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# Phosphorus Fertilizer: The Original and Commercial Sources

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#### **Abstract**

Earlier the original source of phosphorus (P) fertilizer was bones; as time passes, the supply of P fertilizer will get exhausted. Today, rock phosphate is the only raw material in the form of P fertilizers. There are two types of rock phosphates: igneous and sedimentary; both have the same phosphate mineral, i.e., calcium phosphate of apatite group. The general formula for pure rock phosphate is  $Ca_{10}(PO_4)_6(X)_2$ , where X is F<sup>-</sup>, OH<sup>-</sup> or Cl<sup>-</sup>. These minerals are called apatites. The most common rock phosphate mined is fluorapatite, which contains impurities like CO<sub>2</sub>, Na and Mg. Carbonatefluorapatite (francolite) is primary apatite mineral in the majority of phosphate rocks. The high reactivity of some phosphate rocks is due to the occurrence of francolite. The major deposits are found in the US followed by China, Morocco and Russia. The US produced about 33% of the world's rock phosphate, although nearly 50% of the world reserves are in Morocco. P fertilizers are produced from either acid-treated or heat-treated rock phosphate to break the apatite bond and to increase the water soluble P content. There are many commercially available P fertilizers like rock phosphate, phosphoric acid, calcium orthophosphates, ammonium phosphates, ammonium polyphosphate and nitric phosphates.

Keywords: phosphorus, rock phosphate, fertilizer, apatites, fluorapatite

# 1. Introduction

0.12% of earth crust is made up of phosphorus mineral. P is a nonrenewable natural resource present in all types of rock and soils, in all living cells, and however can form complex compounds. Mineral deposits are the major supply of phosphorus. All phosphate mineral was



derived from apatite by weathering. Mostly phosphate is found in different forms like quartz, calcite, dolomite, apatite, Fe-oxide minerals and clay minerals. Apatite mineral is used for manufacturing fertilizers. Extraction of phosphorus depends on the physical properties of the rocks and its geological setting.

#### 1.1. Historical overview

Since ancient times man used natural resources such as manures, vegetables material, and bones as fertilizers. In 1840 Liebig, the German chemist, suggested the formation of superphosphate by dissolving bones in sulfuric acid that made the P more available to plants. This practice becomes so popular that bone supply is restricted in a very short time. To overcome this problem, some workers started extraction of phosphorus from rocks; in 1847 the first commercial production of P rocks from the mining of coprolites began in Suffolk in Great Britain and peaked in 1876 when about 25,000 metric tons were mined.

### 1.1.1. World phosphate reserves and resources

Presently all the Phosphate reserves that are found all over the world are not "mineable" deposits, as mining of them are not economically feasible. The United States is the highest phosphate-producing country in the world, while Morocco and China are the second and third countries with respect to phosphate production. Australia and Canada are recently known sites of phosphorus mining. There are rich deposits of phosphate found in Mongolia and Peru that will fulfill the need in the future. Florida phosphate industry becomes one of the major producer and exporter of phosphate fertilizer due to good transportation and industrial infrastructure facility in America and also because a substantial layer of phosphate is only 15 to 50 feet below a soft overburden. The phosphate mining in Central Florida overshadowed other sources because of low cost of mining, large deposits and the good quality of phosphate content of Florida rock. Florida is presently providing approximately 75% of the nation's supply of phosphate fertilizer and about 25% of the world supply. In 2000, mining operations began in Ontario, Canada, of North America. Florida's phosphate is part of a deposit that stretches across the state and up the coast to the Chesapeake Bay. The phosphate mining is expanded from Central Florida to Polk and Hillsborough counties, south, to Hardee, DeSoto, Manatee and Sarasota counties. In Northern Florida phosphate deposits are present in Hamilton, Columbia and Suwannee counties.

