Chapter One: General introduction

1.1 Overview

Phosphorus (P) is an essential nutrient for plants and is necessary for several metabolic processes. The concentration of plant available P is low in most soils hence the fertilization with P fertilizers is needed. Rock phosphate has been the main raw product for the production of P fertilizers since the last century until today. The actual worldwide P resources can maintain the present rate of consumption not longer than 100 years (Berg and Schaum, 2005; Cordell et al., 2009; Steen, 1998; Stewart et al., 2005). The increasing world population and the consequent higher demand of food makes it necessary to find ways to recycle P resources. However, the simple application of sewage sludge or municipal wastewaters to the land has a high public reject, mainly due to the possible content of hazardous products. A way to solve this problem might be the recovery of P by separating it from pathogens, antibiotics and heavy metals. To improve our understanding about how we can reuse P, it is not only necessary to know the technology to achieve that goal, but also to understand the interactions between products applied to the soil and the different P forms in soil. A better knowledge of the soil P is desirable to use P resources in an efficient way. In the following sections the current situation of P resources, recycling alternatives, P dynamics in soils and different methods to evaluate soil P will be described.

1.2 Phosphorus reserves, consumption and new scenarios and technologies

Phosphorus is a non-renewable resource and has no substitute for agricultural purposes (Cordell et al., 2009; Steen, 1998). According to Cordell (2009), P is obtained mainly from rock phosphate mine. Recent approaches calculate that with the current rate of consumption P will be exhausted in about 50-100 years (Steen, 1998). Furthermore, the fertilizer industry has recognized that the remaining rock phosphate reserves are of lower quality and the cost of P fertilizer production is increasing (Cordell et al., 2009; Runge-Metzger, 1995). Beside of a low quality of P reserves the amount of wastes generated during its production is increasing (Steen, 1998).

1.2.1 Global phosphate rock reserves

Phosphate rock deposits are found throughout the world, however the most important reserves are in the northern hemisphere. According to Steen (1998), the information about reserves of rock phosphate are uncertain and are treated as privileged information. More than 30 countries are currently producing phosphate rock for the international market (Steen, 1998; USGS, 2009). Tab. 1.1 shows the more important producers of phosphate rock.

Tab. 1.1. World mine production, reserves and reserve base of rock phosphate. Reserves are defined as those mines exploitable at cost below 40 US dollar per ton and reserve base as deposits that can be processed at a cost below 100 US dollar. (Data from USGS (2009) and definitions about reserve and reserve base were taken from Steen (1998) and Stewart et al. (2005)).

Country	Mine production		Reserves	Reserve base
	2007	2008	Thousand metric tons	
	Thousand metric tons year^{-1}			
Morocco	27,000	28,000	5,700,000	21,000,000
China	45,400	50,000	4,100,000	10,000,000
USA	29,700	30,900	1,200,000	3,400,000
South Africa	2,560	2,400	1,500,000	2,500,000
Jordan	5,540	5,500	900,000	1,700,000
Australia	2,200	2,300	82,000	1,200,000
Russia	11,000	11,000	200,000	1,000,000
Israel	3,100	3,100	180,000	800,000
Syria	3,700	3,700	100,000	800,000
Egypt	2,200	3,000	100,000	760,000
Tunisia	7,800	7,800	100,000	600,000
Brazil	6,000	6,000	260,000	370,000
Canada	700	800	25,000	200,000
Senegal	600	600	50,000	160,000
Togo	800	800	30,000	60,000
Other countries	8,110	10,800	890,000	2,200,000
World total	156,000	167,000	15,000,000	47,000,000

The largest phosphate rock reserve in the world is located in Morocco with an estimate of 5.7 billion tons and with a reserve base of about 21 billion tons. In the worlds second place is China with the largest production and reserves. Among Morocco, China and USA control 3/4 of the global phosphate rock reserves (Tab. 1.1).

