**Ricardo Alfonso Cabeza Pérez** 

Phosphorus dynamics in soil and plant availability of fertilizers from phosphorus recycling evaluated in field and pot experiments





Phosphorus dynamics in soil and plant availability of fertilizers from phosphorus recycling evaluated in field and pot experiments

Dissertation to obtain the Ph. D. degree in the International Ph. D. Program for Agricultural Sciences in Göttingen (IPAG) at the Faculty of Agricultural Sciences, Georg-August-University Göttingen, Germany

Submitted by

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To my parents and brothers A mis padres y hermanos, gracias por todos estos años de amor y apoyo

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X

Symbol	efinition				
Chapter two					
TSP-60	Reference fertilizer triple superphosphate, 60 kg of P ha <sup>-1</sup>				
TSP-100	Reference fertilizer triple superphosphate, 100 kg of P ha <sup>-1</sup>				
Chapter three					
TSP-60	Reference fertilizer triple superphosphate, 60 mg of P kg <sup>-1</sup> soil				
TSP-200	Reference fertilizer triple superphosphate, 200 mg of P ka <sup>-1</sup> soil				
For all chapters					
P-0	Control unfertilized				
MAP-Sb	Phosphorus recovery as magnesium-ammonium-phosphate from Seaborne sewage sludge treatment plant				
MAP-Gf	Phosphorus recovery as magnesium-ammonium-phosphate from				
	Gifhorn sewage sludge treatment plant				
MAP-St	Phosphorus recovery as magnesium-ammonium-phosphate from				
	Stuttgart sewage sludge treatment plant				
Sinter-P	Phosphorus recovery by sintering of animal by-products				
Sl-ash	Phosphorus recovery by burning of sewage sludge				
Cupola slag	Phosphorus recovery by smelting of sewage sludge and dust from animal meal				
MB meal ash	Phosphorus recovery by mono-incineration of animal by-products				
MCP	Mono calcium phosphate				
MoAP	Mono ammonium phosphate				
CAL-P	P extracted by calcium-acetate-lactate method				
b	Buffer power of P in soil				
CL	P concentration in soil solution				
рК <sub><i>sp</i></sub>	Solubility product				
RFE	Relative fertilizer efficiency, %				
IEP	Isotopically exchangeable phosphorus				
Resin-P <sub>i</sub>	Soil P extracted by anion exchange resins				
NaHCO <sub>3</sub> -P <sub>i</sub>	Soil P extracted by 0.5 M sodium bicarbonate				
NaOH-P <sub>i</sub>	Soil P extracted by 1 M sodium hydroxide				
HCl 1M-P <sub>i</sub>	Soil P extracted by 1 M hydrochloric acid				
HCl concP <sub>i</sub>	Soil P extracted by hot concentrated hydrochloric acid				
Residual P	Soil P extracted by sulphuric acid and water peroxide				

# List of Symbols and Abbreviations

# **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)).

	Mine pro	oduction	Reserves	Reserve base		
Country	2007	2008	Thousand	housand metric		
Thousand metric tons year <sup>-1</sup>			tons			
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<sub>2</sub>S) 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)<sub>2</sub> (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)).

	CaO	MgO	SiO <sub>2</sub>	$AI_2O_3$	$P_2O_5$	Plant available $P_2O_5$
Siag components				- %		
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

## 1.3.1.4 Phosphorus recovery from sewage sludge: the SUSAN project

The SUSAN project (Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery) tends to obtain a sustainable and safe strategy to recycle nutrients from sewage sludge by thermochemical work (Adam et al., 2009b). The P recovery starts with a mono-incineration of sewage sludge destroying organic compounds and obtaining a high P content, but also heavy metals. In the following step heavy metals from ashes are volatilized in the form of chloride compounds by the addition of a chloride donor (MgCl<sub>2</sub> or CaCl<sub>2</sub>), water (up to 30% of the mixture) and temperature, about 1000°C (Adam et al., 2009b).



Fig. 1.2. Schematic representation of the steps to recycle P with the SUSAN process (Adam et al., 2009b).

The gasified metals are separated from the gas matrix in a gas treatment system. After the separation of heavy metals, a raw material is obtained which can be used in the industry of

fertilizers in a similar way as rock phosphate (Adam et al., 2008; Adam et al., 2009b). Phosphates generated from this process are mainly Mg/Ca-P but Al-P is also possible to find. The P concentration of end product is about 6.0-11.0% (Adam et al., 2008; Adam et al., 2009b).

