated phosphorus recovery rates through struvite precipitation at high enough levels to warrant investment in full-scale facilities. The University of British Columbia in Canada designed and built a pilot project at the Lulu Island Wastewater Treatment Plant in 2006 to predict struvite precipitation levels through saturation index calculations and to identify factors effecting struvite crystallization in fluidized bed reactors (Bhuiyan et al. 2008). Struvite crystals formed within the experimental reactor had molecular structures confirmed as struvite by x-ray diffraction analysis (XRD). Researchers found the harvested struvite pellets were 98.0±1.0% pure struvite and ranged in size from 0.5 to 3.5 mm. The average composition of the reject waters being fed to the fluidized reactor over the two-month experiment period was 76.3 mg/L phosphate, 757.4 mg/L ammonia and 12.31 mg/L magnesium (Bhuiyan et al. 2008). Performance of the pilot-scale phosphorus recovery reactor removal efficiency was calculated comparing the difference of phosphorus concentrations in influent and effluent liquids. With magnesium additions and pH levels controlled at 8.0-8.2, the pilot-scale operation removed 75 to 85% phosphate material from incoming reject water flows (Bhuiyan et al. 2008).

Oxley Creek Wastewater Treatment Plant

A pilot-scale study of the Unitika Ltd. Phosnix struvite precipitation process was undertaken to determine the feasibility for full-scale operation at the Oxley Creek Wastewater Treatment Plant in Australia. The results showed that the process achieved an organic phosphate removal of 94% from reject water influent flows averaging 61 mg/L phosphorus (Munch and Barr 2001). Magnesium hydroxide was added to the influent liquid to stimulate struvite precipitation and pH levels were maintained around 8.5. Produced struvite pellets were 90% by weight pure struvite, confirmed with X-ray diffraction (XRD) analysis. Crystal development was influenced by influent phosphorus concentrations and particle detention time within the reactor. High influent phosphorus concentrations, >200 mg/L, resulted in crystal growth rates around 0.173 mm/d. Low phosphorus concentrations, ranging from 34 to 100 mg/L, had reduced crystal growth rates of 0.061 mm/d (Munch and Barr 2001). Influent phosphorus concentrations were artificially maintained through dilution with clean water at 90 mg/L in the reactor in order to maintain experimentally optimal growth rates during pilot testing. The pilot-scale reactor produced 320 g of struvite pellets per day at an average influent flow rate of 266 gal/d. The resulting product 12.4% inorganic phosphorus, 9.1% magnesium, 5.1% nitrogen and 39% water; it also contained cadmium, lead and mercury in levels below legal limits in Australia, allowing it to be sold as a slow-release fertilizer (Munch and Barr 2001). A wastewater treatment plant with average daily reject water flow rates of 114 thousand gal/d can theoretically produce 0.137 metric tons of struvite each day. Research into marketability of this fertilizer product in Australia denotes a retail price of $300-400 Aus./ton ($193-330 US/ton), meaning Oxley Creek Wastewater Treatment Plant could generate a $15,001.50-25,002.50 Aus./yr ($9,650.97-16,501.65 US/yr) (Munch and Barr 2001).

Full-Scale Struvite Recovery Facilities

With such promising results from numerous pilot-scale studies, struvite precipitation has transitioned from research and development to full-scale operational processes in wastewater treatment facilities throughout the world. The leading global wastewater phosphorus recovery company is Canadian-based Ostara. Their patented Pearl® Process recovers phosphorus and nitrogen from wastewater treatment plants to produce their Crystal Green® fertilizer. The produced fertilizer pellets, needing no further processing than that achieved with the Pearl® fluidized reactor, are marketed as slow-release fertilizers made by struvite precipitation. This inorganic phosphate fertilizer is registered for agricultural use in 34 US states, the United Kingdom, Canada and the

European Union (Cullen et al. 2013). Processing reject waters from wastewater treatment plants through their Pearl® fluidized reactor systems has an average struvite recovery rate of 85% phosphorus and 15% ammonia (Cullen et al. 2013). Unitika Ltd. of Japan performs similar work and sells a slow-release fertilizer marketed as Green MAP II that is widely used locally (Munch and Barr 2001; Liao et al. 2003). Phosphorus recovery via struvite precipitation reactors reduces maintenance at wastewater treatment plants by removing struvite buildup on infrastructure, reduces nutrient loading on the facility, stabilizes sewage treatment processes and generates a profit through sale of slow-release fertilizers (Cullen et al. 2013; Koch et al. 2003).

Saskatoon Wastewater Treatment Plant

Phosphorus concentrations in biosolids increased at the Saskatoon Wastewater Treatment Plant after a biological phosphorus removal (BPR) system upgrade in 1996. The system upgrade was designed to comply with an updated operations permit requiring treated secondary effluent waters to contain a maximum of 0.2 mg/L phosphorus (Ostara 2013a). The facility was able to control the majority of struvite scaling that developed after the system upgrade with a rigorous maintenance program. However, in 2010 the 7.5 mile pipe transporting digested sludge to a drying lagoon became choked off, bringing operations to a stand-still. Traditional struvite scale removal methods of chemical flushing to clean the pipeline failed, and the facility ended up having to replace the pipe (Ostara 2013a). To prevent reoccurrences of this debilitating event, facility managers invested in another upgrade to solve the struvite-scaling problem. By adding an Ostara Pearl® struvite precipitation reactor the facility began producing 457 tons of slow-release fertilizer sold throughout Canada and the United States. The facility experienced multiple benefits from the latest upgrade: a new revenue stream from sale of produced fertilizer; a reduction in struvite buildup; lower maintenance and labor costs associated with struvite scaling management; a reduction in nutrient loading on the plant allowing for increased treatment efficiencies, and a reduction in chemical usage for struvite scaling removal (Ostara 2013a). Installation of one Pearl® reactor capable of treating 1.3 million gallons per day (MGD) of reject waters removed 158 kg/d of phosphorus at an efficiency rate of 66% and 72 kg/d of nitrogen with an efficiency rate of 11% (Ostara 2013a).

