ANDREAS KREUZEDER

MODELLING PHOSPHORUS FLOWS IN SOILS

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Supervisors:
Univ.-Prof. Dr.rer.nat. Claudia R. Binder
Institute for Systems Science, Innovation & Sustainability Research (ISIS)
Karl-Franzens-University Graz

Ao.Univ.-Prof. Dr.phil. Anton Huber
Institute of Chemistry (IFC)
Karl-Franzens-University Graz

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Zusammenfassung

In allen lebenden Zellen kommt dem Phosphor (P) eine zentrale Rolle zu – speziell in der Energieumsetzung und im genetischen Code. Seine herausragende Wichtigkeit macht ihn zu einem essenziellen Nährstoff. Obwohl in der Natur in niedrigen Konzentrationen ubiquitär vorkommend, wird Phosphor als nicht-erneuerbare Ressource betrachtet. Die globalen Vorkommen sind limitiert und auf wenige Länder konzentriert.

Ungefähr 90% der globalen Phosphorproduktion finden als Dünger in der Landwirtschaft Verwendung, wo sie von enormer Wichtigkeit für die Produktion landwirtschaftlicher Güter sind. Durch diese nicht substituierbare Aufgabe als Dünger und die Begrenztheit als natürliche Ressource wird ein neues und historisches Kapitel eröffnet: Eine mögliche Versorgungskrise von Phosphor. Eine solche Krise kann durch die Minimierung von Verlusten und durch maximale Nutzungseffizienz vermieden werden. Zentral in einer solchen Strategie ist die schonende Verwendung von Phosphor als Dünger und die Berücksichtigung der Dynamik in Böden. Diese sind mittlerweile gut erforscht aber aufgrund der Komplexität besteht die Notwendigkeit dieses Verständnis an Praktiker, die für die Anwendung von Phosphor verantwortlich sind, weiter zu geben.

In dieser Masterarbeit wurden die Phosphorflüsse für Österreich durch Anwendung der Stoffflussanalyse (MFA) erhoben. Diese Analyse wurde für das Jahr 2008 durchgeführt und mit Daten von 2001 verglichen. Weiters wurde ein „System-Dynamics-P-Modell“ entwickelt, das auf die Charakteristiken von Phosphor im Boden eingeht. Es zeigt den Einfluss der Bodeneigenschaften, die Effekte von Düngeranwendung und Pflanzenaufnahme sowie deren dynamische Zusammenhänge. Entwickelt als Instrument zur praktischen Anwendung, fördert es speziell für Praktiker das Verständnis der Dynamik von Phosphor im Boden.

Die beiden zentralen Resultate dieser Masterarbeit sind:

1. Die Flüsse von Phosphor in der österreichischen Landwirtschaft sind signifikant höher als bisher angenommen. Weiters sind von 2001 bis 2008 die Importe von Phosphor durch Mineraldünger sowie der jährliche Aufbau des Bodenbestands um 5-10% gesunken.
2. Die Zusammenhänge von Anorganischem Phosphor, Phosphor in der Bodenlösung und organischem Phosphor lassen sich durch ein dynamisches Equilibrium von 500 : 1 : 250 beschreiben. Dieses Gleichgewicht wird hauptsächlich durch Parameter wie pH-Wert, Humusanteil, Tonanteil und Anteil von Mineralien die Phosphor komplexieren (Al, Fe, Ca) verschoben.

Abstract

In all living cells phosphorus (P) is a central component for the energy conversion system and in the genetic code. Its outstanding importance makes it an essential nutrient. Although ubiquitous in nature in low concentrations, it is considered a non-renewable resource. The global resources of phosphorus are limited and concentrated in only a few countries.

Around 90% of the global phosphorus production is used as fertilizer in agriculture where it is of great importance for the production of agricultural goods. This pivotal role as a fertilizer and the finiteness as a natural resource led to a new episode of historic importance: A possible upcoming phosphate crisis. Only by decreasing the losses and increasing the efficiency of phosphorus use such a crisis may be prevented. The nucleus of such a strategy is the use of phosphorus as fertilizer and its dynamics in soils. These dynamics are well investigated by now. Due to their complexity there is a need to provide additional means to facilitate the knowledge especially for practitioners, who are directly on the forefront of phosphorus use and thus sustainability.