#### 1.4 Phosphorus dynamics in soil

#### 1.4.1 The soil solution

The reactions and interactions between soil compounds take place in soil solution (Lindsay, 1979). The plants take up the nutrients from soil solution producing a depletion of the plant nutrients (Barber, 1995) and the soil must be able to replenish the P of the soil solution many times over the crop cycle to maintain an optimal concentration for plant growth (Pierzynski et al., 2005). Then a new equilibrium for the nutrients taken up by plants is reached. Plant nutrients in soil solution are buffered on the surfaces of minerals, a small amount of these nutrients can be depleted to the soil solution and become available for the plants (Lindsay, 1979). The soil compounds are very variable and control the intricate equilibrium in soil solution, for this reason a part of P may precipitate in less soluble forms (precipitation-dissolution) others may be sorbed by the soil particle surface (sorption-desorption), immobilized by biological fixation (immobilization-mineralization) or react in dependence on the soil pH and oxidation-reduction conditions (Pierzynski et al., 2005).

#### **1.4.2** Phosphorus cycle and phosphorus forms in soil

The natural P sources in most soils are primary minerals derived from apatite (Pierzynski et al., 2005). However, weathered soils have more stable minerals of P that are associated with elements such as Al and Fe (Pierzynski et al., 2005; Walker and Syers, 1976). As it can be seen in Fig. 1.3, Walker and Syers (1976) established a pattern for the P changes, where the P associated with Ca ( $P_{Ca}$ ) is the main P compound in young soils (in a geological scale), decreasing over time to obtain a more stable P form which is considered to be occluded by Fe or Al hydrous oxides or strongly adsorbed by allophane in soils derived from volcanic ashes (Crews et al., 1995). The soils in natural systems are not subject to large inputs of nutrients and the P forms are very stable (Stevenson and Cole, 1999) and as it can be seen in

the scheme of Walker and Syers (1976) the organic P ( $P_o$ ) is relatively stable over time. The dynamics of P described by the authors are more useful from the ecological point of view whereas a more appropriate characterization for plant nutrition is given by the solubility of P in soil and the adsorption/desorption processes.



Fig. 1.3. Walkers and Syers scheme of P transformation over the time. From Walker and Syers (1976).

# 1.4.3 Phosphorus concentration in soil solution and P dissociation depending on pH value

The concentration of phosphorus in soil solution is usually around 0.03 to 0.5 mg L<sup>-1</sup> (1  $\mu$ M to 16  $\mu$ M) which is very low (Barber, 1995). It is also possible to find high concentration of P in soil solution (1 mg L<sup>-1</sup> or 32  $\mu$ M) in soils that have been fertilized (Brady and Weil, 2002). In some cases where the soil has been heavily fertilized the concentration of P in soil solution can reach 7 to 8 mg P L<sup>-1</sup> (Pierzynski et al., 2005).

The principal forms of P in soil solution depending on the pH value are  $HPO_4^{2-}$  and  $H_2PO_4^{-}$ , divalent and monovalent anion of orthophosphate respectively (Fig. 1.4) (Barber, 1995; Brady and Weil, 2002; Havlin et al., 2005).

Typically, the orthophosphate form  $HPO_4^{2-}$  is predominant in soils with high pH (>7.2) and  $H_2PO_4^{-}$  in acid to neutral soils (pH 4.0-7.2) (Pierzynski et al., 2005). The point where the two species are in equilibrium (50% of each species is present in soil solution) is called *p*K or formation constant and is numerically equal to pH of the solution (Lindsay, 1979).



Fig. 1.4. Influence of pH on the orthophosphate forms in soil solution. From Lindsay (1979).

The equation that relates the amount of orthophosphate species in a specific pH is given by the following formula (Lindsay, 1979):

Eq. 1.

$$\frac{(H_2 P O_4^-)}{(H P O_4^{2-})(H^+)} = 10^{7.2}$$

According to Pierzynski et al. (2005), complex ions of P such as  $CaHPO_2^{\circ}$  or  $CaPO_4^{-}$  are present in soil solution, and in alkaline soils these can represent a substantial part of P in soil solution and it can be quickly converted to orthophosphates. In general, the orthophosphate forms of P are recognized to be taken up by plants, although there are evidences about the uptake of organic P compounds as nucleic acid and phytin also (Bowman and Cole, 1978; Havlin et al., 2005).

## **1.4.4** Phosphorus precipitation and adsorption

The P availability depends on many soil factors. The pH value of soil solution, type and amount of clay minerals and oxide minerals such as Al and Fe are among the more important

(Stevenson and Cole, 1999). Thus, the input of P in a soil implies the dissolution in the soil solution and subsequent precipitation and adsorption (Havlin et al., 2005).

In acid soils, P precipitates as secondary minerals of Al and Fe which are highly insoluble, as Ca-P in soil near to neutral pH, which are partially P available and in calcareous and some alkaline soils as hydroxyapatite carbonated which are highly insoluble (Stevenson and Cole, 1999). In acid soil there is sufficient Al or Fe in solution to cause a chemical precipitation of  $H_2PO_4^-$  as insoluble hydroxyl phosphates (Brady and Weil, 2002). The reaction is described by Eq. 2.