Nine Springs Wastewater Treatment Plant

The Nine Springs Wastewater Treatment Plant in Madison, Wisconsin, a BNR facility with gas harvesting for cogeneration of electricity, struggled with struvite scaling in the digester and dewatering machinery of the solids treatment processes. Traditional and costly struvite management attempts, of utilizing glass-lined piping and ferric dosing, failed to solve the problem (Ostara 2014). The added chemicals from ferric dosing exited the facility with produced biosolids and resulted in leaching issues when beneficially reused in land applications, exacerbating water pollution issues in the region. To combat the struvite problems and maintain liquid effluent phosphorus discharge limits of 0.03 mg/L, the Nine Springs facility installed two Ostara Pearl® reactors with total reject water treatment capacities of 1.8 MGD (Ostara 2014). The fluidized bed struvite precipitation reactors remove 949 lb/d of phosphorus and 429 lb/d nitrogen with annual struvite fertilizer production of 1,375 tons. The upgrade also accomplished reductions in nutrient loading rates to the plant by treating reject waters, reduced chemical usage for solids treatment thereby saving money and creating a new source of income (Ostara 2014).

Slough Sewage Treatment Works

The BNR 15MDG capacity Slough Sewage Treatment Works along the Thames River in Berkshire, UK spent £200,000/yr (~$298,832 US) to remove nuisance struvite formations within the facility's infrastructure (Ostara 2013b). Over concern of chemical dependence and cost, facility managers looked into alternative systems to meet the same ends of struvite control and phosphorus removal at reduced operational costs. After installation of a single Ostara Pearl® reactor the facility experienced: reductions in chemical dosing, increased facility performance by increased capacities due to struvite scale removal, and the new ability to beneficially reuse biosolids due to the reduced phosphorus concentrations which now met regulation standards for land application. Reactor operations remove 55 kg/d of phosphorus, 25 kg/d of nitrogen and produce 160 ton/yr of struvite fertilizer product (Ostara 2013b).

Rock Creek Advanced Wastewater Treatment Facility

The Tualatin River Watershed in Oregon covers 712 square miles, encompassing a variety of ecosystems including plains lands, forests, mountains, agricultural areas and dense urban centers. Five tributaries drain into the Tualatin River and are each protected as sensitive ecosystems (Tualatin River Watershed Council 2015). The 35MGD BNR Rock Creek Advanced Wastewater Treatment Facility, situated within this protected region, must maintain secondary effluent discharge phosphorus rates of 0.1 mg/L (Ostara 2012). In 2011 two Ostara Pearl® reactors were installed to save ratepayer costs by recovering and selling phosphorus from biosolid production instead of expending resources to dispose of it as a waste product. The installed systems treat 0.6MGD of reject water, remove 605 lb-P/d, 891 mg-NH_4/d, 275 lb-N/d and produces 875 ton/yr of struvite fertilizer (Ostara 2012). This dramatically reduced struvite buildup, lowering maintenance costs. Reject water nutrient loading was also dramatically reduced, improving facility efficiency. Additional savings were realized from the reduction in chemical usage, lower produced biosolids, and disposal costs. Moreover, the phosphorus concentrations in the produced biosolids have also decreased (Ostara 2012).

Durham Advanced Wastewater Treatment Plant

Durham Advanced Wastewater Treatment Plant operated by Clean Water Services in Tigard, Oregon is a 20MGD capacity EBNR facility with a secondary effluent phosphorus discharge limit of 0.1 mg/L to surface waters (Ostara 2009). A facility upgrade including the addition of three Ostara Pearl® reactors came online in spring of 2009 with a total reject water treatment capacity of 0.45MGD. The reactors remove 450 lb-P/d, 1,025 mg-NH_4/d, 165 lb-N/d and produce 475 tons/yr of struvite fertilizer (Ostara 2009). Facility operation improvements resulting from reactor installations include: reduced metal salt additions for chemical phosphorus removal, phosphorus biosolid concentration reductions, and reduced nutrient loading by treating reject waters (Ostara 2009).

Nansemond Wastewater Treatment Plant

Hampton Roads Sanitation District's BNR Nansemond Wastewater Treatment Plant in Suffolk, Virginia discharges secondary effluent into the James River, which drains into the environmentally sensitive and protected Chesapeake Bay. The Sanitation District set company goals to reduce nutrient loading into Chesapeake Bay to protect the delicate aquatic environment. In order to meet these new goals the Nansemond facility needed to reduce the composition of its effluent discharge to total nitrogen levels of 8 mg/L and total phosphorus to 1 mg/L (Ostara 2010a). Ostara reactors were determined to be the key to allow Nansemond to meet the new company goals. Three Pearl® reactors were installed, capable of treating 1.5MGD of reject water, remove 500 lb-P/d, 475 mg-NH_4/d, 166 lb-N/d, and produce 430 tons of struvite fertilizer annually (Ostara 2010a). Reject water loading rates to the facility have been reduced, metal salt additions for chemical phosphorus removal processes decreased, and biosolid phosphorus concentrations have declined.

York Wastewater Treatment Plant

The York Wastewater Treatment Plant in York, Pennsylvania, a 20MDG BRN facility, discharges secondary effluents into Codorus Creek, which also feeds Chesapeake Bay. This facility must maintain effluent phosphorus levels at 0.8 mg/L to protect the sensitive Chesapeake Bay environment (Ostara 2010b). Prior to installing two Ostara Pearl® reactors the facility annually spent $400,000 to control nuisance struvite formation within facility infrastructure (Ostara 2010b). Once the reactors began operating, struvite buildup and associated maintenance expenses decreased, nutrient loading rates from reject waters declined, metal salt use for chemical phosphorus removal decreased, biosolid phosphorus concentrations decreased, and nutrient loading to Codorus Creek from secondary effluent discharges were reduced. The Pearl® reactors remove 282 lb-P/d, 635 mg-NH_4/d, 128 lb-N/d from reject waters and produce 400 tons of struvite fertilizers annually (Ostara 2010b).

International Wastewater Treatment Facilities

A full-scale struvite recovery system in Fulkuoka, Japan removes 80% of phosphorus with sewage influent phosphorus concentrations of 245 mg/L (Mavinic et al. 2007). Another facility at the Shimane Prefecture Lake Shinji East Clean Center of Japan achieves 90% phosphorus removal efficiencies through struvite precipitation systems and has a treatment capacity of 1.3MGD (Mavinic et al. 2007). Trevison Municipal Wastewater Treatment Plant in Italy also operates a full-scale struvite recovery system with total phosphorus removal rates averaging 54% of influent reject water flow concentrations (Mavinic et al. 2007).