Historically the USA has been the largest producer and consumer of rock phosphate and phosphate fertilizers and its reserve according to the U.S. Geological Survey (USGS) (2009) is sufficient at current production rates for the next 75 years. In order to prevent the export of rock phosphate and to secure the domestic consumption, the government of China has imposed a tariff of 135% to rock phosphate exported (Cordell et al., 2009). The worldwide phosphate rock production capacity will increase in about 30% until 2013, for 2010 new mines will open in Australia and Peru and in 2011 in Namibia and Saudi Arabia (USGS, 2009). Other countries in which mines already exist like Brazil, China, Egypt, Finland, Morocco, Russia and Tunisia will expand their activities.

1.2.2 Phosphorus consumption, population trends and nutrition

Historically, P demand has been influenced by a conjunction of factors; among the more important are population and economic growth, prices, policy and agricultural production. According to Cordell (2009), the high level of fertilization in the last century in European countries and North America has secured an optimal P level in soils and in these regions the demand for P fertilizers has been stabilized and may decrease in the future. However, in emerging countries the situation is different. Increase of life expectation and decrease of child mortality have enhanced food production and the demand for fertilizers (Steen, 1998). For the year 2050 a population of around 7.4 to 10.6 billion is expected (Fig. 1.1), which will be concentrated in large cities in developing countries (Cordell et al., 2009; Steen, 1998; UN, 2004). According to Cordell (2009), the popularity and consume of milk products and meet in India and China will increase and consequently the demand of P will be higher. New scenarios are possible for agriculture; the high oil price has promoted the incorporation of crops to produce Bio-fuels (FAO, 2008). European and some developing countries are sponsoring the adoption of new crops and technologies to provide an energy security, to reduce gas emissions and to create new opportunities for the farmers (Steenblik, 2007). Another special situation is observed in countries with extreme poverty where food production is required both in quantity and quality and for increasing the agricultural production it is necessary to enhance the soil fertility. Currently there are about 800 million people suffering food scarcity (300 million are children), over 40% of African people cannot secure a basic daily diet and water resource is an increasing problem (Millenium-Project, 2005). Nevertheless, the P supply has not been recognized as a worldwide issue (Cordell et al., 2009).

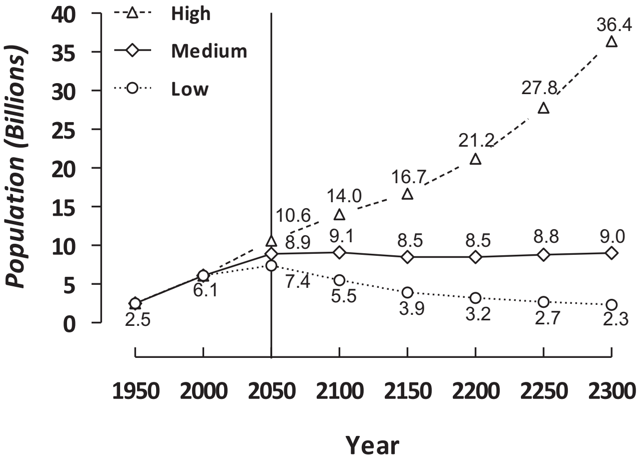

Fig. 1.1. Estimated world population: 1950-2000, and projections: 2000-2300, under three different scenarios; high, medium and low population growth. From United Nations (2004).

1.3 Phosphorus recycling

Reuse of wastewaters and sewage sludge is not an attribute of our modern society. In ancient times, the movement of people to urban areas led consequently to the production of large quantities of human excreta which required the handling. Kirchmann (2005) described that ancient cultures implemented channel systems to evacuate wastewaters. Famous until our days is the “Cloaka maxima” in Rome an example of the necessity to transport wastes outside the city. Another interesting example of handling of organic human wastes was developed in ancient Asiatic cultures (China, Korea and Japan), where wastes were incinerated to transport them to the land, a careful treatment, storage and recirculation of urine were used to prevent the mineral losses (Kirchman et al., 2005). However, the middle age was characterized for a lack of good hygienic practices in the European cities. Poor hygiene and the absence of handling of human waste brought an increase in diseases, laws and fees were introduced to reduce the odor, pollution and to improve the health of the citizens (Kirchman et al., 2005). For example, in some medieval cities of Germany the farmers that brought agricultural products to the cities should return to the Farm with municipal wastes (Wilson, 1976). According to Kirchmann et al. (2005), the introduction of toilets in European cities which were discharged into water bodies near towns resulted in water eutrophication. As a consequence the wastewaters began to be handled in sewage plants to clean and remove nutrients.