# 1.1.2. Discovery of phosphate in Florida

Some three decades ago in 1880, Dr. C. A. Simmonsin of England, who owned a rock quarry for building stone in Hawthorne, sends some of his rocks to Washington, DC, for analysis. The analysis determined the presence of phosphate in the rock samples, and in 1883 he made the first attempt for mining phosphate in Florida. But it was in 1889 by Albertus Vogt and others in Marion County who began the production of the first hard rock by the Marion Phosphate Company. This was later in 1890 followed by the Dunnellon Phosphate Company, in which Vogt had ownership interest, and in this way the area was flooded by thousands of prospectors, and the great Florida phosphate boom had begun. By 1894 more than 215 phosphate mining companies were operating statewide. The boom brought wealth. But in

1900 due to consolidation and capitalization, this number had dwindled to about 50. In 1881, Captain J. Francis LeBaron, chief engineer of the US Army Corps, during his survey of Peace River of Polk County, analyzed river pebbles and confirmed the presence of phosphate, but at that time this discovery did not catch much attention. In 1886 John C. Jones and Captain W. R. McKee, of Orlando, discovered high grade phosphate along the Peace River which led to the formation of an association known as the Peace River Phosphate. Mining activity along the Peace River proceeded both in the river itself and on the adjacent land. The so-called river pebble mining was the first to be exploited. In 1888, the first shipment of Peace River phosphate pebble was launched by Arcadia Phosphate Company about a year ahead of the Peace River Phosphate Company. This phosphate discovery was kept relatively quiet. Rumors of no phosphate in Central Florida spread as a result; Polk County's phosphate deposit took a back seat the first 15 years to the hard rock region to the north. The Florida Phosphate Company and the Pharr Phosphate Company were the two phosphate mining plants found in pebble district till 1890. In 1891 Pharr started shipment of land pebble for the first time; due to this there occurred a boom in the rate of river pebble production in 1893. Phosphate mining came to North Florida in the 1960s when Occidental Petroleum Company was looking for a way to get into the fertilizer business to get profit. Occidental went north and opened a mine in White Springs where it mined phosphate until 1995, when the Potash Corporation of Saskatchewan (PCS) purchased the operation. Nowadays Mosaic and PCS Phosphate, White Springs, are the two phosphate mining companies in Florida, and the third one are US Agri-Chemicals which produce phosphate fertilizers in Central Florida.

#### 1.1.3. Florida's phosphate deposits

A blanket of phosphate deposits covers much of the Peninsular Florida has a large phosphate deposits which consists of approximately equal parts phosphate rock, clay and sand, averages 12 to 15 feet in thickness. The matrix is buried beneath a soil that is 15–30 feet deep. By the end of 1999, approximately 300,000 acres of land, or more than 460 square miles, had been mined in Florida. Polk County is the heart of the Bone Valley mining region, and the mineable deposit in this area stretches to Hillsborough, Hardee, Manatee, and DeSoto counties. The large depositions were also found in mining in North Florida's Hamilton County from a mineable area that extends into Columbia and Suwanee counties. Similar deposition is found in both the areas. Mining in Central Florida has been moving south. As sites mine out, the draglines move to where the contiguous deposit of phosphate pebble is found. Toward the south the quality of rock decreases which brings technological challenges for the mining industries. During the past years, mining is slowed down in Polk County's southern fringe. In 2000 closing of IMC Clear Springs and Noralyn mines conveyed a close to active. Currently phosphate mining companies has opened new mining sites in Manatee, DeSoto and Hardee counties.

#### 1.1.4. Florida phosphate products today include

## 1.1.4.1. Diammonium phosphate (DAP)

The fertilizer that quickly became the item of commerce as most widely used by the growers today, and it had the highest concentration of phosphate and nitrogen at 18 N–46P<sub>2</sub>O<sub>5</sub>–0K<sub>2</sub>O.

# 1.1.4.2. Monoammonium phosphate (MAP)

This fertilizer is essentially the same as DAP, but it has a lower concentration of nitrogen at  $11 \text{ N}-52P_2O_5-0K_2O$ . It is completely water soluble and has granular material; it mixes well and frequently serves as an ingredient in bulk-blended fertilizers.

# 1.1.4.3. Granulated triple superphosphate (GTSP)

It is very similar to the superphosphate fertilizer that provides 46% P<sub>2</sub>O<sub>5</sub>, some calcium and sulfur to plants. GTSP is formed by reaction of phosphate rock with phosphoric acid.

#### 1.1.4.4. Superphosphoric acid

It's an acid used to make a concentrated or fluid fertilizer. PCS is the acid produced only by Florida Company in North Florida.