Benefits

Wastewater Industry

Incorporating struvite precipitation phosphorus recovery systems to wastewater treatment can reduce chemical usages required for chemical phosphorus removal systems as well as those used to combat struvite scaling problems (Batstone et al. 2014; Molinos-Senante et al. 2011; *Case Study: Slough* 2013; Chanan et al. 2013; Petzet and Cornel 2011; Hao et al. 2013; Koch et al. 2003; Shu et al. 2006; Marchi et al. 2015; Bergmans et al. 2014). Researchers estimate cost savings achieved with struvite precipitation processes range from \$500 to \$2500 for every 260 thousand gallons of wastewater treated; these savings are associated with reduced maintenance and materials used to remove struvite scaling problems (Chanan et al. 2013). Struvite scaling problems cause reduced hydraulic pumping capacities for impacted equipment and if not addressed will result in equipment failure (Koch et al. 2003). Traditional struvite scale removal often causes prolonged downtime for sections of the treatment process, reducing treatment capabilities of plants. Recovering phosphorus with struvite precipitation equipment alleviates these issues (Shu et al. 2006; Marchi et al. 2015).

Struvite fluidized bed reactors precipitate phosphorus before solids dewatering processes and divert it from biosolids production. Reduced phosphorus concentrations in sludge and biosolids reduce produced volumes, anywhere from two to eight percent (Chanan et al. 2013). Smaller volumes of produced biosolids decrease transportation costs to landfills or agricultural sites (Chanan et al. 2013; De-Bashan and Bashan 2004; Marchi et al. 2015; Koch et al. 2003; Bergmans et al. 2014; Forrest et al. 2008; Shu et al. 2006). Precipitating 1 kg/d of struvite can reduce biosolid disposal volumes enough to reduce utilized landfills space by 0.000063 m^2 (Shu et al. 2006). At current population levels global struvite fertilizer production from wastewater treatment plants could amount to 3.114 Mt, saving 198,000 m^2 (~49 acres) of landfill space (Shu et al. 2006; Andreev et al. 2013). Lower phosphorus concentrations in produced biosolids also allows the material to be beneficially reused more; lowered phosphorus concentrations often meet the requirements imposed upon materials applied to agricultural fields (Molinos-Senante et al. 2011; De-Bashan and Bashan 2004).

While struvite recovery systems target phosphorus removal from reject waters, the chemical precipitation process requires a combination of elements. For struvite crystals to form within a fluidized bed reactor there must be a balance of phosphorus, magnesium and ammonium of 1:1:1 (Chanan et al. 2013; Xavier et al. 2014; Bergmans et al. 2014; Munch and Barr 2001; Acelas et al. 2014). Magnesium concentrations in wastewater are too low for struvite precipitation and are therefore added through chemical inputs. Necessary ammonium concentrations already exist within wastewater and is also removed during struvite formation, removal rates of ammonium have been recorded as high as 50% from reject water influent flows to reactors (Koch et al. 2003).

Phosphorus Production for Industry

Recovered phosphorus from wastewater facilities, in the form of slow-release struvite pellet fertilizers, can be sold to agriculture production operations as substitutes for traditional phosphate rock fertilizers (Chanan et al. 2013; Koch et al. 2003). As a fertilizer product, struvite pellets have demonstrated lower contaminant and impurity concentrations compared to phosphate rock fertilizers (Forrest et al. 2008). Phosphate rock ores often contain toxic heavy metals and radionuclides, whereas struvite pellets are free of pathogens, heavy metals and radioactive compounds (Muster et al. 2013). Struvite pellets have also demonstrated equivalency, and occasionally superior performance, to phosphate rock fertilizers for delivering inorganic phosphorus to plants (Barak and Stafford 2006). Experiments comparing struvite fertilizer (MAP) efficiency to diammonium phosphate (DAP), the popular phosphate rock fertilizer, demonstrate an application of 36 mg-MAP-P/kg fertilizer results in an equivalent plant biomass growth as an application of 42 mg-DAP-P/kg (Barak and Stafford 2006). The resulting struvite fertilizer efficiency rate is 117% over diammonium phosphate fertilizer (Barak and Stafford 2006).

Limitations

Costs

Wastewater treatment plant upgrades that include struvite recovery systems are not possible for every facility. EBPR and BNR facilities with anaerobic digesters are perfect for these recovery systems. However, Bardenpho aeration systems and MBR plants do not have digesters with reject water byproducts and therefore cannot accommodate struvite recovery systems. Facility upgrades must be economically sound to garner management approval and necessary capital investments. While struvite recovery facilities do produce revenue streams, the return on investment (ROI) is upwards of five years for a 14.5MGD facility (Shu et al. 2006; Jaffer et al. 2002). Struvite fertilizer is also more expensive to produce than phosphate rock fertilizers, $140 to $160 USD per ton for struvite fertilizers compared to $40 to $50 USD per ton for phosphate rock fertilizers (Forrest et al. 2008). However, in cases where market prices of phosphate rock fertilizers are high, it may be economical to recover struvite from wastewater treatment plants; Japan sells struvite fertilizer pellets for $250 US/ton (Forrest et al. 2008; Munch and Barr 2001). Struvite recovery systems provide important sustainability implications by reducing phosphorus fertilizer reliance upon non-renewable limited phosphate rock reserves. However, societal concerns over opportunity costs may hinder wastewater treatment plant upgrades. The public may not be interested in investing in upgrades for wastewater treatment plants, regardless of the reduced aquatic pollution it provides, over investments into public education or health care (Hu et al. 2012).

Struvite pellets as fertilizer sales cover only one third of the annual chemical inputs, not including other operational costs, of a fluidized bed reactor system (Jaffer et al. 2002). Magnesium input costs average $330US per ton of struvite produced (Munch and Barr 2001). However, cost savings are achieved through avoidance of struvite scaling issues. Minimizing struvite scale decreases pumping, operational, pipe replacement, and labor costs (Jaffer et al. 2002). Table 4 lists some of the monetary inputs and outflows relating to installation and operation of struvite recovery systems analyzed at the Wastewater Treatment Plant in Leuven, Belgium.

TABLE 4. POSITIVE AND NEGATIVE MONETARY FLOWS RELATED TO STRUVITE RECOVERY SYSTEM INSTALLATION AND OPERATION AT WASTEWATER TREATMENT PLANTS, TAKEN FROM (Geerts et al. 2015).