This thesis shows the flows of phosphorus in Austria by using the method of material flow analysis (MFA). This analysis was performed for the year 2008 and compared to previously available data from 2001. Furthermore, a System Dynamics P-Model was developed outlining the characteristics of phosphorus and its use in soils. This model considers the complex interactions and processes in soils. It shows the influence of soil properties, the effects of fertilizer use and crop uptake, and their dynamic interrelations. Especially, designed as a hands-on tool it allows to foster the understanding for phosphorus dynamics in soils for practitioners.

The two main findings of this thesis are:

1. The flows of phosphorus in Austrian agriculture are significantly higher than previously expected. Also, the imports of phosphorus through mineral fertilizer as well as the build-up of the soil stock declined by 5-10% from 2001 to 2008.
2. The relationships of inorganic phosphorus, phosphorus in soil solution and organic phosphorus can be described by a dynamic equilibrium of 500 : 1 : 250. This equilibrium is influenced by other parameters, most notably: pH-value, organic matter content, clay content and content of minerals binding phosphorus in complexes (Al, Fe, Ca)

Glossary

Al:	Aluminium
Apoplasm:	In plants, especially roots, the apoplast or apoplasm is the free space outside the plasma membrane
ATP:	Adenosine triphosphate: energy carrier in the cells
Ca:	Calcium
CAL:	Citric Acetate Lactate-Method: is used to determine plant available phosphorus
Calibration:	Using empirical data sets, data from literature or general trends to estimate model factors or behaviour
DNA:	Deoxyribonucleic acid: a bio molecule that carries genetic information
Fe:	Iron (latin: Ferrum)
Flow (Material Flow):	Defines a mass transfer between two processes
Isotope:	Atoms with the same number of protons and a different number of neutrons. Isotopes are often used as radioactive markers
M:	Molarity or molar concentration (mol/l)
MFA:	Material Flow Analysis
Mineral Fertilizer:	Or synthetic fertilizer: composed of inorganic minerals or chemically synthesized
Mycorrhizal symbiosis:	Mutualistic association of fungus and roots of a vascular plant
nes / n.e.s.:	not else specified
Organic Fertilizer:	Fertilizer composed of enriched organic matter
Rhizosphere:	Upper layer of soil that is directly influenced by roots
SD:	System Dynamics
Stock:	Represents a quantity existing at a defined point in time
Symplast:	Is the inner side of the plasma-membrane
P:	Phosphorus
pH-Value:	pH is a measure of the acidity or basicity of an aqueous solution
P_2O_5:	Phosphorus oxide containing 44% phosphorus
Process:	Is a transformation, transport or storage of materials
White Phosphorus:	Very reactive phosphorus allotrope

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1 Introduction

This chapter shows the main theoretical basis of this thesis and current state of research of phosphorus in soils. By outlining the properties, functions in nature and society, chemistry and nutrient behaviour as well as phosphorus in soils and as fertilizer an overview on all relevant topics is given. This extensive introduction is essential in order to put the current developments as well as the results of this thesis in a general context.

This chapter starts with *Phosphorus in Nature*, an introduction of the functions and qualities of phosphorus in nature. The section *Phosphorus in Society* outlines these functions and qualities from a societal viewpoint. The section *Phosphorus in the Environment* emphasizes the role of phosphorus as a resource on the one hand, and as a pollutant on the other. These two narratives represent the major topics related to anthropogenic phosphorus use. The section *Phosphorus Chemistry* describes its properties and behaviour in a chemical sense and shows examples for some of the most important forms of phosphorus in soils. This is the basis for the description of *Phosphorus as a Nutrient* as well as *Phosphorus in Soils*. Here the phosphorus cycling, its movement and the difficulty of the fractionation of phosphorus forms is outlined. The section *Phosphorus as Fertilizer* describes the ways the various forms of phosphorus fertilizers are produced and their properties as well as the overall mass flows related to this use.

The section *Global Fluxes and Material Flow Analysis for Phosphorus* summarizes the current state of research in a global context and with a special focus on Austria. While this leaves dynamic interrelations especially in soils unconsidered the section *Dynamic Modelling the Behaviour of Phosphorus* outlines the currently available models, their area of application as well as strengths and weaknesses.

In the section *Methodical Approach* the overall approach for this thesis is outlined.