Application of sewage sludge directly on the land to improve the soil fertility has several problems and has only been applied successfully in recreation places (parks) and as amendments in degraded soils (Dentel, 2004; Kirchman et al., 2005). The recirculation of P with wastes has been criticized because municipal sludge contains heavy metals and organic compounds of anthropogenic origin (Balmer, 2004; Berg and Schaum, 2005; Kirchman et al., 2005). Another important consideration is related to the high water content present in organic waste (70-80% in sewage sludge), which makes their distribution over longer distances uneconomic (Kirchman et al., 2005). New technologies are being introduced in the treatment of wastewater for reducing heavy metal contents, to recycle nutrients and to produce a product useful as a fertilizer. In Germany the Federal Environmental Ministry (Umweltbundesamt) announced 2003 the support to initiatives to recycle P from wastewaters in sewage works or from sewage sludge incineration ashes (SCOPE, 2003; Umweltbundesamt, 2004).

1.3.1 Processes to recover P in Germany

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

The Seaborne process provides mainly two by-products of sewage sludge; biogas and fertilizers. The process was developed by the Seaborne Environmental Research Laboratory to produce biogas and fertilizers from different biomass products (Cornel, 2002). In this process the sewage sludge is anaerobically digested (Phan et al., 2009). After digestion, the sewage sludge is treated with sulphuric acid to dissolve the solids. The solids not dissolved are separated, dried and incinerated. The ashes can be reverted to the acidification process. In the following step heavy metals are precipitated with the addition of sodium sulphide (Na_2S) and removed them from the flow (Phan et al., 2009). Then nitrogen, phosphorus and potassium are precipitated by various chemical precipitation reactions in a “nutrient removal system” where the pH is adjusted to achieve a value 9, with the addition of NaOH and $Mg(OH)_2$ (Phan et al., 2009). In the step described above, the precipitation of magnesium-ammonium-phosphate (MAP) is obtained. In the process final stage MAP is separated from the flow using a decanter (Phan et al., 2009).

1.3.1.2 Crystallization of P as a calcium phosphate: P-RoC-technology

The “P Recovery from Waste- and Process Water by Crystallization” is described among the alternatives to recover P from wastewaters in Germany (Ehbrecht et al., 2009). The P recovery with this method occurs in a single step with the application of calcium silicate hydrate (CSH) compounds (Berg et al., 2007). According with Berg et al. (2007) and Ehbrecht et al. (2009) the product obtained with this treatment is a poorly crystalline Hydroxylapatite (HAP, $Ca_5(PO_4)_3OH$) which has a high water solubility and can be used as a P fertilizer.

1.3.1.3 Phosphorus recovery from sewage sludge and meat-bone meal: Mephrec process

The Mephrec system to recycle P is a special metallurgic process to generate gas and phosphate slag. The materials that can be used with this process are sewage sludge and meat-bone animal meal as well as ashes from their incineration (Scheidig et al., 2009). According to Scheidig et al. (2009), the input material must be agglomerated to use it in the Mephrec process, the most common form is the agglomeration as a briquette. The Mephrec process has developed a particular method to use sewage sludge, which is dried mechanically and converted to briquettes for using in shaft furnaces. The agglomerated material is smelted in a shaft furnace up to 2000°C using a mixture with limestone or dolomite for the slag formation. The material smelted is granulated with a jet of water (Scheidig et al., 2009). Thus, a special characteristic of Mephrec process is the possibility of using several different materials for P recovering (Scheidig et al., 2009). According to Berg and Schaum (2005), the material obtained with this technology can be used as a fertilizer or as a raw material for the fertilizer industry, and can be considered analogue to the Thomasphosphat production. Some characteristics of this material are shown in Tab. 1.2.

Tab. 1.2. Mineral composition of two products obtained by the Mephrec process (Scheidig et al. (2009)).

Slag components	CaO	MgO	SiO_2	Al_2O_3	P_2O_5	Plant available P_2O_5
				%		
Mephrec slag 1	49.0	3.5	21.0	17.4	4.6	92.7
Mephrec slag 3	50.5	2.5	16.0	14.5	12.0	94.2