Positive Monetary Flows Connected to Struvite Recovery
Sales price of struvite
Reduced aeration cost for nitrogen removal (reduction via feedback flows of reject waters)
Reduced cost for carbon source for phosphorus removal (reduction via feedback flow od reject waters)
Reduced maintenance cost for clogged pipes
Lower sludge disposal cost due to improved dewaterability
Reduced polymer use in the dewatering process
Negative Monetary Flows Connected to Struvite Recovery
Installation investment
Investment in chemical storage and dosing of caustic and magnesium (to allow for bulk delivery and thus reduce chemical-dosing costs)
Operation man-hours
Operation magnesium and caustic consumption
Maintenance
Monetary Flows Not Considered with Struvite Recovery
Research costs and pilot-scale testing
Fixed costs for digestion, dewatering and drying
Possible benefits attributed to lower cadmium and uranium content in the struvite fertilizers as compared to natural phosphate ore
Benefits related to a lower phosphorus content in dried biosolids

Based on the analysis performed at the Wastewater Treatment Plant in Leuven, Belgium, the facility would have an ROI of 10 years with the sale of struvite currently priced at €530/ton ($637US/ton) (Geerts et al. 2015). Installation of a struvite recovery facility demonstrates positive economic returns when maintenance costs and environmental benefits are taken into account (Barak and Stafford 2006).

Chemical Inputs

Struvite crystal formation requires molar ratios of 1:1:1 of magnesium, nitrogen and phosphorus (Koch et al. 2003). Phosphorus and nitrogen are present in wastewater at sufficient concentrations. However, magnesium concentrations are too low for struvite precipitation and must therefore be added. pH levels must also be adjusted to optimal ranges for struvite crystallization, see **Error! Reference source not found.**Figure 14 and Equation 1. The reject water itself has an average pH of 7.0 and high alkalinity (Wu and Bishop 2004; Jaffer et al. 2002). Alkaline waters resist pH adjustments and necessitate large inputs of pH raising caustic chemicals to reach pH breakpoints, such as sodium hydroxide or magnesium hydroxide (Jaffer et al. 2002; Bhuiyan et al. 2008). Magnesium, being the smallest volume of the three elements necessary for struvite formation present in wastewater, is the limiting nutrient for struvite production (Jaffer et al. 2002; Bhuiyan et al. 2008). Magnesium inputs must be optimized and maintained to ensure maximum struvite output from reactors. Magnesium hydroxide ($Mg(OH)_2$) and magnesium chloride ($MgCl_2$) are the two most commonly used magnesium inputs for fluidized bed reactors (Jaffer et al. 2002; Munch and Barr 2001). Each chemical behaves differently in the system; however, one does not appear to be better than the other concerning struvite production rates. Magnesium chloride dissociates faster and enables shorter reaction times in mixing chambers, whereas magnesium hydroxide is cheaper and assists with pH increases (Jaffer et al. 2002; Munch and Barr 2001).

Research into alternatives to chemical inputs for pH adjustments and magnesium is on the rise as interest in struvite precipitation technologies increase. A number of studies have proposed dissolved carbon dioxide (CO_2) stripping during struvite precipitation to increases pH to levels optimal for crystal development (Fattah et al. 2008, 2010; Battistoni et al. 1997; Hiroyuki and Toru 2003). Bicarbonate present in wastewater liquids, formed during secondary aeration treatments, can dissociate into carbon dioxide and hydroxide. Carbon dioxide releases to the atmosphere in gaseous form while the hydroxide aids in increasing aqueous pH, the chemical equation is shown below in Equation 2:

$$HCO_3^- \rightarrow CO_2 \uparrow + OH^-$$

EQUATION 2. CHEMICAL EQUATION OF BICARBONATE DISSOCIATING INTO CARBON DIOXIDE AND HYDROXIDE, TAKEN FROM (Fattah et al. 2008).

Including air stripping techniques to remove carbon dioxide increases pH and in turn reduces caustic input requirements for struvite precipitation, saving money on chemical and bulk storage units (Fattah et al. 2008; Battistoni et al. 1997). An experiment performed on carbon dioxide stripping in struvite reactors demonstrated quantifiable cost savings on caustic chemical addition while still achieving struvite production volumes comparable to systems without CO_2 strippers, results are shown in Table 5. A struvite recovery system without air stripping processes, test run 1, used 1.23 kg/d of caustic additions and removed 2.44E-03 moles of phosphorus with a 90% removal rate, 5.73E-03 moles of nitrogen at a 10% removal rate, and removed 2.19E-03 moles of magnesium at a 66% removal rate. Testing of air stripping techniques incorporated with struvite precipitation processes was conducted. One system, used in test run 2, pulled air from external sources while the other system, test run 3, did not utilize external air sources. Test run 2 used 0.84 kg/d of caustic additions and removed 2.42E-03 moles of phosphorus with a 90% removal rate, 2.98E-03 moles of nitrogen at 5% removal rate, and removed 2.28E-03 moles of magnesium at a 75% removal rate. Test run 3 used 0.91 kg/d of caustic additions and removed 1.55E-03 moles of phosphorus with a 90% removal rate, 7.66E-03 moles of nitrogen at 14.5% removal rate, and removed 1.13E-03 moles of magnesium at a 39% removal rate.

TABLE 5. SUMMARY OF EXPERIMENTAL RESULTS COMPARING PHOSPHATE, AMMONIA AND MAGNESIUM REMOVAL RATES AND COST SAVINGS OF STRUVITE CRYSTALIZING SYSTEMS WITH AND WITHOUT CARBON DIOXIDE AIR STRIPPING, ADAPTED FROM (Fattah et al. 2008).

	Without Strippers	*With Strippers*	
	Run 1	*Run 2*❖	*Run 3*□
Phosphate removal (%)	90	90	90
Ammonium removal (%)	10	5	14.5
Magnesium removal (%)	66	75	39
Molar phosphate removal	2.44E-03	2.42E-03	1.55E-03
Molar ammonium removal	5.73E-03	2.98E-03	7.66E-03
Molar magnesium removal	2.19E-03	2.28E-03	1.13E-03
Molar ratio (Mg:N:P)	0.9:2.3:1	0.9:1.2:1	0.7:4.9:1
Caustic use (kg/d)	1.23	0.84	0.91
Caustic savings (kg/d)	--	0.39	0.32
Caustic savings (%)	--	32	26
Current caustic savings⊙ (US$/d)	--	0.82	0.65
Annual savings at Lulu Island Wastewater Treatment Plant	--	9,965	8,168
Annual savings at Annacis Wastewater Treatment Plant	--	44,518	36,350

❖ Carbon dioxide stripper run with external air.

