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Global Material Analysis on Phosphorus Flows, Supply Horizon and Impact Assessment of Phosphorus Depletion

Análise Global de Fluxo Material do Fósforo Fluxos, Alternativas e Avaliação do Impacto do Esgotamento do Fósforo

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Preface

The present master thesis "Global Material Flow Analysis on Phosphorus flows, supply horizon and impact assessment of phosphorus depletion" was developed in Institute of Chemical Engineering, Biotechnology and Environmental Technology, Faculty of Engineering, University of Southern Denmark(Odense) with the guidance from the Professor Henrik Wenzel and the co-supervisors were Nassera Ahmed, Birgitte Lilholt Sørensen and Sven Sommer.

The master thesis is rewarded with 42 ECTS points during the period from November to 4st of June.

In order to develop this thesis, it was very important to get the help of many people. They were very helpful in giving me relevant information and also answering to the questionnaire interview. I want to thank:

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I thank also my family and friends for all support during my work. This work is dedicated to a special friend, Maria Olinda.

Summary

Different problems are daily discuss on environmental aspects such acid rain, eutrophication, global warming and an others problems. Rarely do we find some discussions about phosphorus problematic. Through the years the phosphorus as been a real problem and must be more discussed.

On this thesis was done a global material flow analysis of phosphorus, based on data from the year 2004, the production of phosphate rock in that year was 18.9 million tones, almost this amount it was used as fertilizer on the soil and the plants only can uptake, on average, 20% of the input of fertilizer to grow up, the remainder is lost for the phosphorus soil. In the phosphorus soil there is equilibrium between the phosphorus available to uptake from the plants and the phosphorus associate with other compounds, this equilibrium depends of the kind of soil and is related with the soil pH.

A reserve inventory was done and we have 15,000 million tones as reserve, the amount that is economical available. The reserve base is estimated in 47,000 million tones. The major reserves can be found in Morocco and Western Sahara, United Sates, China and South Africa. The reserve estimated in 2009 was 15,000 million tone of phosphate rock or 1,963 million tone of P. If every year the mined phosphate rock is around 22 Mt/yr (phosphorus production on 2008 USGS 2009), and each year the consumption of phosphorus increases because of the food demand, the reserves of phosphate rock will be finished in about 90 years, or maybe even less.

About the value/impact assessment was done a qualitative analysis, if on the future we don't have more phosphate rock to produce fertilizers, it is expected a drop on the crops yields, each depends of the kind of the soil and the impact on the humans feed and animal production will not be a relevant problem.

We can recovery phosphorus from different waste streams such as ploughing crop residues back into the soil, Food processing plants and food retailers, Human and animal excreta, Meat and bone meal, Manure fibre, Sewage sludge and wastewater. Some of these examples are developed in the paper.

Resumo

Nestes últimos anos as questões ambientais são cada vez mais estudadas, diariamente fala-se em problemas tais como o aquecimento global, emissão de gases poluentes, poluição de águas. Por outro lado, a depleção de recursos naturais tem menos impacto na comunicação social.

A quantidade de fósforo existente no nosso planeta *versos* a sua utilização constitui hoje em dia um grande problema ambiental. As reservas de fósforo existentes são finitas tais como a do petróleo, e a extracção do fósforo tem sido crescente de acordo com as necessidades mundiais.

O fósforo é um componente essencial para o crescimento das plantas e grande parte do fósforo produzido é utilizado na agricultura como fertilizante. No entanto o ciclo natural do fósforo é muito lento podendo levar um milhão de anos para formar e existir fósforo sob a forma disponível para extracção.

Por esta razão, na presente tese a Análise de Fluxo Material (MFA) feita só é considerado no ciclo do fósforo a quantidade anual extraída, a produção dos diversos produtos contendo fósforo, e os principais fluxos de uso do fósforo.

O grande objectivo da elaboração do MFA foi ter uma noção da ordem de grandeza de fósforo perdido no ambiente, para posteriormente estudar os impactos ao nível do crescimento das plantas bem como nos humanos e animais. O MFA realizado permite concluir que no ano de 2009 a reserva de fósforo em rocha com potencial para ser extraída foi estimada em 15.000 Mt de fósforo, e a produção deste elemento foi de 1.963 Mt, o que significa que as reservas de fósforo terminarão em 90 anos, ou talvez menos.

Nesta tese foram avaliadas hipóteses para os possíveis impactos no caso de não haver fósforo para fertilizar os solos, caso as reservas de fósforo terminem dentro deste século, como previsto por dados estatísticos das reservas existentes e da sua produção anual.

Foi avaliado o impacto causado no crescimento das plantas, se houver um défice de fósforo na terra onde a planta está a desenvolver-se, os dados de diferentes testes comprovam que influenciará o crescimento das plantas, principalmente o crescimento das raízes. No entanto numa entrevista com um especialista nesta área, este é da opinião que a planta irá adaptar-se

desenvolvendo as raízes de modo a procurar fósforo noutros níveis da terra, portanto não terá grande impacto.

Estudou-se também o impacto na produção de agrícola e em discussão com diferentes especialistas agrónomos, de um modo genérico, ao longo do tempo a produção irá decair, pois existe ainda uma quantidade de fósforo disponível no solo (disponibilidade depende predominantemente do pH), quando terminar o fósforo disponível no solo a disponibilidade irá depender da capacidade de adaptação da planta em desenvolver raízes de modo a procurar fósforo noutras camadas da terra.

Inicialmente na equipa de estudo onde estava inserida, supôs-se que se há menos fósforo disponível para a planta nos solos, logo a planta também teria menos fósforo. As plantas contendo menos fósforo iriam causar um impacto na alimentação dos humanos e animais. Mas, diferentes agrónomos são da opinião que a quantidade de fósforo irá manter-se igual nas e mesmo que houvesse um decréscimo os humanos consomem mais fósforo do que realmente necessitam diariamente.

Portanto é necessário procurar soluções pois o maior impacto será na produção agrícola, o que provavelmente irá gerar também conflitos socioeconómicos.

Com vista a minimizar os consumos de fósforo, recuperar fósforo em fluxos que são perdidos para a natureza, já existem em diferentes partes no mundo métodos de reciclagem/recuperação. A Suécia é um bom exemplo, pois tem sanitas próprias para separar a urina das fezes, de modo a recuperar a urina e utilizá-la directamente como fertilizante, visto a urina conter uma elevada percentagem em fósforo. Outro caso de sucesso, é uma empresa que desenvolveu um fungo que é capaz de transformar o fósforo que esteja não disponível para a planta no solo numa forma disponível para absorção da planta.

É obvio que a depleção dos recursos do fósforo é um problema a nível ambiental, mas ainda há vários estudos que podem vir a ser feitos e também é essencial a divulgação desta problemática à sociedade, para uma tomada de consciência colectiva.

List of Contents

List of Figures

List of tables

Abbreviations

MFA – Material Flow Analysis

Mt- Million tones

N – Nitrogen

P – Elemental Phosphorus

P_2O_2- Phosphoric acid

1. Introduction to Project Work

1.1. Problem description

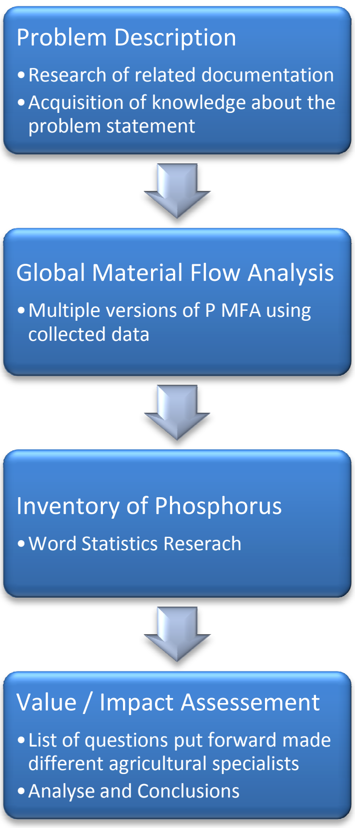
The scope of this work is to present the most important phosphorous flows in the world and analyze consumption impacts on the environment. Phosphorus is very important to the plants growth, and plants are important to feed humans and animals. As phosphate rock is a non-renewable resource and can be exhausted in about 50 – 100 years, it is important to know if we can recycle phosphorous from the waste streams or maybe it will be not enough and we will need to find other solutions.

1.2. Objectives

The general objectives of this Master thesis are:

I. To carry out a global material flow analysis on phosphorous in order to reveal the mass flows.
II. To make the phosphorus resource reserve inventory. The reserve inventory along with the flow analysis should be able to estimate the supply horizon of phosphorus.
III. To carry out a value assessment/impact assessment.

1.3. Project flow diagram



2. Introduction to Phosphorus Problematic

2.1. Phosphate rock and its characteristics

Phosphorus is the eleventh most abundant element in the lithosphere. Owing to its relative reactivity, it is generally associated with calcium (Ca), sodium (Na), fluorine (F), chloride (Cl), metals such as iron (Fe), aluminium (Al), magnesium (Mg), heavy metals, for example cadmium (Cd), radionucleids like uranium (U) etc. In reality almost every element that can be found in the periodic table is represented in phosphate rock.

There are two main types of phosphate rock deposits, igneous and sedimentary, which have widely differing mineralogical, textural and chemical characteristics.

The most prevalent phosphate minerals in these rocks are species of apatite, i.e. calcium phosphate with quartz, calcite, dolomite, clay and iron oxide as gangue components. Igneous rock is often associated with carbonatites and/or alkalic intrusions and is generally low in grade i.e. low concentration of phosphate. The abundance ratio of igneous versus sedimentary rock is 13 to 87. Some 80% of the world phosphate production is derived from sedimentary phosphate deposits.

More than 75% of the globally commercially exploited phosphate rock is surface mined, which can take many forms from manual methods to the employment of highly mechanized technologies, with the remainder recovered by underground mining.

Phosphate content in currently mined rocks can range from over 40% to below 5%. The mined rock is further processed to remove the bulk of the contained impurities and thus upgrade the rock. Consequently, the rock concentrate contains an increased apatite content of an improved quality. The beneficiation process usually allows a concentration of around 1.5x but higher ratios up to 9x are possible with some rocks. After beneficiation, phosphate rock (concentrate) generally ranges from 26% to about 34% P_2O_5 and up to as much as 42%.

Phosphate rock can be beneficiated by many methods, and usually a combination of methods is used. In general, with the lower concentration of phosphate and lower quality deposit, the more waste is generated. Furthermore, more energy and chemicals are required per ton of useful phosphate produced. Consequently, the cost for recovery and beneficiation of phosphate rock increases significantly in relation to lower grade and lower quality deposit. An analysis of production costs must thus be an integral part in the assessment of the lifetime of phosphate deposits and the likely cost of fertilizers in the future.

Most phosphate rock is further processed, but very small volumes are applied directly to acidic soils as fertilizer (NHM, 1998).

2.2.Importance of Phosphorous

While access to water and energy sources are now understood to be limiting factors to achieving global food security, the implications of future phosphate scarcity has not received explicit mention in key dialogues on global food security. Fig. 1 depicts four of the key current discourses on global food security, illustrating that phosphorus is missing from the picture and could be added (Cordell, 2008).

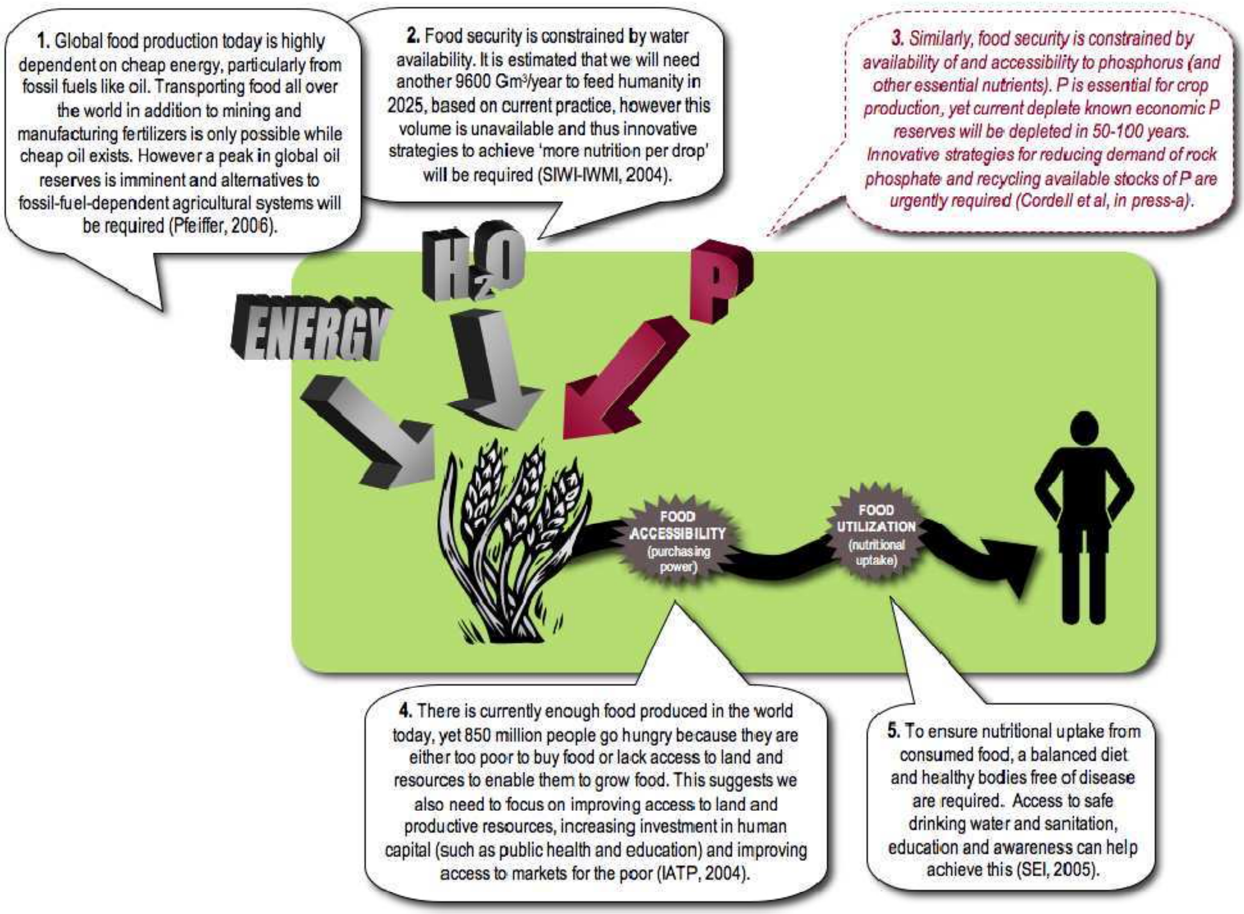


Figure 1 - Dominant discourses on global food security: including accessibility to food, health, energy and water (Cordell, 2008).