1.1 Phosphorus in Nature

As nitrogen and potassium, phosphorus is a major limiting nutrient for the productivity of managed and unmanaged terrestrial and aquatic ecosystems. The cycling of these nutrients has greatly accelerated over the last decades, due to human activities especially in agriculture (Antikainen et al., 2005). The essential nutrient phosphorus is ubiquitous in nature, particularly in soils and sediments, but because of its immobility it can be considered as a non-renewable resource, which has to be mined in order to be used as a fertilizer (Liu et al., 2007). Phosphorus can be found in all living cells as it is part of vital compounds of living matter such as DNA, ATP or phospholipids (Abelson, 1999). It cannot be replaced by any other element and therefore, phosphorus is indispensable for plant growth, cell activities, energy conversion or reproduction (Liu et al., 2007). Because phosphorus is involved in almost all processes of life, there are far-reaching implications related to the availability of this element. This exceeds the fields of agriculture by far and in particular includes food security, fertilization and agriculture, environmental damage by eutrophication, waste treatment, global food supply and demand dynamics, etc. (Cordell, 2010). In agriculture, the use of phosphorus focuses on the fertility increase of soils as well as to sustain the production of crops and other types of plants. On the other hand, the stimulation of biological activity in aquatic systems, generally known as eutrophication, is an important environmental issue related to phosphorus. Nevertheless, over the last years the finiteness of phosphorus resources has crystallized as another major concern (Pierzynski et al., 2005a, P. 185f).

Based on the facts that 90% of the global phosphorus production are used in agriculture and that there is no possible substitute for the use as a fertilizer, the role of phosphorus in agriculture and the related areas - such as production of agricultural goods, food security, environmental impact, etc. - are arguably the most significant ones for a society (Cordell, 2010). Given this pivotal role in modern agriculture there are three major concerns arising from the current use of phosphorus:

(i) The way phosphorus is used.

(ii) The danger of resource depletion.

(iii) Eutrophication

To avoid confusion with different units for phosphorus, in this thesis elemental phosphorus (P) was used, rather than other common types such as P_2O_5 (containing 44% P; commonly used in the fertilizer industry) or phosphate rock (containing 29-34% of P_2O_5). When other units were used it is separately stated. The term phosphate in this thesis refers to PO_4^{3-} in its various chemical forms.

1.2 Phosphorus in Society

From the discovery of phosphorus onwards, this element stood at the centre of a number of discourses, which were recognized on a societal level. Cordell (2010) argues that phosphorus was perceived in multiple ways with changing societal functions. Mainly related to the specific use of phosphorus, functions were associated with contradictory perceptions over the last 200 to 300 years. This includes the use of phosphorus in war (e.g., phosphorus grenades, VX nerve gas), flame retardants, fertilizers, eutrophication, food production, detergents etc. Following this reasoning, Cordell (2010) argues that the newest emerging discourse of the 21st century is global phosphorus scarcity. Today there are several connotations related to phosphorus and some of them seem to be contradictory.

Using Google Alerts, a tool to monitor new content on the internet, the role of phosphorus as a homeopathic drug dominated online discussions in 2010 overwhelmingly. Another major topic related to phosphorus is its use in war, as it was recently used in the Operation Cast Lead in 2008/09 when Israeli forces used white phosphorus in grenades (Human Rights Watch, 2009). The upcoming resource scarcity has gained momentum in online discussions, especially due to the efforts of the Sustainable Phosphorus Futures Network (http://phosphorusfutures.net) and their members. A decade ago, when recognized as an upcoming challenge (Abelson, 1999), this topic and especially the term “Peak-Phosphorus” have now entered the public arena (Elser & White, 2010).

These discussions on the internet reflect the public interest and awareness on these topics. Nevertheless, this perception contrasts with the questions related to phosphorus that researchers and experts address. Eutrophication and erosion seem to be topics that were already addressed publicly two or three decades ago. And resource depletion or phosphorus dynamics in the environment are topics that may have yet to enter the public stage.

1.3 Phosphorus in the Environment

1.3.1 Phosphorus as a resource

The essential mineral phosphorus is ubiquitous in nature, especially in soils and sediments. Föllmi (1996) pointed out the immobility and slow geological conversion rates of phosphorus and therefore, phosphorus is considered as a non-renewable resource. This is also illustrated in the profound fact that phosphorus has to be mined from special ores in order to be obtained in concentrations high enough to be used. Due to the slow (bio-) chemical weathering, the natural levels of phosphorus availability are relatively stable. This is also true for marine phosphorus levels, which respond to changes in continental weathering rates (Föllmi, 1996).