□ Carbon dioxide stripper run without external air.

⊙ Caustic cost USD 2.1/kg.

Cost savings achieved with air stripping in Run 2 amounted to \$0.39kg-US/d and \$0.65kg-US/d. Theoretically applying Run 2 savings to the Lulu Island Wastewater Treatment Plant in Richmond, BC, Canada could result in annual caustic savings of \$9,965 (US), and Run 3 savings could amount to \$8,168 (US). Theoretically applying Run 2 savings to the Annacis Wastewater Treatment Plant in Vancouver, BC, Canada can result in annual caustic savings of $44,518 (US), and Run 3 savings could amount to $36,350 (US). In conclusion, carbon dioxide air stripping results in cost savings to a wastewater treatment plant employing struvite precipitation processes by increasing pH through chemistry instead of caustic chemical additions (Fattah et al. 2010, 2008).

Product Marketability and Societal Acceptance

As with marketing recycled water, there is an‘ick’ factor associated with materials recycled from wastewater streams. Public perceptions need to be addressed when selling struvite pellets recovered from wastewater for agriculture production (Contreras et al. 2013). However, when phosphate rock fertilizers become scarce and prohibitively expensive, the public may be less concerned with struvite fertilizer sources and direct more attention to lower prices and sustainability of the product (Muster et al. 2013). Struvite fertilizer marketing can also rely on the important facts that it contains zero pathogens, heavy metals or radionuclides unlike phosphate rock ores (Muster et al. 2013). Research demonstrates struvite pellets provide equivalent plant biomass growth at lower fertilizer input rates compared to phosphate rock, the material is also slow-release enabling for further application reductions, passing along cost savings to agriculture producers (Barak and Stafford 2006).

Struvite Precipitation to Produce Alternative Phosphorus

Struvite Precipitation Product as Phosphate Rock Fertilizer Substitute

Phosphate Rock Fertilizer Regulations

Phosphate rock ore contains traces of contaminants such as arsenic (As), cadmium (Cd), zinc (Zn), lead (Pb), cobalt (Co), chromium (Cr), Copper (Cu), iron (Fe), molybdenum (Mo), nickel (Ni), and vanadium (V) (Molina et al. 2009). Phosphorus fertilizers derived from phosphate rock ore used in agricultural operations also contain these trace contaminant elements to varying degrees, dependent on ore origins (Molina et al. 2009; Jiao et al. 2012; Chen et al. 2007). Contaminants in phosphorus fertilizers added to agricultural fields compound and pose human health and environmental risks (Jiao et al. 2012; Chen et al. 2007; Molina et al. 2009). During plant development these accumulated contaminants are absorbed from soils applied with phosphorus rock fertilizers. Plant matter containing these contaminants pass the material to humans through food consumption and may present harmful side effects (Jiao et al. 2012). To mitigate potential environmental and health hazards, phosphorus fertilizers have maximum contaminant concentration restrictions connected to the concentration of phosphorus. Higher phosphorus (as phosphorus pentoxide P_2O_5) concentrations can have higher levels of trace contaminants (Jiao et al. 2012; Chen et al. 2007). Regulated contaminant limitations vary between countries is shown in Table 6. Canada has the most restrictions for various trace contaminants: cadmium 20 mg/kg- P_2O_5, arsenic 75 mg/kg- P_2O_5, cobalt 150 mg/kg- P_2O_5, molybdenum 20 mg/kg- P_2O_5, nickel 180 mg/kg- P_2O_5, lead 500mg/kg- P_2O_5, and zinc limited to 1850 mg/kg- P_2O_5. Some states in the United States limit contaminant concentrations; Texas restricts cadmium levels to 39 mg/kg- P_2O_5; California limits cadmium to 200 mg/kg- P_2O_5 and lead to 1000 mg/kg- P_2O_5. Cadmium is widely regulated throughout the world at varying degrees: Australia set limits to 300 mg/kg- P_2O_5, Austria at 275 mg/kg- P_2O_5, Belgium at 200 mg/kg- P_2O_5, Czech Republic at 50 mg/kg- P_2O_5, China at 8 mg/kg- P_2O_5, Denmark at 110 mg/kg- P_2O_5, Finland 50 mg/kg- P_2O_5, Germany 200 mg/kg- P_2O_5, Japan 340 mg/kg- P_2O_5, Netherlands 35 mg/kg- P_2O_5, New Zealand 280 mg/kg- P_2O_5, Norway 100 mg/kg- P_2O_5, Portugal 200 mg/kg- P_2O_5, and Sweden at 100 mg/kg- P_2O_5 (Molina et al. 2009).

TABLE 6. REGULATORY TRACE CONTAMINANT CONCENTRATION LIMITS FOR PHOSPHATE ROCK FERTILIZERS ADAPTED FROM TABLE IN (Molina et al. 2009).

Contaminant	*Country*	*Concentration Limit (mg/kg- P_2O_5)*
Cadmium	Australia	300
	Austria	275
	Belgium	200
	Czech Republic	50
	China	8
	Denmark	110
	Finland	50
	Germany	200
	Japan	340
	Netherlands	35
	New Zealand	280
	Norway	100
	Portugal	200
	Sweden	100
	Canada	20
	U.S.—Texas	39
	U.S—California	200
Arsenic	Canada	75
	U.S.—California	100
Cobalt	Canada	150
Molybdenum	Canada	20
Nickel	Canada	180
Lead	Canada	500
	U.S.—California	1000
Zinc	Canada	1850

Phosphate Rock Fertilizer Products

Phosphate rock based fertilizers come in various forms with different properties; rock phosphate is a low soluble material with an NPK ratio of 0-20-0; triple superphosphate is highly soluble with an NPK ratio of 0-46-0; diammonium phosphate dissolves to a slightly basic solution with an NPK ratio of 18-46-0; monoammonium phosphate dissolves into a slightly acidic solution with an NPK ratio of 11-52-0; ammonium polyphosphate is a slightly acidic liquid with an NPK ratio of 10-34-0; and ortho-superphosphate is a sulfuric acid with a 10% sulfur composition and an NPK ratio of 0-20-0 (Barrett and Arnall 2011; Robertson et al. 2012). Monoammonium phosphate (NH_4HPO_4) is produced through a chemical reaction between ammonia (NH_3) and phosphoric acid (H_3PO_4) composing of 10 to 12% nitrogen 48 to 61% P_2O_5, the inorganic phosphorus compound utilized by plants (International Plant Nutrition Institution 2010). Diammonium phosphate ($(NH_4)_2HPO_4$), the preferred phosphorus fertilizer in the United States, is created by a chemical reaction between phosphoric acid and ammonia with a composition of 18% nitrogen and 46% P_2O_5 (International Plant Nutrition Institution 2012).