#### 1.1.4.5. Phosphoric acid

Phosphoric acid is used in granulation plants where ammonia is added to phosphoric acid to produce the ammoniated phosphate fertilizer. Purified food-grade phosphoric acid is used in making soft drinks.

#### 1.1.4.6. Animal feed supplements

Defluorinated phosphate rock or phosphoric acid is used to make animal feed supplements by combining phosphate rock with phosphoric acid, sodium carbonate and then calcine or react it with lime to get dicalcium phosphate.

#### Sulfuric acid

This acid is used to produce phosphoric acid after reacting with phosphate rocks at phosphate plants.

## 1.2. World resources

Sedimentary marine phosphorites are the principle resources of phosphate rock. The world's largest sedimentary reservoirs are found in North Africa, China, the Middle East, and the United States. Valuable igneous sedimentary reservoirs are also found in Brazil, Canada, Finland, Russia, and South Africa. Substantially large phosphate deposits have been spotted near the Atlantic Ocean and the Pacific Ocean shown in **Table 1** and **Figure 1**. World resources of phosphate rock are more than 300 billion tons. There are no imminent shortages of phosphate rock.

# 1.2.1. History of the development of phosphorus acid and its salts as agricultural chemicals

It was observed that applications of H<sub>3</sub>PO<sub>3</sub> and phosphite (Phi) were less effective as compared to phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and its derivatives on the first crop. With increasing rates of phosphite (Phi), phytotoxic effects were detected on the crop yield. However, nutritive role of

Countries	Mine production		
	2015	2016	
United States	27,400	27,800	
Algeria	1400	1500	
Australia	2500	2500	
Brazil	6100	6500	
China	120,000	138,000	
Egypt	5500	5500	
India	1500	1500	
Israel	3540	3500	
Jordan	8340	8300	
Kazakhstan	1840	1800	
Mexico	1680	1700	
Morocco and Western Sahara	29,000	30,000	
Peru	3880	4000	
Russia	11,600	11,600	
Saudi Arabia	4000	4000	
Senegal	1240	1250	
South Africa	1980	1700	
Syria	750	_	
Togo	1100	900	
Tunisia	2800	3500	
Vietnam	2500	2800	
Other countries	2470	2410	
World total (rounded)	241,000	261,000	

Table 1. Showing world production of phosphate in 2015 and 2016.

Phi in growth response was evident when compared to the zero-P control. Whereas researchers found Phi and H<sub>3</sub>PO<sub>3</sub> treatments beneficial to the second crop, this was due to probable conversion of Phi to phosphate in the soil. In general, better yield was obtained when Phi materials were used on soils with limestone. Further scientific studies related with the significance of H<sub>3</sub>PO<sub>3</sub> and its salts in agriculture did not occur for nearly 30 years, but rather their performance against plant diseases was mentioned [1]. During the disease control analysis, many incidents related to the plant's physical and chemical mobility were observed when the plants were treated with H<sub>3</sub>PO<sub>3</sub> or its salts in the absence of plant pathogens, some of which are described below. Ouimette and Coffey [2] reported that the Phi were more readily absorbed into plant tissues than phosphates—very important in crops with leaf surfaces that resist foliar spray uptake. In a comprehensive review given by Guest and Grant [3] related

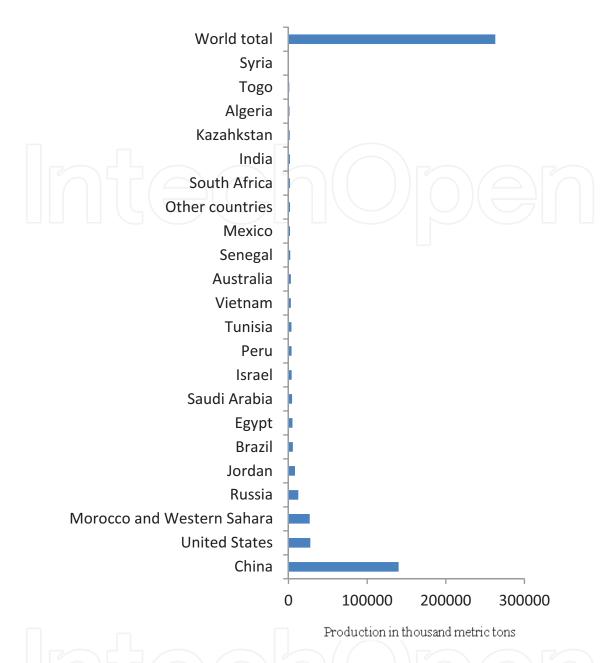


Figure 1. Phosphate rock production worldwide in 2017, by country (in 1000 metric tons).