Phosphorus in the context of food production and the environment is most commonly framed as an environmental pollutant, which together with nitrogen, contributes to eutrophication and algal blooms worldwide. However, phosphorus is simultaneously a critical nutrient input in agriculture whose global reserves are being rapidly depleted. Rarely are phosphorus pollution and phosphate scarcity discussed in the same context.

The risks of not considering systemic links are exemplified by the recent increased global concern about oil scarcity and climate change leading to a rapid production boom of biofuel crops which not only compete with food production for prime fertile land, yet require profuse amounts of phosphorus fertilizers. This sudden increased demand for fertilizers worldwide has contributed to the seven-fold increase in the price of phosphate rock. In this sense, the peak oil problem is being shifted to a peak phosphorus problem, making the 'supra'-system unsustainable in the long-term (Cordell, 2008)

2.3.The utilization of phosphorus

Crop production relied on natural levels of soil phosphorus and the addition of locally available organic matter like manure and human excreta (Maarald, 1998). To keep up with increased food demand due to rapid population growth in the 20th century, guano and later rock phosphate were applied extensively to food crops (Brink, 1977; Smil, 2000b). Fig. 2 gives a broad outline of the evolution of phosphorus fertilizer use for food production.
A long time ago, the Chinese civilization used human excreta as fertilizer, like the Japanese civilization did (Matsui, 1997).
In Europe, soil degradation and recurring famines during the 17th and 18th centuries created the need to supplement animal and human excreta with other sources of phosphorus (Maarald, 1998). In the early 19th century, for instance, England imported large quantities of bones from other European countries. In addition to the application of phosphorus from new sources, improved agricultural techniques enabled European agriculture to recover from the famines of the 18th century (Maarald, 1998). These improvements included crop rotation, improved handling of manure, and in particular, and the introduction of new crops such as clover which could fix nitrogen from the atmosphere.

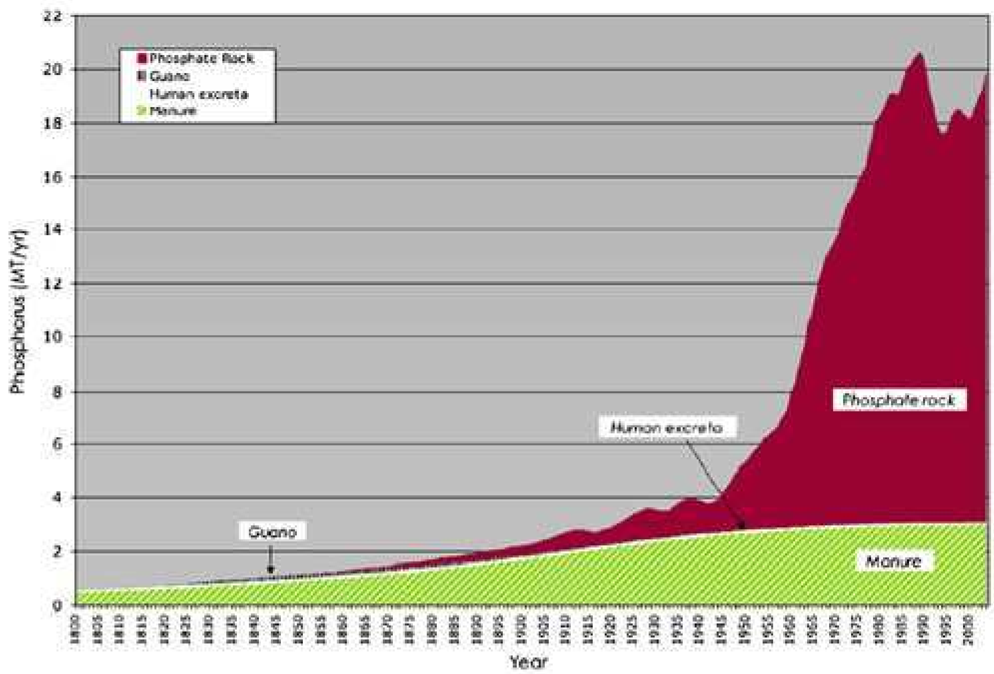


Figure 2 - Historical sources of phosphorus fertilizers since 1800 until 2000, based in calculation from Brink (1997), Buckingham and Jasinski (2004), IFA (2006) and Smil (2000b), (Cordell *et al*. 2009).

In 1840 Liebig formulated the ‘mineral theory’, which replaced the ‘humus theory’ that plants and animals were given life in a mysterious way from dead or decomposing plants and animals (Liebig, 1840; Maarald, 1998). Liebig provided a scientific explanation: nutrients such as nitrogen, phosphorus and potassium were elements circulating between dead and living material (Maarald, 1998). This discovery occurred during a period of rapid urbanization in Europe, when fertilizer factories were being established around growing cities. Food production was local and the factories manufactured phosphorus fertilizers from locally available organic waste products, such as human excreta, industrial organic waste by-products, animal dung, fish, ash, bones, and other slaughterhouse by-products (Maarald, 1998; Neset *et al.*, 2008). However, around the mid-to-late 19th century, the use of local organic matter was replaced by phosphorus material from distant sources. The mining of guano (bird droppings deposited over previous millennia) and phosphate-rich rock had begun (Brink, 1977; Smil, 2000b). World trade in guano grew rapidly, but it relied on a limited resource which declined by the end of the 19th century (Stewart *et al.*, 2005). Phosphate rock was seen as an unlimited source of concentrated phosphorus and the market for mineral fertilizers developed rapidly. At the same time, the introduction of flush toilets in towns meant that human waste was discharged into water bodies instead of being returned to the soil. There were protests among intellectuals that farmers were being robbed of human manure.

Trade in food grew steadily with urbanization and colonization, but insufficient amounts of nutrients were returned to the areas of food production to balance off-takes. By the late 19th century, processed mineral phosphorus fertilizer was routinely used in Europe and its use grew substantially in the 20th. Processed mineral fertilizers such as ordinary superphosphate (OSP) typically contained an order of magnitude greater concentration of phosphorus than did manure (Smil, 2000b). Application of such highly concentrated fertilizers helped rectify the phosphorus deficiency of soils. In the mid-20th century the Green Revolution improved agricultural output in many countries. As well as introducing new crop varieties, the Green Revolution involved the application of chemical fertilizers. This new approach saved millions from starvation and the proportion of the world’s population that was undernourished declined despite rapid population growth (IFPRI, 2002; Cordell *et al.*, 2009).

Nowadays, the use of fertilizers for phosphorus, nitrogen and potassium is indispensable to the increase in food demand.

2.4. Phosphate rock reserves

Before the phosphate rock reserve finishes, a global peak in phosphates reserves can be predicted, and it is estimated to occur on the next 30 years.

Hubbert in 1949 predicted (Hubbert, 1949) that the production of oil resources will eventually reach a maximum rate or 'peak' based on the finite nature of non-renewable resources, after which production will decline. Hubbert and later others contest that the important period is not when 100% of the resource is depleted, but rather when it reaches a maximum production, which occurs when 50% of the resource is still in the ground. After this point, production will decreases, placing upward pressure on prices and increasing international tensions (Campbell, 1997).

This analysis of peak phosphorus is based on estimated P in current world phosphate rock reserves (approximately 2358 Mt P) based on US Geological Survey data and cumulative production between 1900-2007 (totaling 854 Mt P) based on US Geological Survey data (Buckingham and Jasinski, 2006; Jasinski, 2007, 2008) and European Fertilizer Manufacturers Association (2000). The area under the Hubbert curve must equal the depleted plus current reserves, totaling approximately 3,212 Mt P. Units of phosphorus are presented as elemental P, rather than P_2O_5 (containing 44% P) or phosphate rock (containing 29-34% P_2O_5) as commonly used by industry (Stuart *et al.*, 2006).

The data for production is fitted using a Gaussian distribution (Laherrere, 2000), based on the depleted plus current reserves estimate of 3,212 Mt P, and a least squares optimization which results in a production at peak of 28 Mt P/a and a peak year of 2034 (Fig. 3) (Stuart *et al.*, 2006).

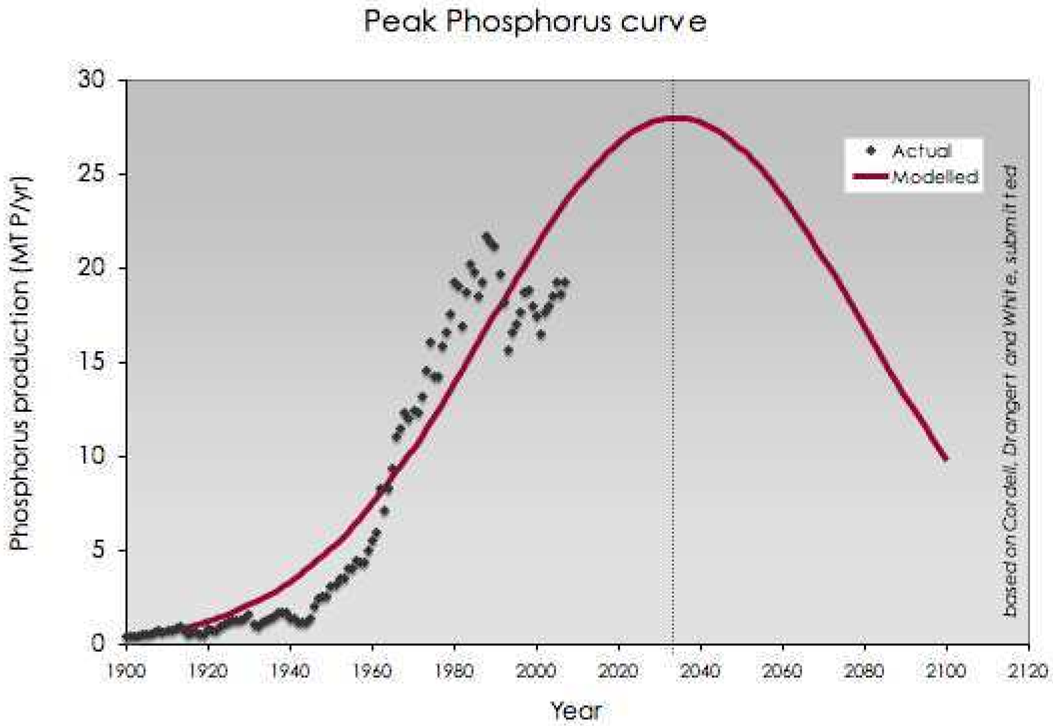


Figure 3 - Peak phosphorus 'Hubbert' curve, indicating that production will eventually reach a maximum, after which it will decline (Stuart *et al.*, 2006).

While it is understood that phosphate rock, like oil and other key non-renewable resources will follow a Hubbert production curve, a key difference between peak oil and peak phosphorus, is that oil can be replaced with other forms of energy once it becomes too scarce. However there is no substitute for P in food production (Cordell, et al, 2009). P cannot be produced or synthesized in a laboratory. Quite simply, without phosphorus, we cannot produce food (Stuart *et al.*, 2006).

Although oil is unavailable once it is used, while phosphorus is an element that can be captured after use and recirculated for use within economic and technical limits. Peak phosphorus is also linked to peak oil. For example, the recent oil price shock and growing concern about climate change has stimulated a dramatic increase in biofuel crop production globally, which in turn increases the demand for phosphate fertilizers, and hence the proximity of the phosphorus peak (Stuart *et al.*, 2006; Cordell *et al.*, 2009).

3. Global Material Flow Analysis (MFA) of Phosphorus

3.1.What a is MFA

Material flow analysis is a method to describe, investigate, and evaluate the metabolism of anthropogenic and geogenic systems. MFA defines terms and procedures to establish material balances of systems (Brunner, 2003). It is an accounting system that captures the mass balances in an economy, where inputs (extractions + imports) equal outputs (consumptions + exports + accumulation + wastes), and thus is based on the laws of Thermodynamics.