Average measurable trace contaminants present in monoammonium phosphates produced in the United States: arsenic ~11.5 mg/kg- P_2O_5, cadmium ~ 2.3 mg/kg- P_2O_5, cobalt ~1.8 mg/kg- P_2O_5, nickel ~1.9 mg/kg- P_2O_5, molybdenum ~11.5 mg/kg- P_2O_5, lead ~6.5 mg/kg- P_2O_5, copper ~0.1 mg/kg- P_2O_5, chromium ~80 mg/kg- P_2O_5, manganese ~135 mg/kg- P_2O_5, iron ~7000 mg/kg- P_2O_5, vanadium ~40 mg/kg- P_2O_5, and zinc ~30 mg/kg- P_2O_5. Average measurable trace contaminants present in monoammonium phosphates produced in Mexico: arsenic ~12.1 mg/kg- P_2O_5, cadmium ~ 4.3 mg/kg- P_2O_5, cobalt ~3.5 mg/kg- P_2O_5, nickel ~6 mg/kg- P_2O_5, molybdenum ~10 mg/kg- P_2O_5, lead ~5.5 mg/kg- P_2O_5, copper ~0.15 mg/kg- P_2O_5, chromium ~85 mg/kg- P_2O_5, manganese ~145 mg/kg- P_2O_5, iron ~9000 mg/kg- P_2O_5, vanadium ~50 mg/kg- P_2O_5, and zinc ~80 mg/kg- P_2O_5. Average measurable trace contaminants present in diammonium phosphates produced in the United States: arsenic ~13.5 mg/kg- P_2O_5, cadmium ~ 3 mg/kg- P_2O_5, cobalt ~2.5 mg/kg- P_2O_5, nickel ~3 mg/kg- P_2O_5, molybdenum ~9 mg/kg- P_2O_5, lead ~8 mg/kg- P_2O_5, copper ~0.5 mg/kg- P_2O_5, chromium ~80 mg/kg- P_2O_5, manganese ~135 mg/kg- P_2O_5, iron ~7000 mg/kg- P_2O_5, vanadium ~35 mg/kg- P_2O_5, and zinc ~42 mg/kg- P_2O_5. Average measurable trace contaminants present in diammonium phosphates produced in the Mexico: arsenic ~16 mg/kg- P_2O_5, cadmium ~ 4.5 mg/kg- P_2O_5, cobalt ~3.5 mg/kg- P_2O_5, nickel ~7 mg/kg- P_2O_5, molybdenum ~7 mg/kg- P_2O_5, lead ~9.8 mg/kg- P_2O_5, copper ~0.1 mg/kg- P_2O_5, chromium ~98 mg/kg- P_2O_5, manganese ~115 mg/kg- P_2O_5, iron ~11000 mg/kg- P_2O_5, vanadium ~38 mg/kg- P_2O_5, and zinc ~39 mg/kg- P_2O_5 represented graphically in Figure 15 (Molina et al. 2009).

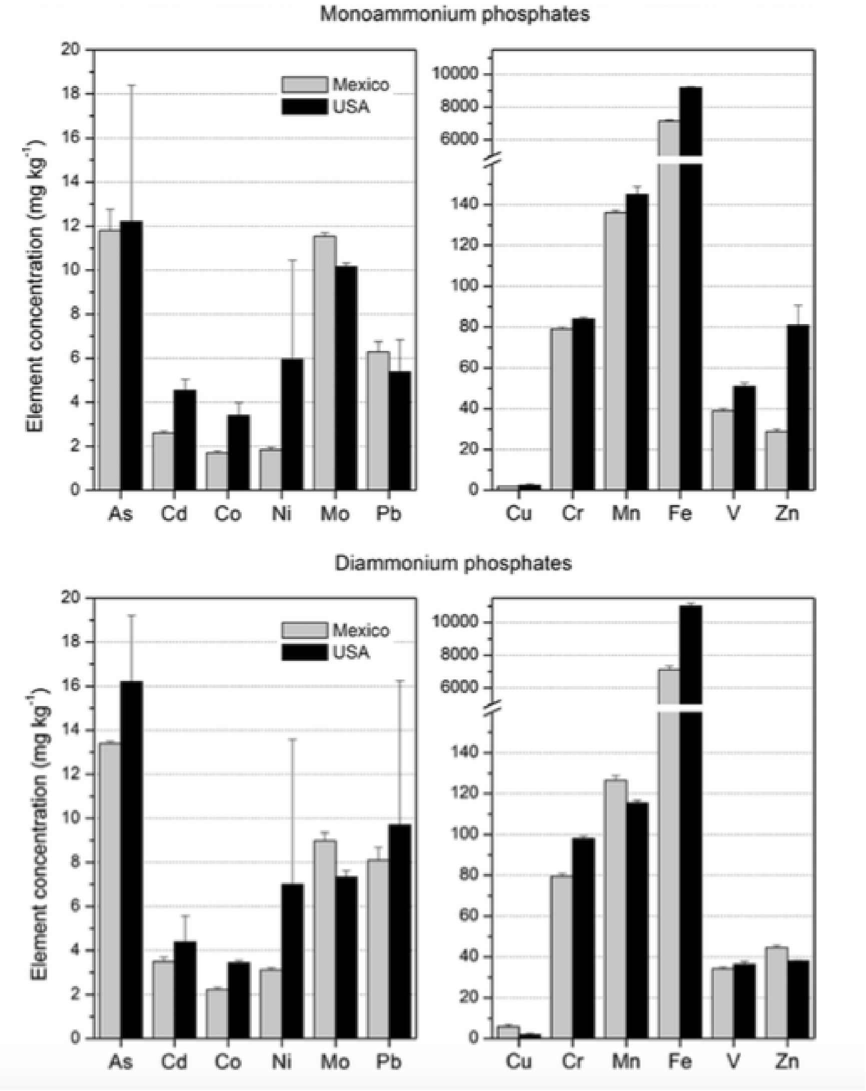


FIGURE 15. CONCENTRATIONS BY WEIGHT OF TRACE CONTAMINANTS PRESENTED IN PHOSPHATE ROCK FERTILIZERS FROM PHOSPHATE ROCK RESERVES IN THE UNITED STATES AND MEXICO, TAKEN FROM (Molina et al. 2009).