with the complex action of phosphonates, several unique features of this chemical group were recounted. For example, Phi is a rapidly absorbing nutrient, which translocates from xylem to phloem according to normal source-sink relationships for nutrient element materials. Guest and Grant [3] reported that the Phi is more persistent as it metabolized slowly in plant tissue as compared with phosphate and does not participate in all the same biochemical pathways as phosphate. Adam and Conrad and Casida [4, 5] confirmed their results through experiments where bacterium *Pseudomonas fluorescens* 195 showed the ability to oxidize Phi and also discharge it in the growth medium as phosphate. Malacinski and Konetzka [6] repeated the same work and reported that a short adaptive period was required before oxidation of Phi by organisms, and this whole process took 14–15 weeks. Bezuidenhout et al. [7] during their study

reported first time that the Phi can also be converted microbially to phosphate within plant tissues and identified three genera of bacteria (Alcaligenes, Pseudomonas and Serratia). These findings complemented the previous observations given by Rothbaum [8] that elemental P in soil was oxidized non-enzymatically under particular temperature and water. Busman et al. [9] reported that the phosphate fertilizer applied to the soil will not be utilized by the crop in the first season. Rothbaum and Baillie [8, 10] observed that Phi was less adsorbed than phosphate by the same soil. This lower 'phosphate fixation' improved growth of Phi-treated soil, with a period gap, as compared to phosphate-treated soil. Rhone-Poulenc Ag Company of the United States expressed concern to the US Environmental Protection Agency (EPA) about classifying a fungicide based on H<sub>3</sub>PO<sub>3</sub> salts as a biochemical pesticide and affirmed the non-enzymatic oxidation of Phi to phosphate occur naturally over time. Lovatt [11] discovered that foliar application of K<sub>2</sub>PO<sub>3</sub> to P-deficient citrus seedlings restored plant growth. This demonstrated that through metabolic processes, Phi was readily taken up by plant leaves and replaced phosphate as a source of Frazier and Waerstad [12] tested the composition and solubility of Phi to analyze the potential of this class of materials for increasing the plant nutrient element content of liquid fertilizers. Albrigo [13] reported the positive response of Phi on winter prebloom foliar of Valencia oranges which were increased flower number, fruit set and yield, plus increased total soluble solids. Additional studies by Lovatt [14] on foliar fertilization of citrus showed that application of K<sub>3</sub>PO<sub>3</sub> in May and July to navel orange significantly increased the number of large-size fruit, total soluble solids and the ratio of soluble solids to acid, compared to control fruit. Biagro Western Sales, Inc., Visalia, CA, took the lead in commercialization of Phi-supplying fertilizer products patented by the University of California Anon and Lovatt [15, 16]. Today farmers are well educated and formed community of producers; they analyze themselves the effect of new Phi products on both soil and crop. In a practical sense, acceptance by discriminating growers is strong evidence that the benefits of H<sub>3</sub>PO<sub>3</sub>-derived fertilizers are standing up to their ultimate test—the real world of agricultural crop production.

# 1.2.2. Rock phosphate: its availability and solubilization in the soil

Rock phosphate is one of the basic raw materials needed in the manufacture of phosphatic fertilizers like single superphosphate, diammonium phosphate, nitrophosphates, etc. Commercial rock phosphate occurs in nature as deposits of apatites (bearing minerals) along with other accessory minerals such as quartz, silicates, carbonates, sulfates, sesquioxides, etc. Four types of rock phosphate minerals are carbonate apatite  $[3Ca_3(PO_4)^2.CaCO_3]$ , fluorapatite  $[3Ca_3(PO_4)_2.Ca(OH)_2]$ , and sulpho apatite  $[3Ca_3(PO_4)_2.CaSO_4]$ . Because of their well-developed crystalline formation property, the apatites of igneous and metamorphic origin are generally regarded as less reactive. However, the apatites of sedimentary rock deposits are soft minerals possessing microcrystalline structure and are of major commercial importance for direct application in the soil [17].