Material Flow Analysis recognizes that material through put is required for all economic activities and hypotheses whether the flow of materials is sustainable in terms of the environmental burden it creates. It accounts for all materials and energy used in production and consumption, including the hidden flows, or ecological rucksack, of materials that were extracted in the production cycle but which never entered the final products. The physical size of these hidden flows is often many times larger than the flows that end up in actual products.

The identification of wastes is a major issue in MFA, as the purpose of conducting a MFA is to minimize the flow of materials while maximizing the human welfare generated by the flow. Its methodology allows the monitoring of wastes that are typically unaccounted for in traditional economic analyses. As such, it is a method for evaluating the efficiency of using material resources.

MFA was develop in Europe, largely at the Wuppertal Institute in Germany, and has been adopted as a methodology by the European Union with respect to its sustainable development program. To date the focus of MFA has been primarily regional or national; a variety of MFA studies have been conducted for both developed countries and economies in transition, including Germany, the UK, Japan, Brazil, Venezuela, Chile and China. EU wide studies have also been conducted, and a global MFA is now underway (The Sustainable scale Project 2003).

3.2.MFA and Relation to Sustainable Scale

MFA is a method for operationalizing the concept of material throughput, and as such is an important contribution to measuring one component of sustainable scale. MFA has proven very useful for demonstrating the negative impacts associated with various specific economic activities. It has highlighted in a very practical way the unsustainability of specific throughputs (e.g. high reliance on non-renewable resources), the incompatibility of absolute levels of input with an equal Earthshare identified within the Ecological Footprint , the displacement of ecological burden to trading partners (generally from developed to undeveloped nations), and the enormous wastes involved in specific products or services.

Continued development of this important tool will likely increase its usefulness in linking economic throughput with ecological limits, especially as it is applied to the global level (Brunner, 2003).

3.3.MFA Procedures

MFA consists of several steps, in general begins with the definition of the problem and the adequate goals. Then relevant substances and appropriate system boundaries, processes, and goals are selected. Next, mass flows of goods and substance concentrations in these flows are assessed. The final step is to present the results in an appropriate way, in this case as a flow chart (Brunner, 2003).

3.3.1. Selection of Substance

There are various approaches to choosing substances relevant for an MFA. By one hand, they depend on the purpose of the MFA, and on the other hand, they depend on the kind of system on which the MFA is based (Brunner, 2003).
In this case study the substance is phosphorous. The phosphorus can be found on the nature in different forms, as we can see on the phosphorous cycle (Fig. 4).

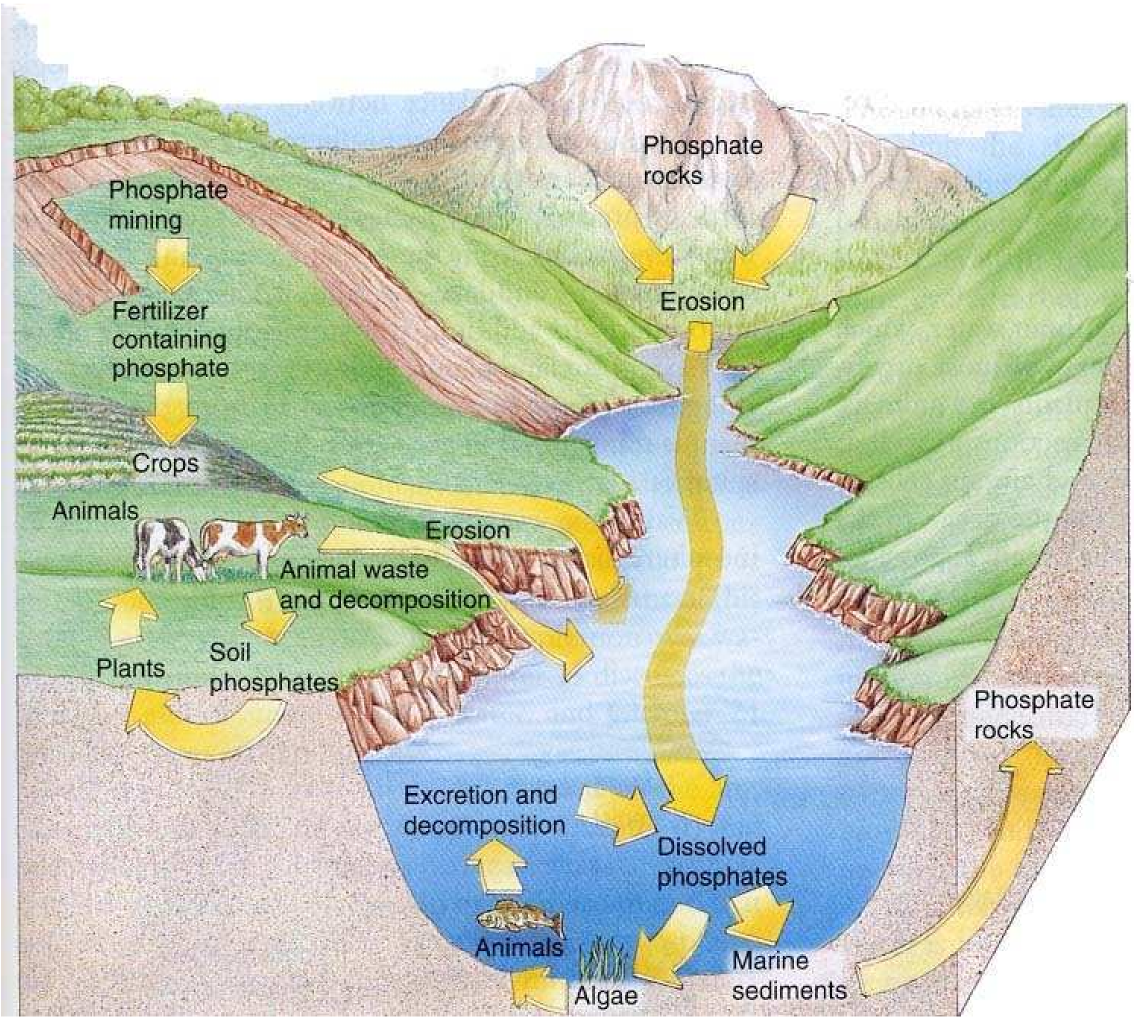


Figure 4 – Nature Phosphorous cycle (vincejtremante.tripod.com).

In the nature phosphorus is found in different forms. In the atmosphere P is present on particulates over land and over oceans; in land P is found on biota, soil, mineable rock, fresh-water (dissolved); finally in the ocean P is present on biota, dissolved (inorganic), detritus (particulates) and sediments.

3.3.1.1. Soil Chemistry

When the phosphate in fertilizers and manure is used on the soil, the phosphate is initially quite soluble and available. Manure contains soluble phosphate, organic phosphate, and inorganic phosphate compounds that are quite available. When the fertilizer or manure phosphate comes in contact with the soil, various reactions begin occurring that make the phosphate less soluble and less available (Fig. 5). The rates and products of these reactions are dependent on such soil conditions as pH, moisture content, temperature, and the minerals already present in the soil.

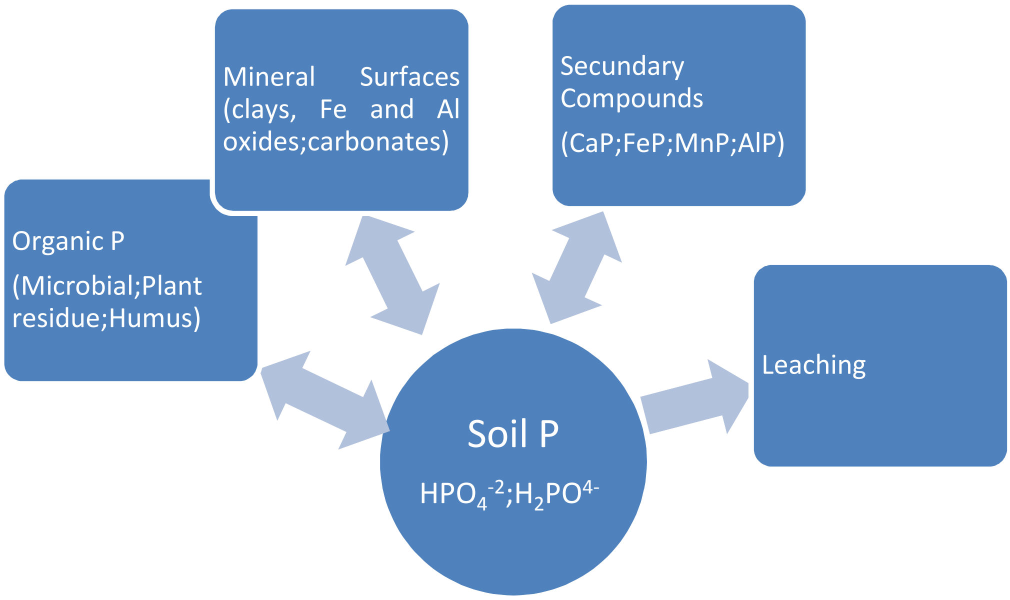


Figure 5 – Scheme showing the interactions on the Phosphorus in soil.

As a particle of fertilizer comes in contact with the soil, moisture from the soil will begin dissolving the particle. Dissolving of the fertilizer increases the soluble phosphate in the soil solution around the particle and allows the dissolved phosphate to move a short distance away from the fertilizer particle. Movement is slow but may be increased by rainfall or irrigation water flowing through the soil. As phosphate ions in solution slowly migrate away from the fertilizer particle, most of the phosphate will react with the minerals within the soil. Phosphate ions generally react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe), and forming compounds that are solids. The adsorbed phosphate and the newly formed solids are relatively available to meet crop needs.

Gradually reactions occur in which the adsorbed phosphate and the easily dissolved compounds of phosphate form more insoluble compounds that cause the phosphate to be become fixed and unavailable. Over time this results in a decrease in soil test P. The mechanisms for the changes in phosphate are complex and involve a variety of compounds. In alkaline soils Ca is the dominant cation (positive ion) that will react with phosphate. A general sequence of reactions in alkaline soils is the formation of dibasic calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite. The formation of each product results in a decrease in solubility and availability of phosphate. In acidic soils (especially with soil pH less than 5.5) Al is the dominant ion that will react with phosphate. In these soils the first products formed would be amorphous Al and Fe phosphates, as well as some Ca phosphates. The amorphous Al and Fe phosphates gradually change into compounds that resemble crystalline variscite (an Al phosphate) and strengite (an Fe phosphate). Each of these reactions will result in very insoluble compounds of phosphate that are generally not available to plants. Reactions that reduce P availability occur in all ranges of soil pH but can be very pronounced in alkaline soils (pH > 7.3) and in acidic soils (pH < 5.5). Maintaining soil pH between 6 and 7 will generally result in the most efficient use of phosphate, as it is shown on Fig. 6 (Busman, 2008).

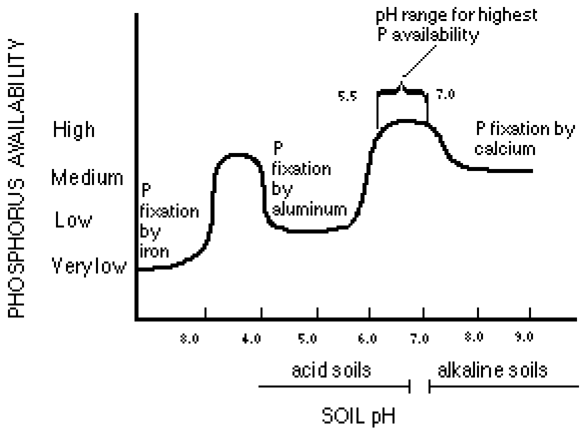


Figure 6 – Correlation between the phosphorus available with soil pH (Busman, 2008).

3.3.2. System definition in space and time

The spatial system boundary is usually determined by the scope of the Project, so the boundary here is global including all streams with phosphorous in world.

Temporal system boundaries are comparatively easier to determine. This is especially the case when average flows and stocks over a longer period of time are of interest. In this case, the time span of investigation, which is identical with the temporal system boundary, has to be extended long enough to outweigh the momentary unsteadiness of the system. Usually in this case of analysis the temporal system boundary is one year (Brunner 2003).

3.3.3. Identification of Relevant Flows and Process

After selecting the substance and defining system boundary, a first rough balance of goods is carried out for the system. (Brunner 2003)

Table 1 - Relevant phosphorus flows on the nature (Jeffrey E. Richey 1982):

Atmosphere (land)	→	Atmosphere (ocean)
Atmosphere (land)	←	Atmosphere (ocean)
Atmosphere	→	Land
Atmosphere	→	Ocean
Land	→	Atmosphere
Ocean	→	Atmosphere
Marine dissolved	→	Biota
Marine detritus	→	Sediment
Terrestrial biota	→	Soils
Mineable rock	→	Soil
Soil	→	Fresh-water
Fresh-water (diss.)	→	Oceans
Fresh-water (part.)	→	Oceans

Other important Processes containing phosphorus:

- Processing of the rock phosphate;
- Private Household and Household, e.g. human feed, detergents, chemical compounds.
- Waste Water Treatment Plant (WWTP), such as excreta and organic wastes, sludge and sewage;
- Animals, such as animal fodder, animal consumption, feed-grade additives and animal manure.

In the flow chart (Fig.7) an overview of all important streams is shown. The flow chart highlights more the human influence instead of influence from the nature.

4. Practical Part

A MFA was done in flow chart presentation taking data from recently MFA from Liu et al. and (2008), Cordell et al. (2009). The year of all data for MFA is 2004.