The geochemical phosphorus cycle has four major components: (i) Tectonic uplift of phosphorus bearing rocks and their weathering, (ii) erosion and chemical weathering of rocks resulting in soil creation and phosphorus deposition to rivers, (iii) riverine transport of phosphorus to flood plains, lakes and oceans, and (iv) sedimentation of organic and mineral matter (Schröder et al., 2010; Föllmi, 1996).

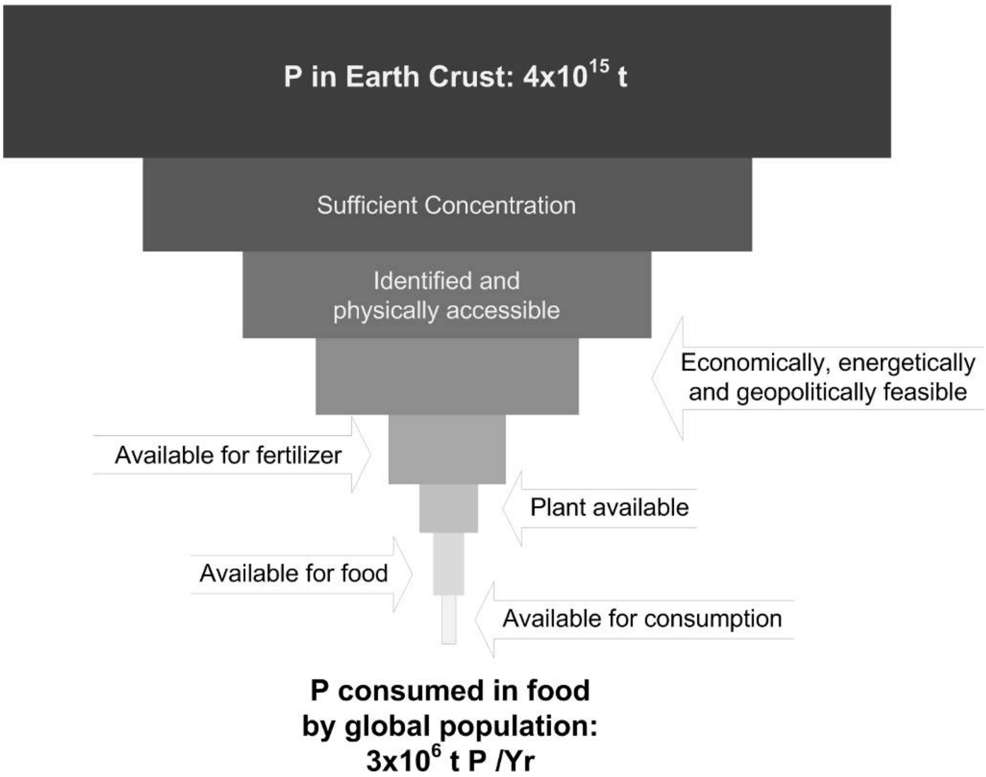

Figure 1: Phosphorus availability bottlenecks (Unit is t P); Source: adapted and redrawn from Schröder et al. (2010)

The so called phosphorus availability bottlenecks, schematically shown in *Figure 1*, illustrate the physical, economic, social and ecological factors limiting the availability of phosphorus. While phosphorus is ubiquitous in the earth crust only a small fraction has a sufficient concentration to be used as phosphorus source. It must then be accessible and mining economically feasible. Even a smaller fraction is available for fertilizer use and even less is available for plants and finally makes its way into agricultural products through fertilization and plant uptake. This combination of factors limits the availability of phosphorus as fertilizer and finally for consumption (Schröder et al., 2010).