#### 1.2.3. *Grades of rock phosphate*

The classification of reserves of indigenous rock phosphate as done by the Indian Bureau of Mines, and the purpose for which each grade can be used is given in **Table 2**.

Grade	P <sub>2</sub> O <sub>5</sub> (%)	Reserve (mt)	Remarks	
High	+30	15.27	Considered for wet production of fertilizers	
Medium	25–30	18.95	Considered mainly for partially acid rock phosphate and for processed phosphates after less beneficiation	
Low	11–25	55.22	Approx. $20\%  P_2O_5$ grade and relatively more reactive material may be considered for partially acidulated rock phosphate production and others for direct application	
Unclassified		170.04		
Total		259.48		

Table 2. Classification of known reserves of indigenous rock phosphate in India.

# 1.2.4. Availability of rock phosphate

Including all grades and types of rock phosphate, the known global resources are in the order of 163,000 million tons. Though globally adequate, rock phosphate is inequitably geographically distributed. Africa holds about 41%, the United States has 21%, former USSR 13%, the Middle East 10%, Asia 8%, and South America 3%, while Australia, New Zealand and Oceania together reported for only 2% and Europe >1%. Phosphate rock resources in India is, however, not very comfortable as it possesses a resource of only 260 million tons (0.19% of the world) of rock phosphate of all types and grades, catering the agricultural needs of 1/6 of the population of the world. Out of the total rock phosphate resource, the country has a predominance of low grade rock phosphate having only 15.27 million tons reserve of high grade rock phosphate (**Table 1**), and the remaining low grade rock phosphate is unacceptable to P fertilizer industry due to its very low P<sub>2</sub>O<sub>5</sub> and high CaCO<sub>3</sub> content [18]. The current annual domestic demand of high grade rock phosphate is of the order of 4 million tons. Out of which 95% is consumed in agriculture sector as a source of P fertilizer. The domestic production of about 1.4 million tons/year of rock phosphate could hardly meet 35% of the total demand, and the remaining (65%) demand is met through imports. P fertilizer industry largely depends on sulfur, phosphoric acid, and ammonia besides rock phosphate. India imports around 1.7 million tons of sulfur, 2–4 million tons of phosphoric acid, 1.5 million tons of NH<sub>3</sub> and 4.9 million tons of rock phosphate for phosphate industry which constitutes a substantial part of our international trade in fertilizer raw material. Thus, the rapidly increasing price of soluble phosphatic fertilizer has raised interest in cheaper alternatives. Under such conditions, we must explore new methodologies for the utilization of indigenous low grade rock phosphate by converting it into a potential resource of P for direct application to the soil. The direct utilization of indigenous rock phosphate deposits could only alleviate the dependence of the country on foreign suppliers.

# 1.2.5. Factors affecting rock phosphate dissolution

Soils has an eminent reserve of total P, but very little amount of P is actually available to the plants to support their growth to fulfill the requirement; continuous application of phosphate

fertilizers is essential for increasing crop yield. Water solubility of phosphate fertilizers depends on both acidic and neutral to alkaline conditions. Several factors that influence the application of rock phosphate as P fertilizer are rate of dissolution, soil characteristics, plant species and fertilizer.

#### 1.2.6. Dissolution

Factors which determine rock phosphate dissolution rate are its lattice composition, accessory mineral type and particle size. Solubility of apatites increased by substituting CO<sub>3</sub><sup>2-</sup> for PO<sub>4</sub><sup>3-</sup> in the lattice structure due to decrease a-dimension of the unit cell, and crystal instability [19]. Silverman et al. [20] reported Calcium carbonate as the soluble apatite as compared to other apatites. Rate of its dissolution increases with the concentration of Ca<sup>2+</sup> and pH at the surface of apatite, and therefore it reduces the rate of rock phosphate dissolution in soil. The rate of dissolution reduced under field conditions due to leaching or plant uptake of calcium ions. The rate of dissolution increases as the particle size decreases; this might be because fine particle size has greater degree of contact between rock phosphate and soil.