In order to understand better the relations between the P on the soil and the P available on the soils, and also to understand the consequences/impact on the crops, humans feed and animal production, a questionnaire was prepared to present to two agricultural specialists, Gitte Rubæk from University of Aarhus and Jan Schjorring from The University of Copenhagen.

5. Results and Discussion

The phosphate rock is a nature reserve, so it is considered as a pool, as the P pool on the soil, this flow chart as the propose to show the relation in use the phosphorus reserve and the consequences on the nature focus on the consequences on the soil. The nature is not so relevant and this study because the natural phosphorus flow occurs very slowly, one single loop of the nature cycle can take over 1 million years (Liu *et al.*, 2008).

5.1.MFA Flow chart

The flow chart (Fig. 7) begins with the transformation of phosphate rock in phosphate ore by mining. Phosphate ore is extracted with an average P content of 13% by surface or strip mining and contains calcium, iron, aluminum, magnesium, silica, sodium, potassium, fluorine, and many others impurities (Lauriente, 2003).

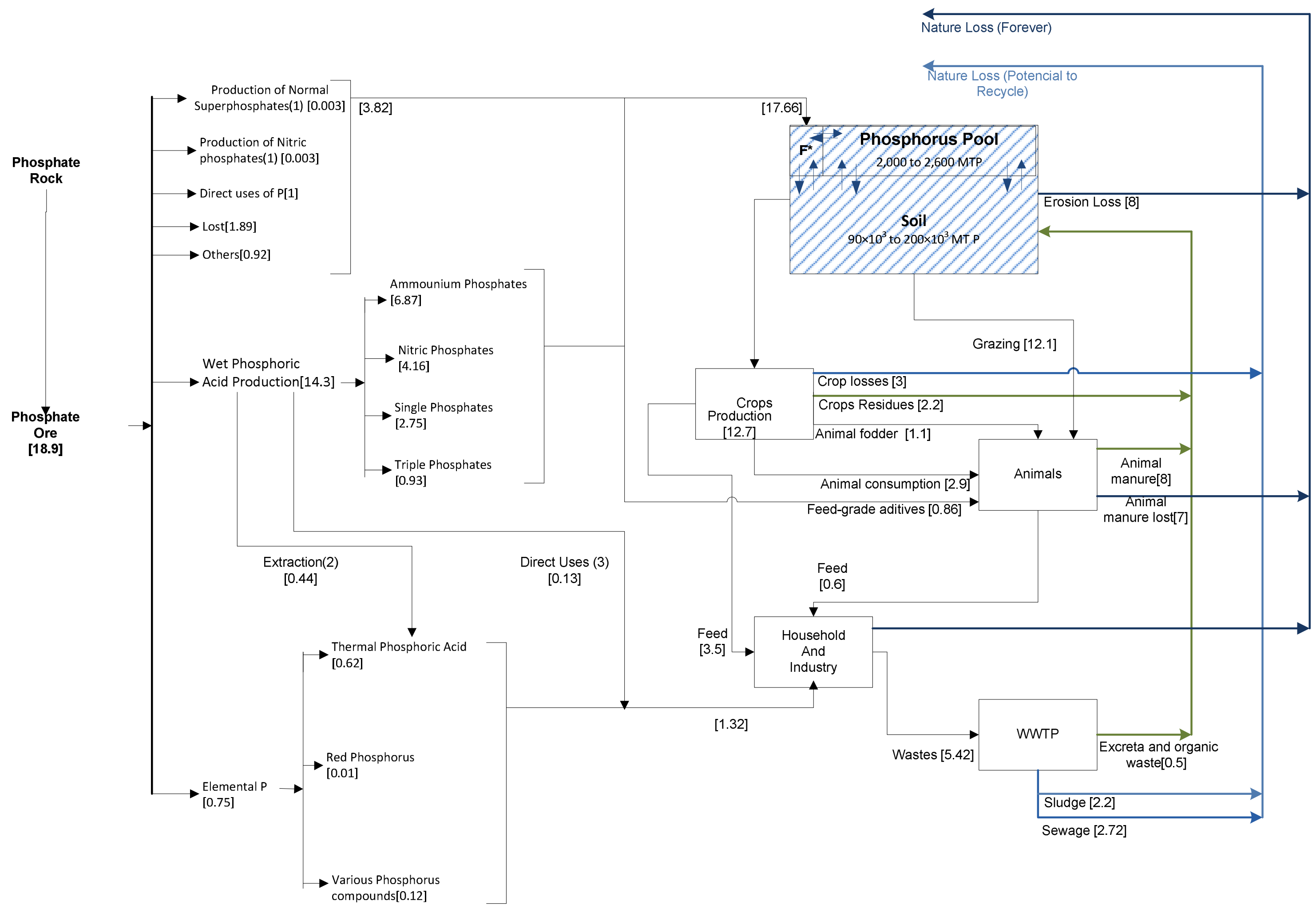


Figure 7 – Global Phosphorus Material Flow Analysis, all values are in Mt of P/yr and from the year 2004.

5.2.Phosphorus flows in production of phosphoric acid

The production of phosphate rock in 2004 was 143 Mt (USGS, 2009), so we have an input of 18.9 Mt of P in the system. Most of the phosphorus produced is used on the world soils as a fertilizer, on the MFA flow chart we can see that 17.66 go to the soil. Recently, Cordell estimated that 8 Mt of P per year is lost by erosion on the soils.

The most common way to produce phosphoric acid is the wet phosphoric acid production and the thermal phosphoric production. Phosphoric acid is the precursor of many of intermediate and end uses of phosphate compounds.

5.2.1. Wet Phosphoric Acid

Wet phosphoric acid is usually produced in large complexes often near the phosphate rock deposits. A large part of the acid is used near the sites of rock production to produce nongranular and granular triple superphosphates and granular ammonium phosphates. However, substantial amounts of wet phosphoric acid are shipped to local and distant plants.

The phosphate ore is digested as slurry with sulfuric acid in multiple reactions tanks or in a compartmented single tank. Slurry from the reaction system is filtered to remove the calcium sulfate that precipitates in the reaction. Conditions during the reactions are controlled to obtain crystals of calcium sulfate that filter at a high rate. The dehydrate wet phosphoric acid process results in the precipitation of byproduct calcium sulfate as the dehydrate form. Other wet phosphoric acid processes are operating at higher temperatures resulting in the precipitation of calcium sulfate in the hemihydrates or the anhydrite form. The filter cake is washed to recover about 95% of phosphoric acid at a concentration usually ranging from 28% to 30% P_2O_5 for the dehydrate process or 40%-50% for the hemihydrates process.

The filter-grade acid is concentrated by vacuum evaporation to 52%-54% P_2O_5 (merchant grade) for shipping and for use in production phosphate fertilizers. For ammonium phosphate production at the site, a concentration of about 40% -45% is sufficient. Wet phosphoric acid, used mainly in preparation of liquid fertilizers, is prepared by concentration to 68%-70% P_2O_5 content (Kauwenbergh, 2007).

The world consumption of wet phosphoric acid was 14.3 Mt of P for 2004. It is a precursor for fertilizers and for industrial phosphates (Villalha *et al.*, 2008).

Wet acid is used to produce the following fertilizers:

• Ammonium phosphates (a world figure of 6.870 Mt of P for 2004; IFA 2006) - normally referred to as APP, it is the most widely consumed fertilizer;

• Nitric phosphates and other nitrogen containing phosphate fertilizers (4.160 Mt of P IFA 2006);

• Single phosphates (a world figure of 2.749 Mt of P for 2004; IFA 2006);

• Triple phosphates (a world figure of 933 thousand metric tons of P for 2004; IFA 2006;Villalha *et al.*, 2008).

5.2.2. Thermal Phosphoric Acid Production

The thermal process first requires the production of elemental phosphorus. In this production, carbon monoxide and phosphorus are produced as gases, together with SiF_4. The phosphorus (product) is condensed, the carbon monoxide is used as fuel or burned as waste, and the SiF_4 is either lost through emissions (older plants) or collected (newer plants). In the production of thermal acid from elemental phosphorus, the major emission is phosphoric acid mist. The mist is mostly recovered, depending on the plant, but some is lost to the air (Villalha *et al.*, 2008).
Thermal acid is of a higher grade than wet acid and is thus used in the food industry and in industrial phosphates, whereas wet acid mostly goes to fertilizer production. Wet acid can be further purified by extraction and used in combination with thermal acid (Villalha *et al.*, 2008).

Wet acid is also purified through extraction (0.44 Mt P/year estimated for 2004) and used in the production of industrial phosphates (technical and food applications), this amount is used in the production of thermal phosphoric acid.
Wet phosphoric acid has a few end uses of its own (0.13 Mt P/year estimated for 2004)—namely, in phosphoric acid fuel cells, as a chemical wet etchant, for metal surface treatment as a pickling agent (to remove oxides on steel), for chemical polishing of aluminum, as a dilute solution in food additives, for catalytic applications, and for waste water treatment (Villalha *et al.*, 2008).

Red and white phosphorus are intermediates used in the production of phosphides, such as aluminum phosphides, and in the production of Phosphine (Villalha *et al.*, 2008).

The production of elemental phosphorus is necessary for the production of thermal phosphoric acid, red phosphorus, and a group of organic and inorganic phosphorus compounds that are categorized under the heading various phosphorus compounds. Elemental phosphorus production totals 750,000 metric tons of P, as an annual estimate, of which 83% goes to thermal phosphoric acid production. The remainder (0.12 Mt P/year estimated for 2004) goes to various phosphorus compounds (Villalha *et al.*, 2008).

Apart from thermal and wet acid production, phosphate rock is also used in the production of normal superphosphates and nitric phosphates (both fertilizers). These forms are produced by acidulation of phosphate rock with sulfuric acid, by acidulation with acid nitric, respectively. For 2004, estimated production figures for normal superphosphates were 0.003 Mt of P (Lauriene 2003), and the same for nitric phosphates. Direct uses of phosphate rock account for 1 Mt of P on 2004 based on estimations from Villalha 2008.

Statistical information indicates that 10% of P is lost in transportation and handling (Lauriente 2003), this figure is 1.89 Mt P/yr in the year 2004. Villalha estimates 0.92 Mt P/yr is used in other uses of phosphate rock concentrate.

5.3.Phosphorus flows on nature and human uses

Most of phosphoric acid obtained by different process is used as fertilizer in crop lands, in Industry and household and also as feed grade additives.

5.3.1. Crop Harvests

The use of phosphates to nourish agricultural soils aims to replenish the removal of phosphorus from soil by harvests and erosion losses. Adopting the average phosphorus contents in crops and the harvest index (Smil, 1999), the global crop production harvested 12.7 Mt P from soils in 2005; on the basis of the world agricultural production database (FAO 2006a).

Given that natural weathering and atmospheric deposition cannot compensate for the amount of phosphorus uptake from soils, application of phosphates, in both inorganic and organic forms, becomes essential to sustain today's harvests. Although most inorganic phosphates applied to soils come from chemical fertilizers, the means of organic phosphorus reuse are diverse. The most direct means is to recycle crop residues in situ. If we assume that roughly half of the annual output of crop residues (mostly cereal straw) is not removed from fields, the amount of the direct reuse of crop residues on the soil is about 2.2 Mt P/yr (Yi Liu *et al.*, 2008).

According with the present flow chart the crop lost is 3 Mt P/yr, this value is consistent with a recent MFA (Cordell *et al.*, 2009).

5.3.2. Animal

The animals are feed using the crop harvests, according to the global Food Balance Sheet (FBS) in 2003, livestock consumed 36% of the harvested cereals (excluding the amount of cereals processed for beer), 21% of the harvested starchy roots, and 20%of the harvested pulses (FAO, 2006b). Consequently, the annual livestock consumption of phosphorus in the harvests accounted for about 2.9 Mt P/yr (Yi Liu *et al.*, 2008).
Apart from the consumption of crop harvests, the animals also graze the vegetation and the input is 12.1 Mt P/yr by (Cordell, 2009).

The animals have an annual consumption via feed additives. Around 6% of global yield of phosphoric acid has been processed as animal feed-grade additives since 2000 (Brasnett, 2002; PotashCorp, 2004), so the input is 0.86 Mt P/yr.

Some part of crop residues is used as animal fodder. The reuse ratio of crop residues (straws of rice, wheat, and corn) as fodder is very different in developed countries compared with developing countries. Given that 70% of world livestock are raised in developing countries, where commercial feeds are less used and the global recycling rate of crops straws as fodder is about 25% (Yi Liu *et al.* 2008), so we have 1.1 Mt P/yr.

If we add all values above the total input on animal is around 17 Mt P/yr, taking in account that in developing countries usually they recycle various industrial byproducts and kitchen organic wastes, the value can be 20% higher (Yi Liu *et al.,* 2008), resulting in a total of 20.4 Mt P/yr.

The phosphorus flux to feed animals (excluding the grazing vegetation consumption) is mainly consumed by animals in confined facilities, whereas the world's cultivated and natural pastures provide a major source of phosphorus for unconfined animals. Probably the maximum recoverable phosphorus for croplands comes from the confined animals (Yi Liu *et al.,* 2008), recently Cordell estimates that 8 Mt of P/yr goes to recycling and 7 Mt of P/yr is lost on landfill and water.

5.3.3. Household and Industry

In this compartment we assume that the household and the Industry are connected, because the amount of production of phosphorus is used to produce chemicals, materials, detergents and posterior used in household.