Global Phosphorus Flows and the Anthropogenic Influence

Today the phosphorus cycle is massively influenced by anthropogenic flows. Falkowski et al. (2000) estimated a natural flux of phosphorus of 3 megatons / year (Mt/a) due to weathering of apatite, the naturally occurring phosphate rock. Human activity additionally caused a flux of 12 Mt/a by the mid-1900s which were released from anthropogenic sources, mainly fertilizers. This represents a 400% increase when compared with pre-industrialized and thus mainly natural flows. This steep increase in the global phosphorus cycling is closely related to significant changes in all other biochemical cycles. Vance (2001) points out that from 1960 to 2000 the world population has grown from 3 to 6 billion people, agricultural production has risen from $1.8x10^9$ to $3.5x10^9$ Mt/a and the consumption of phosphorus fertilizer has risen from 4 to 17 Mt P/a (9 to 40 Mt of P_2O_5). Cordell (2010) estimates the amount of fertilizer to be 14 Mt P/a whereas only 1.4 Mt P/a are used for other, mainly industrial, purposes. Smil (2000) claims that the annual global phosphorus uptake of terrestrial plants is between 70 and 100 Mt P/a which are removed from soils. Although the estimates vary depending on the mode of calculation and data sources a clear trend can be seen. With finite deposits of phosphate rock and the increasing use scarcity seems likely to occur if this development continues.

Most of the extracted quantities of phosphorus are applied as fertilizers in agriculture where the availability declines again due to removal in crops, immobilization in soils or losses (Liu et al., 2007). Nevertheless, fertilization is crucial to keep crop production on high levels because even under perfect conditions soils lose fertility unless the nutrients are replenished. Therefore, new approaches towards the efficiency of phosphorus use and recycling are needed (Abelson, 1999).

The History of Phosphorus as Fertilizer

The history of human population growth is closely related with the ability to produce enough food. That was, in essence, farming technology and the ability to fertilize soils in order to increase the output of crops. Locally available phosphorus in organic matter, manure and human excreta did not meet the increased demand for agricultural products in pre-industrial times. These developments lead to the use of Guano, a manure from bats, seabirds and seals in the mid 19th century, and later on to the use of rock phosphate (Cordell et al., 2009). For some regions and countries Guano played a central role in trade, especially between the mid-19th and mid-20th century. The example of the Republic of Nauru, an island nation in Micronesia, illustrates the rise and fall of the Guano industry. The economy was fully built on Guano exports and the country had once the highest per capita income on earth, but today the reserves are depleted, exports came to a halt and the state faces bankruptcy (Seneviratne, 1999; Jasinski, 2008).

To keep up with crop demands new phosphorus sources were tapped. These included ground basic slag (“Thomasmehl” or Thomasphosphate), a by-product of steel production and later on rock phosphate, which were extensively applied. Additionally, farming technology improved and particularly the introduction of crop rotation, improved handling of manure and the use of new crops helped to produce high yields while effectively using fertilization (Cordell, 2010).