# 1.2.7. Soil properties affecting rock phosphate dissolution

The rate of dissolution of rock phosphate also depends on the chemical properties and type of soil to which it is applied. As compared to other parameters, pH buffering capacity was very important in soil. Earlier studies indicated that the amount of rock phosphate-P decreased with the increase in soil pH. The rate of dissolution of rock phosphate was highly sensitive to Ca<sup>2+</sup> activity in the soil solution. A linear relationship between the log of Ca<sup>2+</sup> activity and log of P in soil solution has been reported by Robinson and Syers [21]. Phosphate retention capacity and soil moisture also affect rock phosphate dissolution of the soil to retain P. Wet soil enhances the rate of phosphate dissolution by allowing the dissolution products. The product transported away from the surface of the rock phosphate particles and recognized the positive effect of organic matter on rock phosphate dissolution.

#### 1.2.8. Influence of plant species on rock phosphate dissolution

Ability of plants to extract P from rock phosphates was recognized by Merril, quoted in Flach et al. [22]. Plants affect the dissolution by the secreting acid or alkali, through Ca uptake, production of chelating organic acids such as citric, malic and 2-ketogluconic acids which complex Ca and deplete P in the soil. Roots of the plants induced change in rhizosphere pH which causes imbalance in the proportion of anionic (usually NO<sub>3</sub>–, H<sub>2</sub>PO<sub>4</sub>–, SO<sub>4</sub><sup>2–</sup> and Cl<sup>–</sup>) and cationic nutrient (K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>) uptake by the plants. The imbalance in the rhizosphere is maintained by the release of either H<sup>+</sup> or OH<sup>–</sup>/HCO<sup>3–</sup>, thus balancing the pH of the rhizosphere. Acidic soil enhances the rate of rock phosphate dissolution. Effective rock phosphate utilization by plant species such as e.g., buckwheat and rapeseed has been responsible for their high Ca uptake. Flach et al. [22] assessed the ability of maize, pearl millet and finger millet to utilize P from rock phosphates by a pot experiment and concluded that plant species influence P dissolution; therefore, choice of crop is very important to maximize the solubility of rock phosphate.

# 2. Phosphorus scarcity

Today growing extraction and consumption of phosphate is exhausting existing deposits, and therefore the rate of P reserves depleting. This means that at a certain point time comes when all the phosphorus reached to the alarming peak and that condition is called 'peak phosphorus' according to literatures. This condition will be calculated on the basis of phosphate rock reserves. Since no consensus was there on the size of these reserves, so nobody knows when will be the peak phosphorus stage will occur. Peak phosphorus has been calculated by the Global Phosphorus Research Initiative (GPRI). In 2009 the GPRI estimated that phosphorus production would peak around the year 2033 and that afterward production will continuously decrease until reserves are depleted within the next 50-100 years. The US Geological Survey (USGS) re-estimated reserves at 60,000 mmt up from previous estimates of 16,000 mmt; the IFDC stated that 'there is no indication of "peak phosphorus" event within the next 20–25 years. The concept of peak phosphorus itself is contested; the main fault in the calculations of peak phosphorus is based on phosphate rock reserves not resources which provide the basis for estimation of static ranges. Phosphate rock reserve data explained by national geological surveys do not point out the absolute quantity of an element which is available for extraction, as the static paradigm would suggest. According to the 'dynamic adaptive paradigm', due to changes in economic feasibility, scarcity in the production of phosphate rock occurs. This paradigm led to scarcity which is a permanent feature of human existence: minerals become scarce as long as they are immensely valued in the society, and how much time and effort it takes to extract them, and they are related to all other goods and services in the society. Shortage of phosphate rock is an important issue when observed from a different angle that is other than relative availability. One of the reasons of fall in phosphate rock exports is the geopolitical turmoil in supplier regions. Scarcity may also result by lack of water available to the mining industry. Price inelasticity of supply, time and investments are the limiting factors which can lead to scarcity of phosphorous rock.