Phosphate rock fertilizers sold in Europe, China and Chile have similar levels of arsenic, cadmium and lead contaminants. European phosphate rock fertilizers contain 7.6 mg/kg-

P_2O_5 of arsenic, 7.4 mg/kg- P_2O_5 of cadmium, and 2.9 mg/kg- P_2O_5 of lead. Phosphate rock fertilizers sold in China contain 13.5 mg/kg- P_2O_5 of arsenic, 2.6 mg/kg- P_2O_5 of cadmium, and 30.0 mg/kg- P_2O_5 of lead. Phosphate rock fertilizers marketed in Chile have 15.1 mg/kg- P_2O_5 of arsenic, 12.3 mg/kg- P_2O_5 of cadmium, and 10.4 mg/kg- P_2O_5 of lead as shown in Table 7.

TABLE 7. ARSENIC, CADMIUM AND LEAD AVERAGE CONCENTRATIONS BY WEIGHT OF PHOSPHATE ROCK OF FERTILIZERS SOLD IN EUROPE, CHINA AND CHILE ADAPTED FROM SIMILAR TABLE PRESENTED IN (Jiao et al. 2012).

Region	*Concentration (mg/kg-P_2O_5)*		
	Arsenic (As)	*Cadmium (Cd)*	*Lead (Pb)*
Europe	7.6	7.4	2.9
China	13.5	2.6	30.0
Chile	15.1	12.3	10.4

Struvite Precipitation Fertilizer Products

Struvite crystals formed in reject water from pilot-scale treatment studies were 96.2 to 97.5% pure struvite, measured at the Annacis, Lulu Island and City of Penticton wastewater treatment facilities (Britton et al. 2005; Mavinic et al. 2007). Crystal formations contained trace amounts of calcium, iron, aluminum, potassium and carbon trioxide contaminants (Britton et al. 2005; Mavinic et al. 2007). An Annacis facility pilot-project produced struvite with contaminant concentrations representing 5.03% by weight of the produced material (Mavinic et al. 2007). Lulu Island wastewater treatment plant pilot-scale study produced struvite with smaller contaminant concentrations, at 3.37% of the total weight (Mavinic et al. 2007). The pilot-scale study performed at the Penticton facility demonstrated the lowest contaminant concentrations at 0.05% total weight (Britton et al. 2005).

Environmental Benefits

Struvite fertilizer production and use can slow down the depletion of phosphate rock reserves. Phosphate rock fertilizer use increases at an annual rate of 2.5%, limited global reserves cannot keep up with an indefinitely increasing demand (Barrett and

Arnall 2011; Rhodes 2013; Mo and Zhang 2013; Molinos-Senante et al. 2011). Phosphorus continuously enters wastewater streams from human excretions and recovery of the material, as a ready to use fertilizer product, provides a sustainable phosphorus fertilizer for agricultural industries (Koch et al. 2003). Struvite fertilizer use may result in reductions for phosphate rock fertilizers causing a conservation of phosphate rock ore and resources used to process ores into fertilizer (Ostara 2009). Decreased phosphate rock fertilizer demands would mean conservation of water and energy used for ore mining and processing along with subsequent reductions in greenhouse gas emissions (Mo and Zhang 2013; Ostara 2009). Substituting 475 tons annually of phosphate rock fertilizer for struvite fertilizer can reduce greenhouse gas emissions by 4000 tons (Ostara 2009). It requires less energy, about 1/7th less, to produce struvite fertilizers versus phosphate rock fertilizers (Ostara 2012).

Unlike many phosphate rock fertilizers, struvite is not soluble in water (Molinos-Senante et al. 2011). The lack of solubility greatly reduces runoff from agricultural fields into nearby surface waters, thereby reducing eutrophication incidences (Molinos-Senante et al. 2011; Hao et al. 2013; De-Bashan and Bashan 2004). Struvite recovery at wastewater treatment plants reduces phosphorus concentrations in produced biosolids, bringing it to a level compliant with land application regulations. Instead of disposing of phosphorus rich biosolids at finite landfill sites, the material could be beneficially reused (Molinos-Senante et al. 2011; De-Bashan and Bashan 2004).

Functionality of Product

The properties of struvite, insolubility and slow-release, allows it to be used as a high-grade slow-release agriculture fertilizer (Molinos-Senante et al. 2011; Hao et al. 2013; Forrest et al. 2008; Shu et al. 2006; Pastor et al. 2008; Xavier et al. 2014; Uysal et al. 2010). The slow release of phosphorus nutrients from struvite, in comparison to release rates of phosphate rock fertilizers, allow for longer contact time with plants providing more efficient delivery of phosphorus (Shu et al. 2006; Barak and Stafford 2006). Insolubility properties further extend contact times between fertilizer and plant roots as nutrients are not washed away with watering or rain (Shu et al. 2006). A reduction in fertilizer application volume to agriculture fields for struvite fertilizer could be observed, due to increased nutrient delivery efficiencies and reduction in material losses (Uysal et al. 2010; Barak and Stafford 2006; Bhuiyan et al. 2008; Munch and Barr 2001). Struvite also has less trace element composition, preventing soil degradation and ensuring food crop safety through reduced fertilizer contaminant additions (Bhuiyan et al. 2008; Mavinic et al. 2007; Britton et al. 2005; Muster et al. 2013; Forrest et al. 2008). With a nutrient composition of 9.8% magnesium, 7.3% ammonium and 38.8% phosphate struvite provides a variety of nutrients essential for plant growth (Mohajit et al. 1989). Nitrogen (N), phosphorus (P) and potassium (K) are the major macronutrients involved in plant development, magnesium is also important for development as a micronutrient and is needed on a smaller scale. In some instances, due to soil composition, magnesium fertilizer additions are required along with NPK for optimal plant growth, in these situations the benefits increase for struvite fertilizer as it already contains magnesium, phosphorus and nitrogen (Munch and Barr 2001).