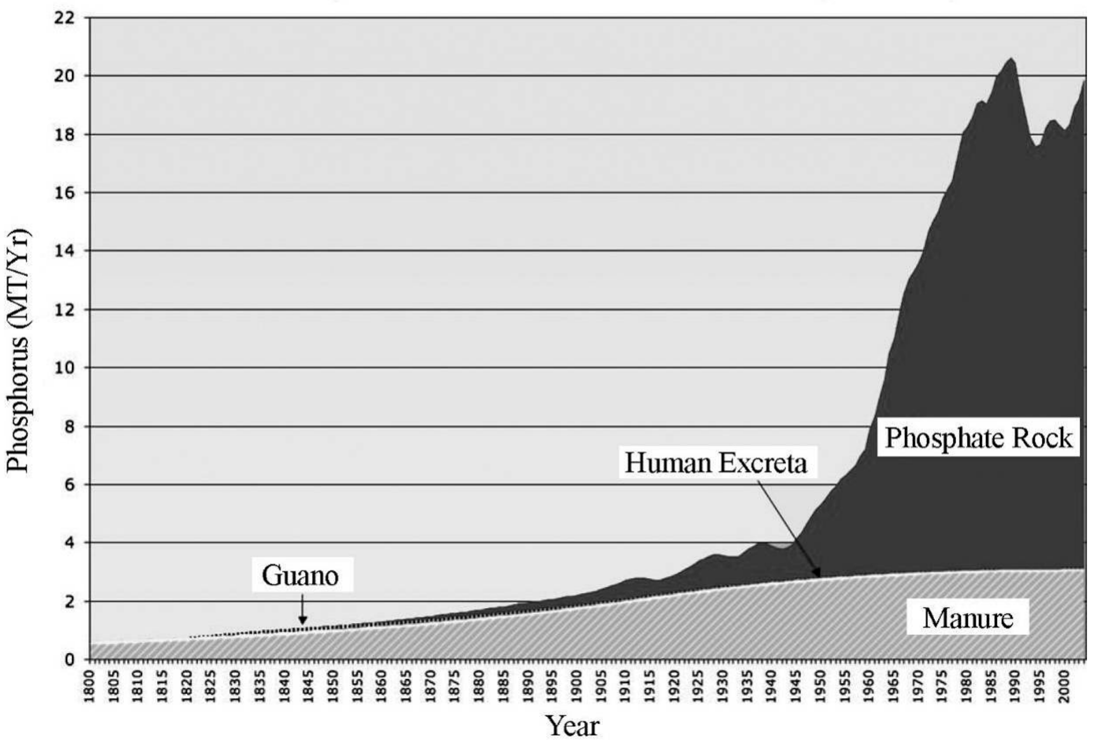

Figure 2: Historical global sources of phosphorus fertilizers from 1800 to 2000; Source: adapted from Cordell et al. (2009)

The historical development of phosphorus consumption as a fertilizer is shown in *Figure 2*. The steep increase in phosphate rock use from 1950 to 1980 is obvious. Although Guano (dotted line) was central to the beginnings of professional fertilization, its absolute share of phosphorus production has always been small. Compared to the large amount of phosphorus from phosphate rock, human excreta (white line) and manure (shaded area) represent a relatively small share of the total supply nowadays.

Predictions for future phosphorus demand usually assume a rising world population and thus increased demand for agricultural production, which will also drive up the world’s phosphorus production. Furthermore, there is a new possible use for phosphorus in lithium-iron phosphate rechargeable batteries. $LiFePO_4$ is known as an environmentally compatible and economically viable lithium battery cathode material that has also been used as an anode-material (Kalaiselvi et al., 2004). If such batteries were commonly used for car batteries and individual transport would convert to electric mobility, the demand for phosphorus would increase sharply.

A possible upcoming Phosphorus Crisis and Phosphorus Prices

The dependency of agriculture on rock phosphate and a rising demand of a rapidly growing world population and changing consumptions patterns, especially in the form of more meat consumption, have driven the demand for phosphorus fertilizers and will continue to push the demand in the future.

Phosphorus from cheap and high-quality sources, meaning high concentrations of easy accessible rock phosphate without contaminants, will become increasingly scarce while food production in most countries is dependent on these imports. Without these fertilizers, agricultural output will decline while the demand is rising. The vulnerability of the EU to such a phosphate crisis has been recognized only recently (Schröder et al., 2010).

Such a scenario becomes increasingly disruptive when market dynamics are considered. Parallel to the term peak-oil, a so called peak-phosphorus scenario, a scenario of peaking supply and rising prices, has been developed by Cordell et al. (2009). It is hard to predict whether this peak-shaped behaviour will be seen in reality or if the estimated peak is in fact reached by 2035 but if this occurs the effect would be tremendous.

It has to be noted that the phrase peak-phosphorus itself and the efforts from a network of researchers has brought broader public attention to the topic of phosphorus scarcity. Articles in professional journals and popular-science media such as Foreign Policy (Elser & White, 2010), the Energy Bulletin (Déry & Anderson, 2007) and The Sunday Times (Lewis, 2008) have fuelled the awareness for this topic which is the first step in countering such a development.

Besides a possible peak-phosphorus scenario the prices of phosphate rock have proven to be very volatile. In 2007 the price for the raw material phosphate rock increased by 400% in only half a year but went back to earlier levels later on in 2008 (Jasinski, 2008). The prices for phosphate rock from Morocco, the world’s biggest exporter, even went up 800% from beginning of 2007 until September 2008, and returned back to earlier levels in the summer of 2009. Strikingly, only very little information is available that looks into the market dynamics of phosphorus demand and supply. Most forecasts only consider the supply side and expect a business-as-usual demand. This neglects future adaptations and developments especially in developing countries (Cordell, 2010).