In the year 2004 the global production of phosphorus for uses in industry was 1.32 Mt/yr of P (Villalha *et al.*, 2008).

Calculations based on Smil (2000a, 2002) suggest the total phosphorus content in annual global agricultural harvests 7 Mt P/yr is processed for feed and food fibre, 2.9 Mt of P/yr goes to feed animals (it was mentioned above) and 3.5 Mt of P/yr goes to the food commodities (Cordell *et al.*, 2009).

If we assume a global average dietary consumption of 1,400 mg P/capita, human excreta contains about 3.3 Mt P/yr, of which urban and rural populations generate 1.6 Mt P/yr and 1.7 Mt P/yr, respectively (Liu *et al.*, 2008). Cordell estimates that the organic solid waste from food communities is around 1.2 Mt of P/yr. Adding 3.3 Mt P/yr from human excreta, 1.2 Mt P/yr and consider that all P produced from industry (to make detergents and chemicals) is waste, the amount of household and industry is 5.82 Mt P/yr.

There is also an output from the household and industry to the nature loss, this output is for example garden wastes, animal excreta (pets), and data from this amount of P loss was not available.

5.3.4. Waste Water Treatment Plant (WWTP)

It is now even more important to recycle P from waste streams, in chapter 7; different ways to recycle P from waste streams is shown.

It is estimated that 0.3 Mt P/yr can be recycle from the organic wastes (Cordell et al., 2009). It is also estimated that 10% (0.3 Mt P/yr) of human excreta can be recycle from human excreta, either intentionally or not, we have some examples from poor urban farmers in Pakistan diverting the city´s untreated wastewater to irrigate and fertilize the soils. These small amounts contribute a recycle flow of 0.5 Mt P/yr. The remainder is lost on landfill as sludge and organic waste (1.2 Mt P/yr as sludge and 1 Mt P/yr as organic waste), on MFA flow chart is a total of 2.2 Mt P/yr (Cordell et al. 2009), and going backwards on mass balance we obtain 2.72 Mt P/yr lost as sewage (Cordell et al., 2009).

The P content on the sludge and sewage can be recovery, is not considered as a loss on the nature.

5.4.The phosphorus resource reserve inventory

The present agriculture is dependent on regular imputs of phosphate fertilizer derived from mined rock to replenish the phosphorus removed from the soil by growing and harvesting of crops.

Every year the mine production increases because the world population is growing and the crops are not only for food supply but also for diferents uses, for example the production of biodiesel. As we can see on Fig. 8 untill the 1940s the utilization of phosphate rock was stable, but since 1950 the use has increased and the peaked production was in 1988 with 166 Mt of phosphate rock. During the 1990s, production dropped to low values (30 % decline) due to social-economic-political problems in the Eastern Block countries and also due to environmental pressures (Villalha *et al.*, 2008). From 2001 onward, there has been growth at a rate that is projected to continue into the future (Lauriente 2003).

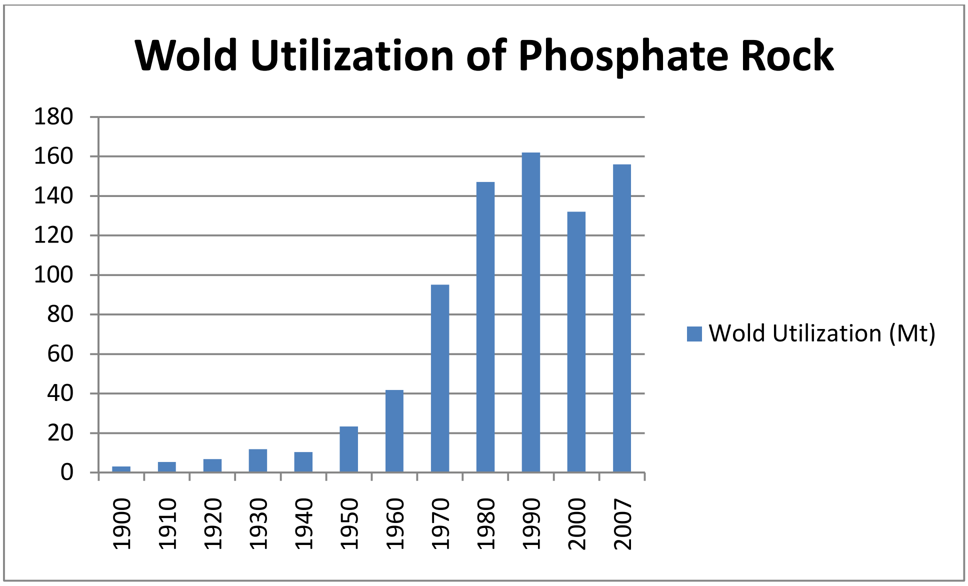


Figure 8 – World Production of Phosphate Rock in Mt over the years, data from statistics of USGS.

Three new phosphate rock mines are planned for development over the next decade in Florida to replace existing mines. The permitting process, however, has been delayed by opposition from local governments concerned about environmental and water use issues. In Idaho, one company received approval from the U.S. Forest Service to expand its mine and another company was developing a new mine to replace its existing mine that is near depletion. Worldwide phosphate rock production was estimated to have increased, primarily in China and North Africa (USGS, 2009).

Table 2 – Mine production in 2007 and a estimation of 2008 in the diferent countries of the world, also the reserves and the reserves base. All data are in milions metric tonnes of phosphate rock (USGS, 2009).

	Mine Production		Reserves	Reserve base
	2007	**2008** (estimated)		
United Sates	29.700	30.900	1,200	3,400
Australia	2.2	2.300	82	1,200
Brazil	6	6	260	370
Canada	0.700	0.800	25	200
China	45.400	50	4,100	10,000
Egypt	2.2	3	100	760
Israel	3.1	3.100	180	800
Jordan	5.540	5.500	900	1,700
Morocco and Western Sahara	27	28	5,700	21,000
Russia	11	11	200	1,000
Senegal	0.600	0.600	50	160
South Africa	2.560	2.400	1,500	2,500
Syria	3.700	3.700	100	800
Togo	0.800	800	30	60
Tunisia	7.800	7.800	100	600
Others Countries	8.110	10.800	890	2,200
World total (rounded)	**156**	**167**	**15,000**	**47,000**

China, United States, Morocco and Western Sahara, Russia are the biggest producer of mine production of phosphate rock. Phosphate rock resources occur principally as sedimentary marine phosphorites. The largest sedimentary deposits are found in northern Africa, China, the Middle East, and the United States. Significant igneous occurrences are found in Brazil, Canada, Russia, and South Africa. Large phosphate resources have been identified on the continental shelves and on seamounts in the Atlantic Ocean and the Pacific Ocean. High phosphate rock prices have renewed interest in exploiting offshore resources of Mexico and Namibia (USGS, 2009).

Reserves of phosphorus can be reserve base or reserve. Reserve Base, representing the part of the identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices (Fig. 9). Reserves, representing the part of the reserve base which could be economically extracted or produced at the time of determination (Fig. 10). The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials (USGS, 2009).

The availability of the reserves is affect also for political problems in the world. China has one of the most reserves of phosphate rock, and they have enough phosphate rock for own uses, the remained can be exported, but the export taxes from China government are very high, so the price of phosphate rock reach high values (questionnaire interview with Schjoerring, 2009).

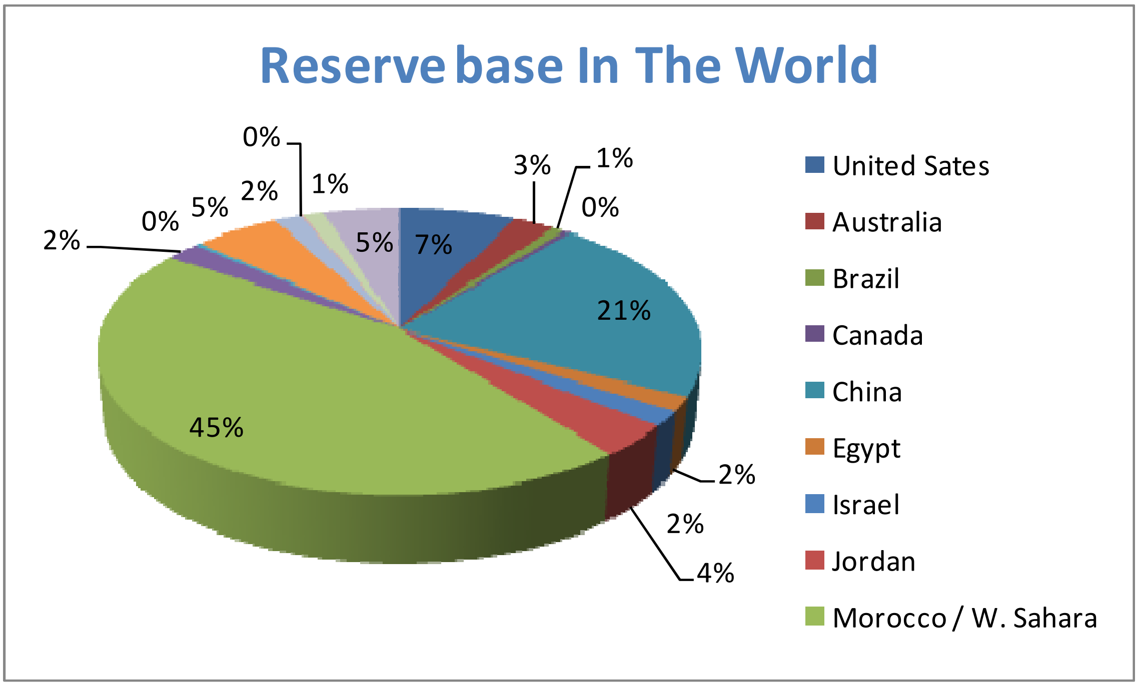


Figure 9 - Graphic showing the percentage of reserves base of P in the world (USGS, 2009).

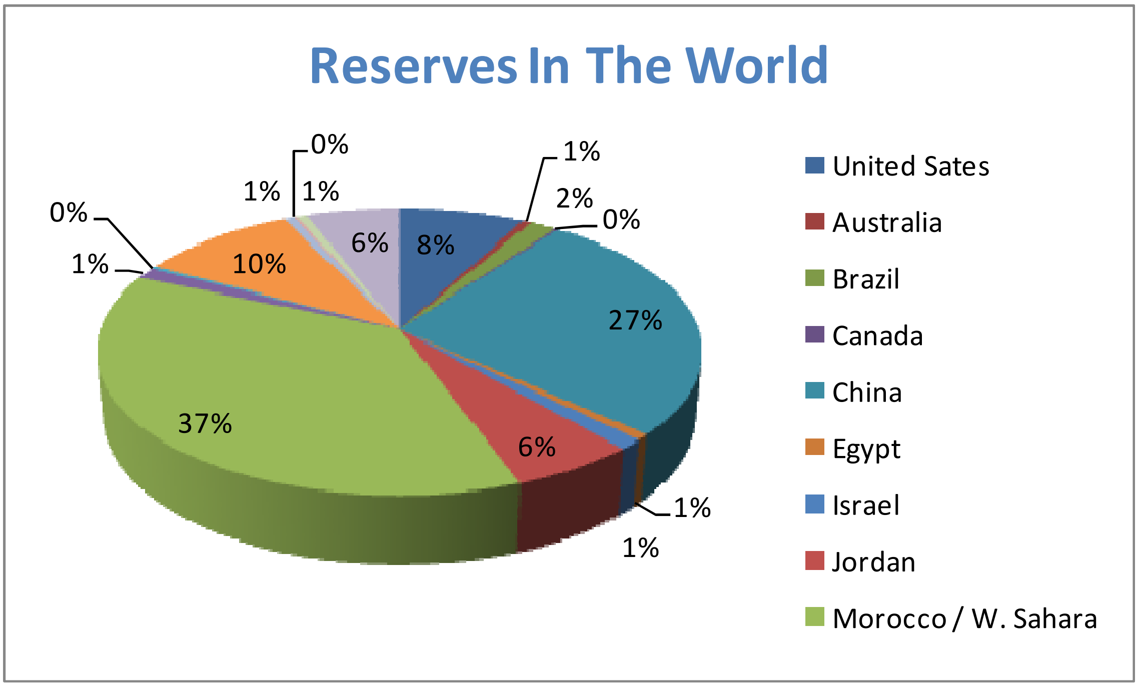


Figure 10 – Graphic showing the percentage of reserves of P in the world (USGS, 2009).

The reserve estimated in 2009 was 15,000 Mt of phosphate rock or 1,963 Mt of P. If every year the mined phosphate rock is around 22 Mt/yr (phosphorus production on 2008 USGS 2009), and each year the consumption of phosphorus increases because of the food demand, the reserves of phosphate rock will be finished in about 90 years, or maybe even less.