Potential Production Capabilities

Wastewater treatment plants throughout the world can produce a combined three megatons (three million metric tons) of phosphorus annually with struvite precipitation technologies (Childers et al. 2011; Dana Cordell, Drangert, and White 2009; Koppelaar and Weikard 2013; De-Bashan and Bashan 2004; Bradford-Hartke, Lant, and Leslie 2012; Shu et al. 2006). Pilot-scale testing supports this recovery estimation by recovering 90% of ortho-phosphate in domestic wastewater through struvite precipitation harvesting methods (Koch et al. 2003). These recovery rates will increase as human populations grow; for every additional one billion people excrement rates will add another 0.38 million tons of phosphorus to wastewater treatment plants (Shu et al. 2006). As of May 2015 the world population level of 7.3 billion people excretes enough phosphorus, if recovered, would correlate to 3.114 megatons of struvite fertilizer produced annually. Shown in Table 8 is the breakdown of phosphorus recovery rates for an increasing global human population. Beginning with 6 billion people and a phosphorus recovery potential of 2.62 megatons, 7 billion people provide enough resources to recover 3 megatons, 3.38 megatons can be recovered from a population of 8 billion, 3.76 megatons from 9 billion people, 4.14 megatons from 10 billion people and

4.52 megatons recoverable phosphorus from the 11 billion people predicted to be living on earth by 2100 (Andreev et al. 2013).

TABLE 8. HUMAN POPULATION INCREASES INCREASE AVAILABLE PHOSPHORUS IN WASTEWATER TO BE RECOVERED, ADAPTED FROM TABLE IN (Shu et al. 2006).

Human Population (billion)	*Recovered P_2O_5 (megaton)*
6	2.62
7	3
8	3.38
9	3.76
10	4.14
11	4.52

Conclusion

Current phosphorus removal systems are comprised of chemical precipitation techniques and EBPR treatment methods (Acelas et al. 2014; Bhuiyan, Mavinic, and Koch 2008; Shu et al. 2006). Chemical precipitation involves adding ferrous elements to wastewater to combine with the dissolved phosphorus. The chemically precipitated material adds to the volume of solids in the wastewater treatment system and is removed during solids treatment processes. Biosolids with phosphorus and ferrous elements do not degrade easily in the natural environment and disposal is often restricted to landfill deposition (Shu et al. 2006; Uysal et al. 2010). EBPR systems bind phosphorus to biosolids through microbial activity in secondary treatment, however phosphorus is re-released into liquid form during anaerobic digestion (Acelas et al. 2014). Phosphorus rich liquid from anaerobic digesters cycle back through the entire treatment facility as reject water (Liao et al. 2003; Munch and Barr 2001; Xavier et al. 2014; Pastor et al. 2008).

Utilization of struvite precipitation at wastewater treatment facilities instead of chemical precipitation and combined with EBPR systems for phosphorus removal recovers phosphorus in a solid form separate from biosolids production and can be used as a fertilizer product.

Sustainable Phosphorus Future

Recovering phosphorus from domestic wastewater could supply three megatons of phosphate fertilizer annually, however this production alone cannot support current annual global needs of 25 Mt (Bradford-Hartke et al. 2012; Cordell and White 2013). Despite the inability of struvite fertilizer to fulfill global demands, it is important to invest in struvite precipitation treatments at wastewater treatment facilities. The quality of phosphate rock ore used for fertilizers is degrading as natural reserves are rapidly depleted; the high-grade ore will be consumed leaving lower grade material for future needs (Sverdrup and Ragnarsdottir 2011). Low quality ore increases processing costs due to higher contaminant concentrations. As phosphate ore reserves dwindle a scarcity develops, further increasing phosphate fertilizer prices. Even with technological advancements in ore processing and mining operations, the future is presented with a shortage of phosphorus that is essential for food production (Cordell and White 2013).

As previously mentioned, struvite precipitation from domestic wastewater cannot fulfill the entirety of global demands, but combined with other reuse measures and production and use efficiency improvements of phosphate fertilizers, struvite can assist with creating a sustainable phosphorus future. The graph in Figure 16 visually demonstrates a possible sustainable future for phosphorus, with phosphorus recovery and reuse from human excreta by employing technologies such as struvite precipitation as one of the components. Phosphorus supplies can be augmented and substituted with material recovered from human excreta in domestic wastewater, animal manures, crop residues and food wastes. Decreases in global consumption as well as increased efficiency in agriculture, food production, and mining and fertilizer production will also be necessary to ensure phosphorus resources for future generations.

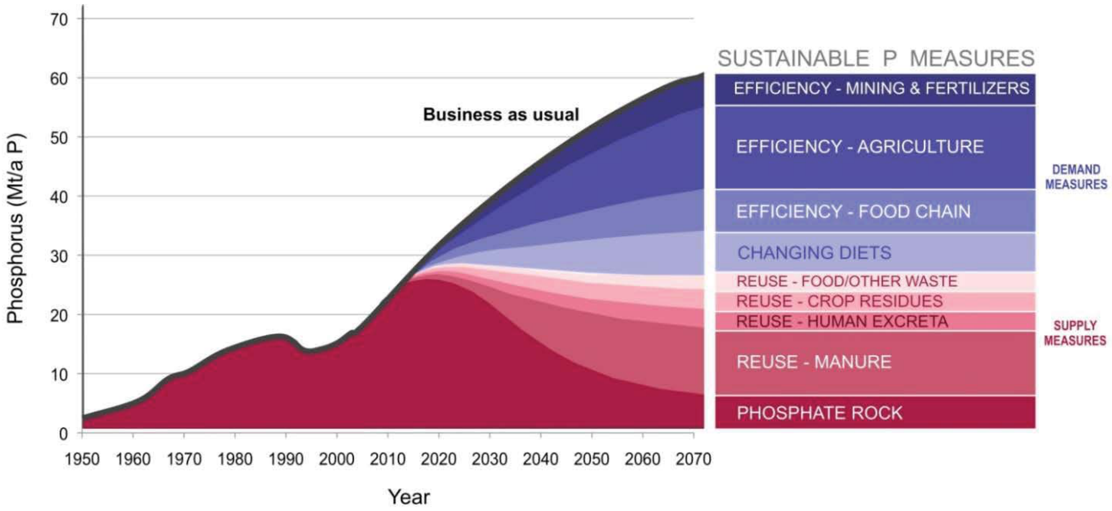


Figure 16. Projected global phosphorus demands with suggested source diversification and efficiency improvement to generate a sustainable future for phosphorus, taken from (Cordell and White 2013).

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