Global Phosphate Rock Production

The world’s phosphorus reserves are very unevenly distributed, which is directly reflected in the worldwide production, leaving 65% of the total in 2007 in only three countries (Jasinski, 2008). Geostrategic aspects also contribute to the complex nature of phosphorus supply due to the concentration of phosphate rock, the primary phosphorus source, only in a few countries. Unresolved political disputes make matters even more complex especially in Western Sahara where the world’s biggest reserves with estimated 5.7 billion t of phosphate rock are located (Cabeza Pérez, 2010). Even more, the fertilizer demand is expected to rise faster than the increase in production capacity (Jasinski, 2008). While the phosphate produced in the US is mainly used domestically, China has imposed high export tariffs of 135% to phosphorus exports in 2008 and Morocco has become the most important exporter of phosphate rock. However, phosphate rich regions in this country are located in the occupied region of Western Sahara. Although condemned by the United Nations, Morocco defies UN resolutions and continues its occupation (Cordell, 2010). Weikhard & Seyhan (2009) argue that an increasing integration of markets in agriculture and urbanization have separated production and consumption processes of phosphorus even more. This process is likely to be continued and will increase the effects of this uneven distribution of phosphorus reserves.

A slight increase compared to the years before took place in 2007, with a total world production of phosphate rock of 156 Mt, more specifically in China (45.4 Mt phosphate rock), the United States (29.7 Mt phosphate rock), and Morocco (27.0 Mt phosphate rock) being the leading producing countries, accounting for 65% of the world total (Jasinski, 2008). Concerning the future availability different estimates of years with available phosphorus can be found. Jasinski (2008) from the U.S. Geological Survey estimates that, at current production rates, the world's combined phosphate rock reserves will be sufficient for another 75 years. The estimates of remaining reserves and predictions of the time to last until a general scarcity is seen, vary heavily from 60 to 130 years (Schröder et al., 2010). Reasons are scarce data, non-transparent assumptions and inconsistent use of terms and units (Cordell, 2010).

Phosphorus Recycling

Given the conditions – a rising worldwide phosphorus demand, limited reserves, and a high dependence – it becomes clear that the vulnerability of food production to changes in the fertilizer supply has to be decreased. Especially, since there is no substitute for phosphorus in agriculture, in a possible phosphate crisis the prices for food production would soar while fertility of agricultural soils would decline and increasingly widen the gap between rich countries who can afford expensive fertilizer and those who cannot. Thus minimizing the losses of phosphorus has to be a primary target.

These facts also stress the importance to develop novel ways of utilizing new sources of phosphorus like recycling. This should not only prolong the resource life-time but also increase the share of a resource for developing countries (Weikhard & Seyhan, 2009). Various technologies for phosphorus recycling have been developed.

The first forms of phosphorus recycling reach back to ancient times when the need for a treatment of human excreta was discovered. Early systems of waste incineration (especially in Asia) as well as the first channel systems to transport wastewaters out of a city, indicate that people were aware of the need of treatment, storage and recirculation of nutrient-containing waste (Kirchmann et al., 2005). According to Kirchmann et al. (2005) the recirculation of wastes and wastewaters, however, has significant negative side effects such as heavy metal contamination or the recirculation of organic compounds of artificial origin.

In recent years new technologies and the awareness for the need to recover phosphorus from waste and wastewater have initiated the interest in new ways to extract phosphorus from new sources and to bring it in forms with fertilizer-similar properties. Cabeza Pérez (2010) has identified four recovery processes from sewage sludge, which would be feasible in Germany. Because sewage sludge has a high concentration of phosphorus it has the highest potential to be used as an additional phosphorus source. Here, they are briefly described to show the different approaches of extracting phosphorus:

(i) Seaborne Process: Precipitation as magnesium-ammonium-phosphate (MAP).

This process provides mainly two by-products: biogas and fertilizers from different biomass products.

(ii) P-RoC-technology: Crystallization of phosphorus as calcium phosphate.

This single-step method with the application of calcium silicate hydrate leads to a product of poorly crystalline Hydroxylapatite, which can be used as a fertilizer.

(iii) Mephrec process: Phosphorus recovery from sewage sludge and meat-bone meal.

This special metallurgic process generates gas and phosphate slag and can be used for sewage sludge and bone meal as well as for their ashes. The flexibility in raw materials is the strength of this method, which leads to a product that can be used as a fertilizer and is considered analogue to Thomasphosphat production.

(iv) SUSAN project: Phosphorus recovery from sewage sludge.

During this thermo-chemical method, the sewage sludge is first incinerated and the heavy metals are removed to obtain a product that can be utilized similarly to phosphate rock.