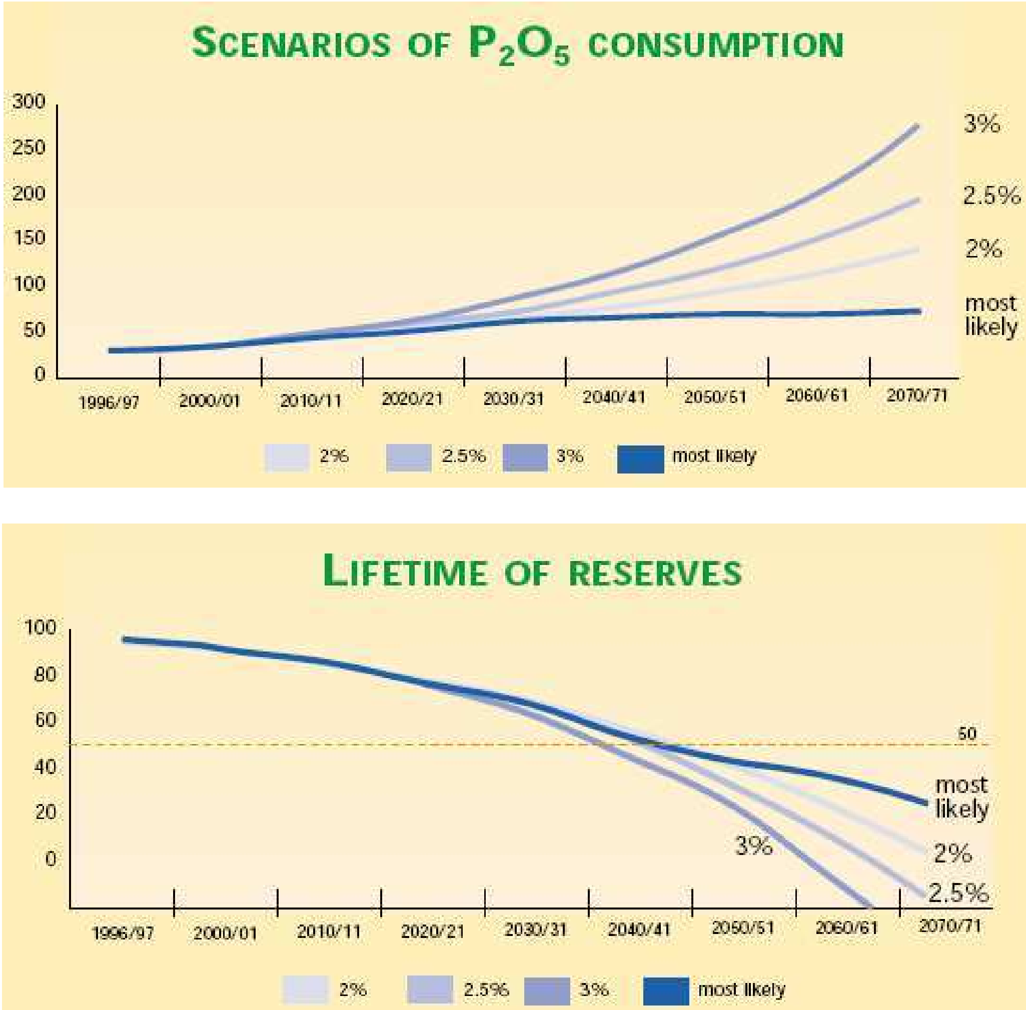


Figure 11 - Relationship between various scenarios for P_2O_5 consumption and the lifetime of reserves, assuming 2%, 2.5%, 3% and the most likely increase in P_2O_5 consumption (EFMA, 2000).

The two graphics above highlights very well that the use of phosphoric acid is increasing on the next years as the lifetime reserves is drop, and the year 2060, the phosphate rock could be exhausted at worst.

6. Value assessment/impact assessment

In this chapter will discuss the different impacts in case of depletion of phosphate rock and its effects on the crop yields, humans and animals. It will show some ways to recovery P from waste streams and also technologies in order to reduce the environmental impact.

The amount of phosphorus in the world's soils is roughly 90×10^3 to 200×10^3 Mt P, according to various estimates. Although the total phosphorus content of soils is large, only a small fraction is available to biota in most soils. This constitutes an available phosphorus pool containing 2,000 to 2,600 Mt P. A larger amount, in the range of 27×10^6 to 840×10^6 Mt P, can be found in the oceans. The sea water contains 80×10^3 to 120×10^3 Mt P, and the rest is accumulated in sediments (Liu *et al.*, 2008).

The distribution, dynamics, and availability of phosphorus in soil are controlled by a combination of biological, chemical, and physical processes. These processes deserve special attention, as a considerable proportion of the applied phosphate is transformed into insoluble calcium, iron, or aluminum phosphates. On average, only a small proportion, perhaps 15% to 20% of the total amount of phosphorus in the plant, comes directly from the fertilizer applied to the crop. The remainder comes from soil reserves (Schjoerring; Yiu et all.2008)

If the input of fertilizers in the soils is around 18 Mt P per year (data from the MFA flow chart) and 20% of P on the plant comes from the fertilizers. Considering that the amount of P consumed for crop production is 12 Mt of P per year, the crops only use 2.4 Mt P/yr from the fertilizers. We can thus conclude that per year we have 15.4 Mt P/yr of losses from the fertilizer input as show in Fig. 12.

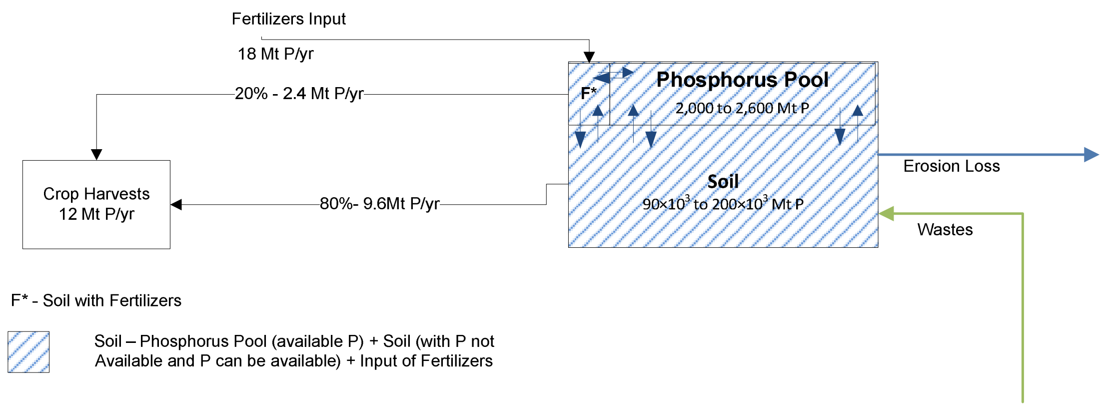


Figure 12 – Zoom of MFA flow chart showing how much fertilizer is used on the plants.

6.1. Consequences of phosphorus depletion

A deficit of phosphorus affects not only plant grow and its development but also the crop yields, along with affecting the quality of seeds. Deficiency can also delay the ripening of crops which can set back the harvests, risking the quality of the product.

To successfully produce the next generations of plants, seeds or grains must store phosphorus so that the seedling has enough to develop its first roots and shoots. Then, as the root system develops, the growing plant will be able to take up the phosphorus it requires from the soil, providing the adequate reserves (EMFA, 2000).

The effect on crop yields can be seeing (Table 3) on the simple experiment done in 1899 on fertilizer deficit soil in England.

Table 3 – Results of an experiment done in England (EMFA, 2000).

	None	**Nitrogen**	**Nitrogen plus Phosphorus**
		Yield, t/ha	
Winter wheat grain 1900 – 1919	1.56	1.83	2.25
Spring barley grain 1900 – 1919	1.29	1.69	2.10
Mangold roots 1906 – 1919	15.60	17.60	40.40

Analyzing the results of the experiment, we can see that with only nitrogen the crop yields are better, but by also adding phosphorus the final result is much better. So phosphorus addition increases the production 2.3 times.

6.1.1. Plant nutrition

The relationship between plant nutrition, soil texture, root growth, and the availability of nutrients in the soil can influence the efficient use of phosphorus in agriculture.

Plant nutrition, is considered in terms of the individual elements required by the plant. These include nitrogen, phosphorus, potassium, carbon, sulphur, hydrogen and many others. Plant roots take up all nutrients from the aqueous solution in the soil apart from carbon, hydrogen and oxygen, which are acquired from carbon dioxide in the air via the leaves and the water in the soil (Fig. 13) (EFMA, 2000).

The root hair is very important for the nutrients uptake to the plant, if the soil is not fertile in phosphorus, it can influence the development of root plant. On a document of EFMA is shown an example of root development of the same plant on different soils. On Fig. 13 is evident the development of root plant on fertile phosphorus soil (a) and the poor development on soil without phosphorus (EFMA, 2000).

But as is shown on plant (b) the roots can be less developed but agricultural specialist believe that the plant can adapt in case the soil P is not available, for example the main root hair is more extended to uptake P from other soil layers with no deficit on the plant (Questionnaire Interview with Schjoerring, 2009).

(a) (b)

Figure 13 – Root Hair development on soil with P (a) and on the poor soil P (b). (From EFMA, 2000)

6.2.Questionnaire

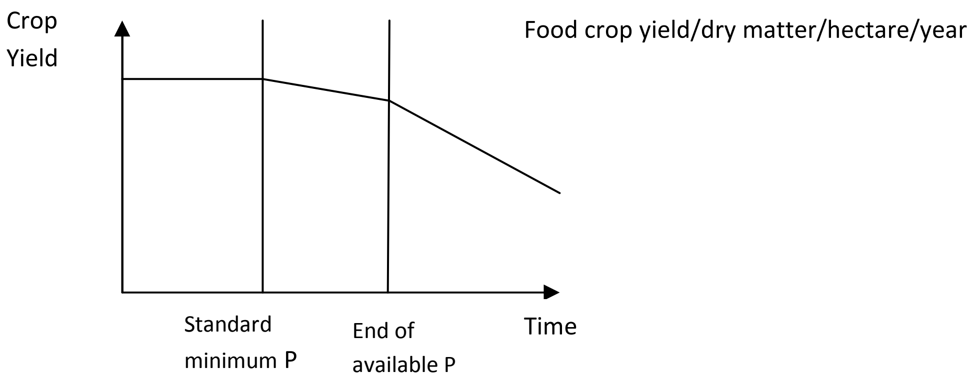
In order to understand better the relations between the P on the soil and the P available on the soils, and also to understand the consequences/impact on the crops, humans feed and animal production, a questionnaire was prepared to present to two agricultural specialists, Gitte Rubæk from University of Aarhus and Jan Schjorring from The University of Copenhagen.

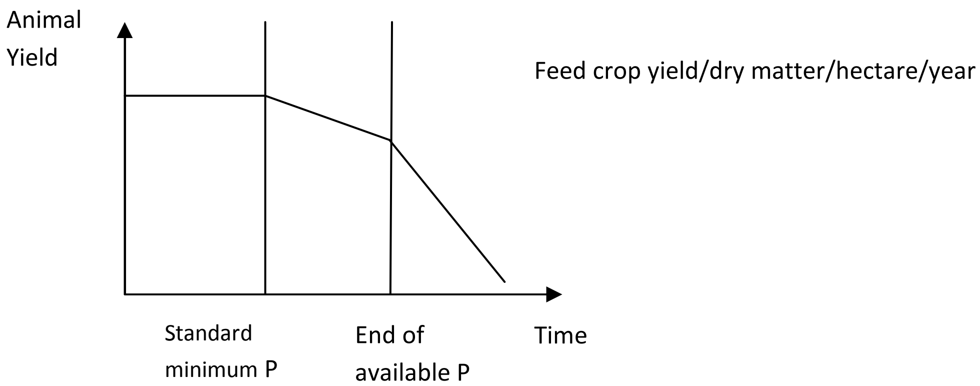
The main questions are as follows:

1) From the P pool in the soil, I would like to have more information/understanding about the equilibrium between the P available and the P not available for plants.
    a. What happens to the crops yield when the minimum P dosage stops but P available to plants is present in the soil?
    b. What happens to the crops yield (both for humans and animals) when the minimum P dosage has stopped and the P available to plants in no more present in the soil?

We suppose that when the minimum P dosage stops, there will be a gradual drop in crop yields (for both humans and animals), however, after the P available to plants in the soil has been used up, there will be a gradual drop in crop yields, but a big drop on animal yield, because we think that not only the crop yield will be drop, put also the P percentage contained in the crops (if there is less available P on the soil influence the uptake plant). So if the P Percentage in the crops is less, possible will be influenced the development of the animals. On the humans we think that a drop of P on the crop yield will not influence, because the P intake of the humans it's bigger than recommended daily intake.

The following diagrams highlight this hypothesis.





2) We understand that the changes in the P pool are based on the differences in space and time, depending on various places, soil types, crops etc. How should be explained the above hypothesis keeping this in mind?
3) There are several technologies available for mitigating the problem of P depletion and decrease of P in the P Pool. Some of them are –
    a. Enhancing P recycling – from waste streams such as Meat & Bone Meal, wastewater sludge, human excreta, etc.
    b. Enhancing P uptake – from the addition of an enzyme that enhances phosphate fertility.
    c. Enhancing P uptake of plants by genetic modifications.
4) Do you have any information about Danish experiences and test fields which were being studied for soil fertility with regard to P without the addition of any fertilizer. I was informed about such studies by my supervisor.

From the answers that we got from the agricultural specialists, the hypothesis is discussed with different scenarios projecting the consequences if the phosphorus reserves are depleted. These are some of the qualitative projected scenarios.

6.2.1. Hypothesis for the consequences on the crops

The impacts of phosphorus depletion on crop yields depends on the different kind of soils such as overfertilized soils, tropical soils where the availability of P is reduced, the type of crops produced. Agronomists agree that the differences in the input of P will affect the crop yield and the reduction in P input will lead to reduction in crop yield.