# 3. Phosphorus sustainability

Nowadays the good news is that crisis can be averted. Almost 4/5 of the phosphorus mined for food production never actually reaches the food on our forks. We can therefore invest in renewable phosphate fertilizers or innovations in on-farm efficiency to safeguard our farmers, our agriculture and food consumers. In every sector recycling of phosphorous is efficiently taking place from agriculture and mining to sanitation sector to changing diet (**Figure 2**) [23]. To meet long-term phosphorous demand of society, we have to face the technical and institutional challenges for implementing practical solutions. An integrated, context-specific approach should be developed over partial measures. Technologies and practices with effective policy instruments (regulatory, economic, facilitation) are required to encourage and bear such measures.

Food demand is rising globally with no slowing down in sight. Especially in China and other rapidly growing economies, more demand for meat and dairy means more demand for

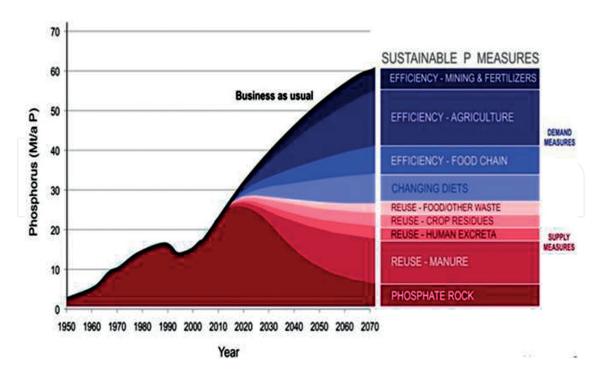


Figure 2. Sustainable phosphorus measures: Efficiency, recycling and changing diets.

fertilizers, while human body only needs around 0.4 kg of P each year. 22.5 kg of phosphate rocks are mined to meet the requirement of phosphate for each person's diet. For growing population water and energy are considered as critical for meeting future demands of food for increasing population. However, there is no approximated value of phosphorus scarcity in future as a limiting factor. Thus far we can say that without phosphorus, there would be no food and life on earth. There is no single international body responsible for managing global P resources currently in the long term, unlike oil, water and nitrogen.

# 4. Phosphorus recovery

Phosphorus can be recovered and used over and over again if present in sufficient concentrations dissimilar to oil, which is lost once it is used. Between the phosphate reserves and the food which we eat, up to 80% of P is lost in the process from production of fertilizers, application of phosphate on fields, in food processing and final consumption. With the increasing efficiency of phosphorous, we have to carry on recovery process of P from residues of crops, waste food items in dumpsters, manure, human excreta, struvite and other sources such as bone meal, ash and algae. A key opportunity to meeting the goal of global food security lies in the often overlooked link between addressing hunger and sanitation. In agriculture P plays a critical role as a nutrient, and but on the other hand, it is also considered as an environmental pollutant due to sewage emerging from human settlements. Human activities produce 3 million tons of P each year. If this P is recirculated back in agriculture fields from where they first came, we can maintain balance in sustaining food production in the decoupled communities which are dependent on globalized P fertilizer markets.

# 5. Conclusions

It may be concluded that evolution of phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) and its salts as fertilizers owes much to both the early investigators searching for phosphate replacements and to the many scientists who later sorted out the relevant facts about plant response to Phi through phytopathological research. In recent years, scientific aroused their interest in the nutrient properties of H<sub>2</sub>PO<sub>2</sub>-derived products which stimulate their commercialization of H<sub>2</sub>PO<sub>2</sub> as fertilizers. Trails of these fertilizers on crops have given fruitful results. The nutritive properties of Phi products proved to be a useful addition to producers' resources. Phi fertilizers elicit positive responses to crop like it enhances flowering and fruit set in cirrus and are converted to phosphate through oxidation process. H<sub>3</sub>PO<sub>3</sub> derivatives give similar responses as that of orthophosphate in fertilization of crops, despite sometimes delayed. Phosphorus acid-derived fertilizers provide a more readily available source of P than that which occurs in soil. Phi products provide more phosphorus to plants as compared to phosphate fertilizers due to their high efficacy of phosphorus uptake through plant foliage. Earlier concept of not using phi as P fertilizers is now changed due to positive results recorded by the scientist about the use of these products as fertilizers. Thus we can reduce a lot of financial burden from our economy by reducing the import of rock phosphate and other by-products required in the manufacture of commercial P fertilizer.