1st case: General soils:

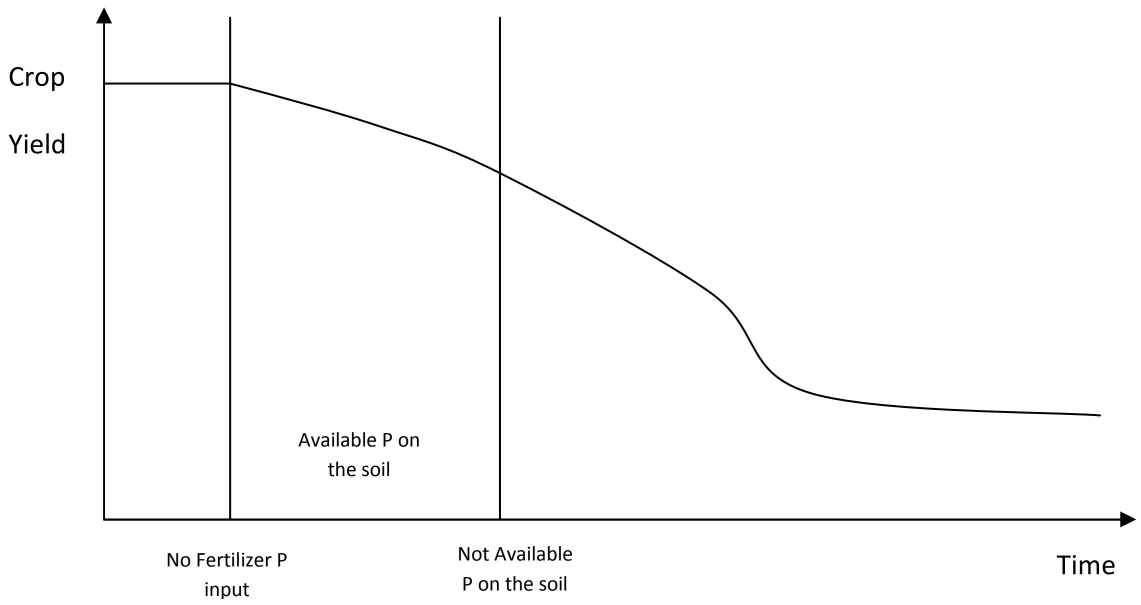


Figure 14 – Graphic showing the possible consequence on the crop yields in case of no fertilization during a long time, on general soils.

If the input of fertilizer stops, on general soil, the crop yields will drop until P is available on the soil. After reaching the time that is not P available on the soils the crop yields will decline more (fig. 14), but both agronomists, agree that in these case the plants will have a period of adaptation, and the roots hair will be longer to uptake P from other levels of the soil.

2st case: Overfertilized soils:

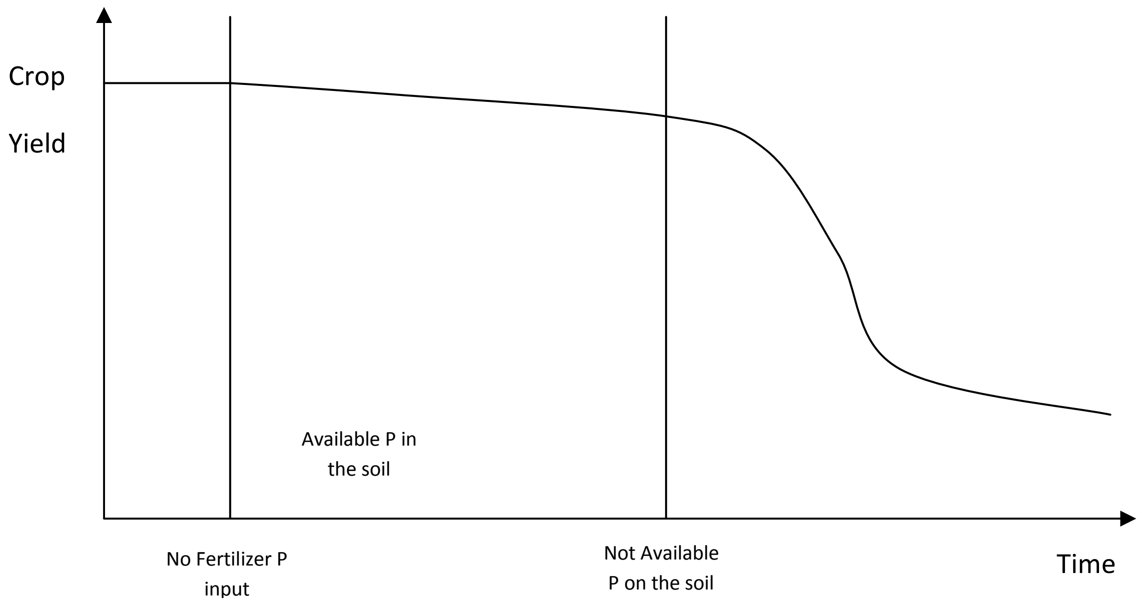


Figure 15 – Graphic showing possible consequence on the crop yields in case of no fertilization during a long time, in overfertilize soils.

In case of overfertilize soils, e.g. recycle animal manure , or an input of P fertilizer above of requirement needs of the soil, it is not expect a big drop of crop yields and the time of P available on the soil will be bigger than in general soils (Fig. 15). In this situation it will take longer to finish the P available.

3rd Case: Too Low available P in the soil

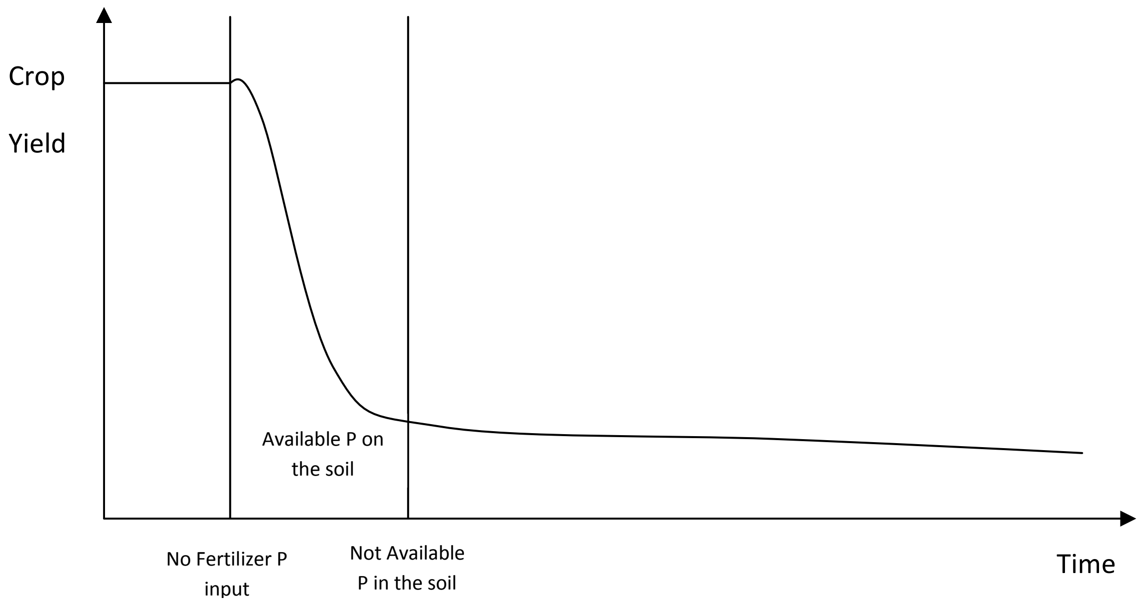


Figure 16 – Graphic showing possible consequence on the crop yields in case of no fertilization during a long time, on too low available P on the soil.

If the soil has too low available P, as tropical soils, the P is not available in solution but it is adsorbed with different compounds, it is expected a reduction on the start and then a steep reduction when it is finishing the P available. However, it will be an equilibrium at a level too low to sustain viable production, and then a very low level of yield (Fig. 16). The lag phase between no fertilizer P input and not available P on the soil will be shorter than the soils described above.

6.2.2. Consequence of Human and Animal

Humans and animals also need to obtain an adequate supply of phosphorus from their food and feeding stuffs. Phosphorus deficiency affects many of the essential processes on which the life of an animal depends, just as it does in plants. Phosphates are added to the diet of pigs and poultry to ensure they do not suffer any deficiency, and to prevent health problems, weak bones and impaired fertility.

Because much of the phosphorus ingested by animals is excreted in the faeces, animal manures, when properly used, are valuable sources of phosphorus. Phosphorus is the second most abundant mineral element in the human body (the first is calcium), accounting for more than 20 percent of the body's minerals. Calcium phosphates, for example, are the major constituent of the skeletal bones and teeth and contain 85% of the body's total phosphorus. Lack of phosphorus not only affects bone structure, but also appetite, growth and fertility (EFMA 2000).

Above, on the questions, we thought that we will have a decrease not only on the crops yields but also a big impact on animals, but the decreased input of phosphorus will reduce grain yield much more than the P percentage in the grain.

On the Human, even the percentage in the grain is less, it will not be such big impact in the humans, because the typical daily consumption is 1,500 mg P/capita for adults. This is well above the dietary reference intake (DRI), the amount a human individual should take in each day, as recommended by the Food and Nutrition Board of the Institute of Medicine, a part of the U.S. National Academy of Science. The U.S. recommended intakes are 700 mg/capita for adults over 18 years of age, 1,250 mg/capita for young adults between 9 and 18 years of age, and 500 mg/capita for children (Villalha *et al.*, 2008).

As an answer of the questionnaire Schjoerring believes that the impact on animals doesn't make sense, e.g. the monogastric animals, like pigs, they are not able to digest the P content on the crops, for which they are given P supplements in their feed. Less P in the crops will mean either additional supplements will need to be provided to the animals or there may be less loss of P to the environment via animal excreta causing lesser environmental impacts.

6.3.Long-Term Experiments in different countries

A different experiment has been performed in order to evaluate soil and crops performance with or without fertilizer.

6.3.1. Denmark

In Denmark it has being developed a study about crop and soil P (in eight fields experiments initiated in 1975) to long-term P fertilization strategies at typical Danish agricultural soils. One of the main objectives was to determine for how long P fertilization could be omitted without affecting yields, carried out by Gitte Holton Rubæk and Erik Sibbesen.

The P treatments were 0 kg P $ha^{-1}year^{-1}$, 15 kg P $ha^{-1}year^{-1}$, 30 kg P $ha^{-1}year^{-1}$ and 70 kg P $ha^{-1}year^{-1}$ every fifth year as super phosphate. Nitrogen was also applied as well other plant nutrients, lime and pesticides according to needs.

The effects of P and N fertilization on crop yields were tested with an ante-dependence analysis of covariance on the relative yields. With this analysis it is possible to deduct information on where the time profiles of the treatments differ from each other. This analysis is a modified multivariate analysis, and therefore it does not depend on variance homogeneity, independence of data or sphericity of the residuals as traditional or adapted univariate analysis or variance do. The first step in the ante-dependence analysis is determination of the order or structure of ante-dependence. This means determining the lowest number of previous measurements, which improves the model significantly, when include as covariates. If the order of covariance is one, only the measurement of the preceding year will be included in the analysis as covariate. If the order of ante-dependence is two, the two preceding years will be included as covariates and so on. An ante-dependence structure of zero will result in a univarate analysis of variance with no correction on previous years.

Table 4- The order of ante-dependence and overall effects of N and P fertilization on the relative yields at each experimental site (Rubæk and Sibbesen, 2000).

Site	Before 1990				1990 and onwards		
	Years included in the analysis	Order of ante-dependence	Effect of N fertilisation	Effect of P fertilisation	Years included in the analysis	Order of ante-dependence	Effect of P fertilisation
Rønhave	75-89	0	***	n.s.	90-97	1	*
Roskilde	75-89	1	***	n.s.	90-97	0	n.s.
Ødum	76-89	1	***	n.s.	90-94	1	n.s.
Askov	75-89	0	***	n.s.	90-94	0	n.s.
Højer	75-87	0	***	n.s.	-	-	-
Tylstrup	75-89	2	***	n.s.	90-94	0	***
Borris	75-89	1	***	n.s.	90-94	1	***
Lundgård	75-89	2	***	n.s.	-	-	-

*** indicates significance at P<0.0001,
** indicates significance at P<0.001,
* indicates significance at P<0.05
n.s. indicates no significance at P<0.05

Note: P is in kg P $ha^{-1}year^{-1}$.

Analyzing the table 4 with data of this long-term experiment it was proved that P-fertilization had no significant overall effects on the crop yields at any experimental sites before 1990. From 1990 and onwards the overall effect of P fertilization were significant at Rønhave, Tylstrup and Borris. In all cases, except at Borris in 1992, the yields were significantly lower in the 0 kg P $ha^{-1}year^{-1}$ treatment then in 30 kg P $ha^{-1}year^{-1}$.

The percentage of P in the crop components in general varied little among treatments, but there was a tendency to lower P concentrations in the 0 kg P $ha^{-1}year^{-1}$ in the later years at the stations were also yields were depressed (Rubæk and Sibbesen, 2000).

6.3.2. Finland

Since 1978 a farm in southern Finland is being used to analyze the growing of cereals without fertilization of potassium and phosphorus, during thirty years. The soil had been cultivated conventionally for decades before the experiment started.

The goal of this project was to investigate how long it would take before a deficiency of the major nutrients phosphorus and potassium occurred under conditions associated with traditional crop production methods.

The design of the experiment consists of two factors with two levels each: without and with phosphorus and potassium fertilizer (36 and 70 kg ha^{-1} yr^{-1}, respectively) as well as without and with an extra superphosphate application (P 36 kg ha^{-1} yr^{-1}). The treatments were replicated at least 4 times. They were arranged in plots of 20 by 15 m or 5 by 15 m (extra superphosphate). Nitrogen has been applied at 100 kg ha^{-1} yearly.

On the end, the results of the total dry matter yield (grain + straw) decreased from about 5000 kg ha^{-1} to a level of 3000 kg ha^{-1} when only nitrogen was applied. After 30 years of nitrogen and phosphorus fertilizer the yield level was 4000 kg ha^{-1}. NPK application kept the yield level almost constant. The surplus annual P rate of 70 kg ha^{-1} seemed to increase the yield a little more.

Over thirty years a significant depletion of P and K in soil occurred when they were not given in fertilizers. This caused a reduction in crop yield. An abundant P application has exceeded the crop uptake very clearly prevented the yield reduction but did not raise the extractable P concentration in the soil. Severe K deficiency did not start to appear until 20 years of growing cereal without fertilizer K. K application compensating for the uptake by the crop did not prevent the decrease of its extractable concentration in this soil, but this decrease did not affect crop yield (Jaakkola, 1997).

7. Options for sustainable phosphorus use and management

Common responses to resource scarcity problems include higher prices, more efficient resource use, the introduction of alternatives, and the recovery of the resource after use. The use of phosphorus is becoming more efficient, especially in Europe. Farmers in Europe and North America are increasingly avoiding over fertilization, and are plugging straw and animal manure into agricultural soils, partly to recycle phosphorus (Cordell *et al.*, 2009).

At this moment, it is important to figure out if it is possible to reduce the waste streams from P cycle, and if it is not possible to reduce the waste, it is important to develop methodologies to recover P from waste streams or recycle.
On chapter 3, analyzing the MFA flow chart we can see that a large amount of P is lost in the nature during the cycle. Before the phosphorus reserve be exhausted, is important to reduce, as possible, the depletion of P.

The phosphorus can be recovered from the food production and consumption system and reused as a fertilizer either directly or after intermediate processing. As example, P can be recovered and/or reused from:

- Plugging crop residues back into the soil;
- Food processing plants and food retailers;
- Human and animal excreta;
- Meat and bone meal;
- Manure fibre;
- Sewage sludge;
- Wastewater.

To increase the life expectancy of world´s phosphorus resources we have two possibilities, recycling by recovery from municipal and other waste products, the second one is improving the efficient use in agriculture of both phosphatic mineral fertilizer and animal manure (Cordell *et al*., 2009).

Some countries have already programs to recycle waste. At least a municipal waste water treatment plant in Portugal is processing the sludge to sell as fertilizer. In some cities from Pakistan and Asia, more than 25% of urban vegetables are irrigate with them own wastewater (Cordell *et al.,* 2009). There are different studies about reuse and recycle of rich phosphorus streams, on this chapter it will be mentioned some of them.

7.1. Phosphorus Recovery from Biological Sewage sludge ash using a wet sulfuric acid process

The aim of Michael's project (Phosphorus Recovery from Biological Sewage sludge ash using a wet sulfuric acid process) was to examine phosphorus recovery from biological sewage sludge ash using a wet sulphuric acid process as recovery method. Different process steps as well as specific parameters influencing the possibility of recovering phosphorus from sewage sludge ash were identified:

- The waste water treatment process
  - Use of precipitation chemicals
  - Phosphorus content of the sludge

- The incineration process
  - Incineration temperature

- Recovery of phosphorus by the sulphuric acid
  - Acid concentration
  - Temperature
  - Stirring
  - Particle size

Biological waste water treatment produces sewage sludge with higher phosphorus concentration than traditional waste water treatment and furthermore elimination of precipitation chemicals minimizes the iron and aluminum content this is highly desirable when recovering phosphorus. Analysis of dried sewage sludge Analysis of ash from biological sewage sludge from Helsingborg, VA-Verket shows that the ash contains 37 % P_2O_5. This is almost twice the amount of the phosphorus in ash from traditional sewage sludge and above the minimum criteria for P_2O_5 in low grade rock phosphate. Biological sewage sludge ash is reported to have an iron content of as little as 1.6%. The iron content in Helsingborg ash is 5.7% this is 23% lower than ash from Lynetten incineration plant. The biological sewage sludge ash fulfilled all threshold values given by the Danish sludge regulations.

The incineration temperature influences the plan availability of the phosphorus. When incineration temperature is increased from 500^oC to 700^oC the plant availability decreases. Incinerating dried, biological sewage sludge from Helsingborg at a temperature of 875^oC, the amount of plant available phosphorus is reduced by a factor 40. Phosphorus is found as hydroxyapatite in the ash.

A series of experiments of phosphorus recovery from biological sewage sludge were carried out. The main influential parameters on the sulphuric acid recovery process are stirring, particle size, sulphuric acid concentration and temperature. The experiments showed that it is possible to recover 40 % of the phosphorus in the ash. High sulphuric acid concentration may have caused coating and hampered the recovery of phosphorus. The produced phosphoric acids had an average P_2O_5 concentration of 4.4 %. Analysis showed that the threshold values in the Danish Sludge regulation were fulfilled. After a concentration step yielding a tenfold increase in P_2O_5 concentration the threshold values were still fulfilled and furthermore specifications for low grade rock phosphate were fulfilled.

The technical feasibility analysis states that biological waste water treatment without addition of precipitations chemicals is technical feasible when the discharge threshold value for phosphorus given by the local municipalities is above 0.4 mg P/L. Incineration of sewage sludge is well established and considered technical feasible. Recovery of phosphorus from sewage sludge ash as phosphoric acid by reaction with sulphuric acid is considered technical feasible and 40 - 90% recovery is expected.

The economical feasibility analysis states that the process generates a surplus of 240 DKK per ton of sewage sludge ash, with a total depreciable plant cost of 29,340,000 DKK (Michael, 2009).

7.2.Reuse of human an animal excreta

As was mentioned on chapter 3, human excreta can be reuse intentionally or not. Since a long time the Chinese people used the human excreta to fertilize the soils. Nowadays, technologies are being developed to recovery human urine. According with Swedish and Zimbabwe studies the nutrients of one persons' urine is sufficient to grow 50- 100% of the food requirements of another person (Cordell et all.2008).

Urine is a very useful waste, it can be use as a fertilizer because content a lot of the most important nutrients to fertilize the soil, with a percentage of 80% of nitrogen, 55% of phosphorus and 60% of potassium , as it is shown on Fig. 17 an example from Sweden.

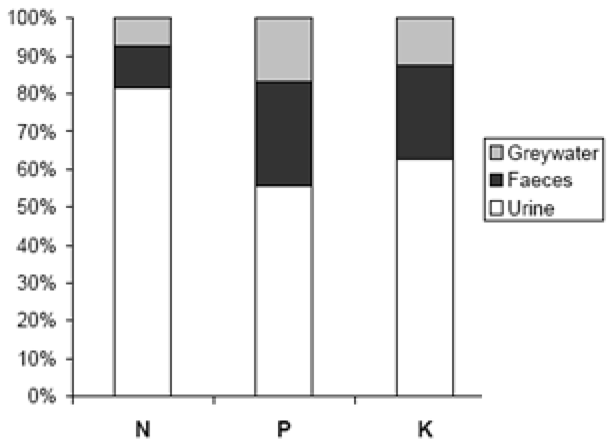


Figure 17 – Content of major plant nutrients and volume in Swedish domestic waste water. Daily mean excretion per person and day is: 14 g N, 2 g P and 4 g K in a volume of 150-200 liter. (Graphic from WHO 2009).

Sweden is a good example of reusing urine, on the beginners of 1990 porcelain urine-diverting toilets ware introduced. This system constitutes on separate flushing mechanism for the urine and faeces or the flush rinses both bowls. The faeces may also be collected dry for composting.

The urine is usually collected in a tank placed underground or in a basement under the house. When the tank is full the urine is transported to a farm for later use as a fertilizer on agricultural land. Before its utilization the urine is stored either in the housing area or near the field, on the Fig. 18 is shown a scheme. For individual households the urine may also be utilized in the garden directly from the collection tank, without separate storage. Investigations were conducted on both small-scale and large-scale systems (WHO, 2009).

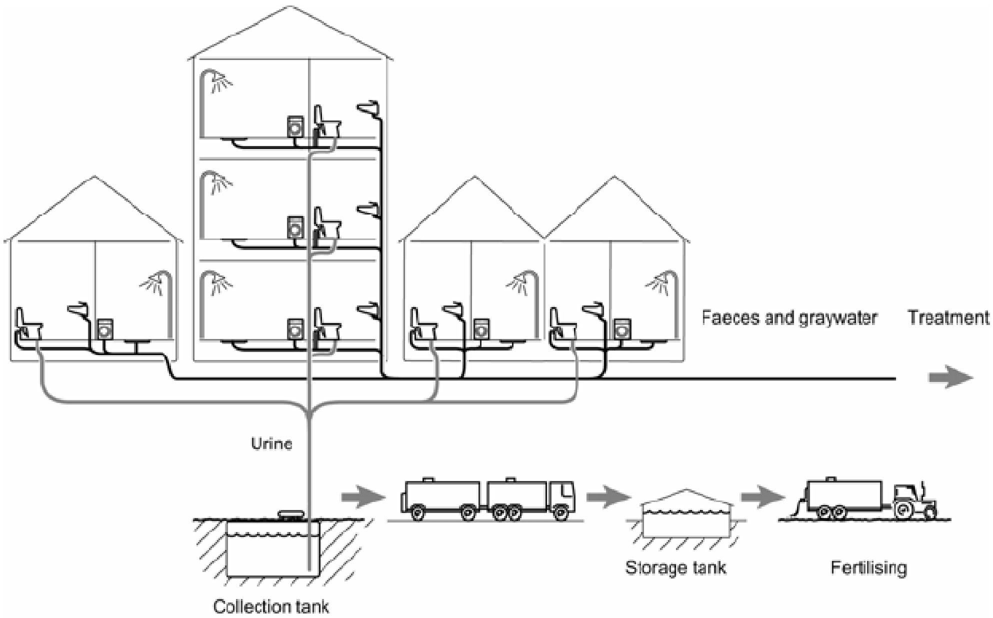


Figure18 – Swedish scheme to recovery human urine. (From WHO 2009)

Nowadays, not only in Sweden is being develop reuse of human excreta. In Zimbabwe was developed toilets that make compost for the crops, most of the rural population of Africa do not have access to safe and reliable toilets , so it is a good way to create sanitary safety and reuse the nutrients to the crops with low-cost (EcoSanRes 2007).

World Health Organization (WHO) has guidelines in order to minimize the risks for transmission of infectious diseases and as a part of risk management. These guidelines are recommendations an them involve parameters such the possible pathogens on the urine depending on the temperature and time of storage, and recommended crops (WHO, 2009).

7.3.Novozymes

Consider that at this moment P exists in two main pools of phosphorus, the phosphate rock reserve and the phosphorus pool on the soil (P available to plants uptake). Taking account that one day the reserve may be finished, is important to have an idea of how the problem can be managed.

On the soil we have phosphorus unavailable to fertilize, however there is on the market a fungus able to transform the phosphorus available (Fig. 19).

When phosphate fertilizer is applied at the time of planting, it can quickly bind with calcium, magnesium, and iron minerals in the soil, resulting in the phosphate being inaccessible to the crop. In that moment JumpStart can be applied on the soils.

Figure 19 – JumpStart is a phosphate inoculant. (Novozymes 2009)

JumpStart is a fertility management tool that is applied as a seed treatment to the seed prior to planting or with the seed at planting. The active component in JumpStart is a naturally occurring soil fungus – *Penicillium bilaii*. As the seeds germinate and develop a root system the JumpStart fungus and the plant form a mutually beneficial relationship. The fungus grows and multiplies along the crop roots, thriving off the root exudates and releasing organic acids into the soil. These acids break the bonds holding the phosphate nutrient in a mineral form, releasing the phosphate into a form the plant can access. The result is enhanced phosphate uptake allowing the crop to achieve its yield potential.

Cool soils, during direct or early seeding, can reduce phosphate availability due to the limited mobility or movement of phosphate in the soil. Poor early season phosphate availability can reduce early growth. JumpStart is active in cool soils as low as 4 °C and supplies an immediately available source of phosphate to developing seedlings, resulting in quicker emergence and early vigor.

JumpStart has been commercially available to North America farmers for more than 10 years, where it was used on approximately 5.0 million acres in 2008. In over 450 split field trials conducted in North America over the last 15 years, "JumpStart" has shown an average 5% to 7% yield increase on a number of different crops (Novozymes, 2009).

8. Conclusions

As a main conclusion of this work the phosphorus is a real environmental problem nowadays, in my opinion it is important to develop more research work in different points of the world. It is important work with farmers in order to inform the best ways to apply the fertilizers on the soil to reduce as much it is possible the use of fertilizers and maybe develop international rules.

The MFA flow chart can show that we have a lot of waste streams and they can be recovered and reduce the need of phosphate rock and also the phosphate's losses on the soil.

It was discussed that the phosphorus depletion can reduce the crop yields and the plant must develop root to find P on another soil level. However it will not interfere on human and animal consumption.

Companies like Novozymes, Kommunekemi and also techniques like the human excreta recovery from Sweden are a good example how we can reduce waste streams rich in P and reduce environmental impacts, such eutrophication. But we still have to develop more techniques, as example there are now some genetic modification studies.

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