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#### References

[1] MacIntire WH, Winterberg SH, Hardin LJ, Sterges AJ, Clements LB. Fertilizer evaluation of certain phosphorus, phosphorous, and phosphoric materials by means of pot cultures. Agronomy Journal. 1950;42:543-549

- [2] Ouimette DG, Coffey M. Phosphonate levels in avocado (*Persea americana*) seedlings and soil following treatment with fosetyl-Al or potassium phosphonate. Plant Disease. 1989;73:212-215
- [3] Guest D, Grant B. The complex action of phosphonates as antifungal agents. Biological Reviews. 1991;66:159-187
- [4] Adam F, Conrad JP. Transition of phosphate to phosphate in soils. Soil Science. 1953;75:361
- [5] Casida LE. Microbial oxidation and utilization of orthophosphite during growth. Journal of Bacteriology. 1960;80:237-241
- [6] Malacinski G, Konetzka WA. Bacterial oxidation of orthophosphite. Journal of Bacteriology. 1966;**91**:578-582
- [7] Bezuidenhout JJ, Darvas JM, Kotze JM. The dynamics and distribution of phosphite in avocado trees treated with phosetyl-Al. South African Avocado Growers' Association Yearbook. 1987;10:101-103
- [8] Rothbaum HP, Baillie WJH. The use of red phosphorus as a fertilizer. Part 4. Phosphite and phosphate retention in soil. New Zealand Journal of Science. 1964;7:446-451
- [9] Busman L, Lamb J, Randall G, Rehm G, Schmitt M. The Nature of Phosphorus in Soils [Internet]. 1997. URL http://www.extension.umn.edu/Documents/D/C/ DC6795. html. Communication and Educational Technology Services, University of Minnesota Extension Service; St. Paul, MN
- [10] Larochelle DA. Letter to OPP/USEPA with Attachment by Helfant L, Castellino S. Dated July 18, 1996. Rhone-Poulenc Ag Company; Research Triangle Park, NC
- [11] Lovatt CJ. Foliar phosphorus fertilization of citrus by foliar application of phosphite. In: Citrus Research Advisory Committee (ed.). Summary of Cirtus Research. Rierside, USA: University of California; 1992. pp. 25-26
- [12] Frazier AW, Waerstad KR. Crystallography and equilibrium solubility for ammonium and potassium orthophosphites and hypophosphites. Fertilizer Research. 1992;32:161-168
- [13] Albrigo LG. Foliar application of major elements for flowering and fruit set. Indian River Citrus Seminar, 50th Anniversary. 1997
- [14] Lovatt CJ. Managing yield with foliar fertilization. Citrograph. 1998;84:8-13
- [15] Anon. Nutri-Phite P soil; Nutri-Phite P+K; and Nutri-Phite P foliar. In: Nutri-Phite? Visalia, CA: Fertilizer Product Labels. Biagro Western Sales, Inc.; 1996
- [16] Lovatt CJ. Formulation of phosphorus fertilizer for plants. U.S. Patent No. 5, 514, 200. 1996
- [17] Biswas DR, Narayanasamy G. Research note: Mobilization of phosphorus from rock phosphate through composting using crop residue. Fertilizers News. 2002;47(3):53-56

- [18] McLean EO, Ssali N. Effect of phosphorus rate and form with combination with lime and gypsum on yield and composition of German millet and alfalfa form highly weathered soil. Soil Science. 1977;123:155-166
- [19] Lehr JR, McClellan GH. TVA Bulletine. Y-43. Muscle Shoals, Albama: Tennessee Valley Authority (TVA); 1972
- [20] Silverman SR, Ruth KF, Jeanne DW. Quantitative determination of calcite associated with carbonate bearing apatites. U.S. Geological Survey; 1951. pp. 211-222
- [21] Robinson JS, Syers JK. Effects of solution calcium concentration and calcium sink size on the dissolution of Gafsa phosphate rock in soils. Journal of Soil Science. 1991;42:389-397
- [22] Flach EN, Quak W, Diest AV. A comparison of the rock phosphate-mobilizing capacities of various crop species. Tropical Agriculture. 1987;64:347-352
- [23] Cordell D, White S. Sustainable phosphorus measures: Strategies and technologies for achieving phosphorus security. Agronomy. 2013;3(1):86-116. http://www.mdpi.com/2073-4395/3/1/86