Eq. 2. 
$$Al^{3+} + H_2PO_4^- + 2H_2O \rightleftharpoons 2H^+ + Al(OH)_2H_2PO_4$$

The precipitation occurs when solution P exceeds the solubility product ( $K_{sp}$ ) of the specific mineral that contains P, while adsorption processes occur with low solution P concentrations (Havlin et al., 2005). Both, precipitation and adsorption are a continuous sequence and their distinction is difficult.

In acid soils the P adsorption is related mainly to Al and Fe oxides as well as hydrous oxide minerals that are on the clay surfaces (Havlin et al., 2005). The adsorption process can be separated into:

1. Non-specific adsorption of anions by simple coulombic interaction with Al-OH<sub>2</sub> or Fe-OH<sub>2</sub> groups, also called *outer sphere* where the anions can be exchanged for other ones (Brady and Weil, 2002).

2. Specific adsorption, where the anion is incorporated as a ligand (in the coordination shell of an Al or Fe atom also called *inner sphere*) (Brady and Weil, 2002). Phosphorus is adsorbed to Al or Fe oxide surface by interacting with  $OH^-$  and/or  $OH_2^+$  groups (Fig. 1.5 and Fig. 1.6). If  $H_2PO_4^-$  is bonded with one Al-O-P bound, the structure is considered a labile P and can be desorbed but when  $H_2PO_4^-$  is linked to two Al-O (a stable binuclear bridge) then a stable form of P is formed and the desorption will be more difficult (*difficultly available P*) (Havlin et al., 2005; lñiguez and Val, 1984; Stevenson and Cole, 1999; Wada and Gunjigake, 1979).



Fig. 1.5. Adsorption of phosphate at hydrous oxide surfaces through a ligand binding mechanism (Stevenson and Cole, 1999).



Fig. 1.6. Phosphorus sorbed on hydrous ferric oxide gels (Stevenson and Cole, 1999).

Phosphorus can also be adsorbed in calcareous soils by the replacement of  $CO_3^{2-}$  for  $PO_4^{3-}$  on calcium carbonate surfaces (Havlin et al., 2005).

According to Stevenson and Cole (1999), the adsorption process is influenced by clay mineralogy and can be graded as follows: amorphous hydrous oxides > goethite = gibbsite > kaolin > montmorillonite. The high rate of P adsorption of amorphous hydrous oxides in low pH has been recognized in many investigations on Andosols with high content of allophanes (Borie and Zunino, 1983; Iñiguez and Val, 1984; Wada and Gunjigake, 1979), however these cases of P adsorption probably depends more on the high specific surface area of amorphous minerals than on pH value (Iñiguez and Val, 1984; Wild, 1988). In highly weathered soils the precipitation in Al and Fe phosphates can occur readily (Stevenson and Cole, 1999) and are more intense in soils with large amounts of iron oxides such as Oxisols (Wild, 1988), which are found mainly in tropical and subtropical regions (Brady and Weil, 2002).

Precipitation as well as adsorption depends on the pH of the soil solution and both are collectively called P fixation (Brady and Weil, 2002; Havlin et al., 2005). The foregoing indicates that P in a soil will be bound or contained in different chemical forms or P fractions.

## 1.4.5 Phosphorus fractionation

A P fractionation procedure is a characterization of different P pools extracted with different chemical solutions (Hedley et al., 1982; Tiessen and Moir, 1993). It is based on the assumption that plant available soil P is removed first by mild extractants, while difficult available P can only be removed by stronger solutions such as acids or alkali (Buehler et al., 2002). This approach also allows certain conclusions about the fate of P fertilizers applied to the soil (Chang and Jackson, 1957; Pheav et al., 2003), about the P dynamics under different tillage systems (Redel et al., 2007) and it is useful in studies related to the aging<sup>1</sup> of P in soil and pedogenesis (Cross and Schlesinger, 1995; Smeck, 1973; Syers and Walker, 1969; Tiessen et al., 1984; Walker and Syers, 1976; Williams et al., 1969).

An early procedure to obtain different fractions of soil P was developed by Chang and Jackson (1957), where the fractions are extracted with solutions of different chemical composition and increasing the chemical strength. In that work, the goal of the authors was to extract different fractions of soil P, taking into account that P compounds in soil can be present in four main forms according to their chemical nature:

- 1. Calcium phosphate
- 2. Aluminum phosphate
- 3. Iron phosphate and
- Reductant-soluble phosphate extractable after removal of the first three P forms (occluded P) (Chang and Jackson, 1957).

The classification described above does not provide any information about the availability to plants. However it allowed the development of a methodological approach to understand the soil P dynamics. Previously, other authors tried to obtain a method to fractionate P in soils, however, the P linked to Al and Fe were not differentiated (Chang and Jackson, 1957). In the sequential extraction proposed by Chang and Jackson (1957) to distinguish Al-P from

<sup>&</sup>lt;sup>1</sup> Reduction of P solubility in soils.

Fe-P the soil is extracted by a solution of neutral ammonium fluoride which can dissolve only Al-P and not Fe-P. The procedure can be summarized as follows:

- 1. Primarily use of 1 N NH<sub>4</sub>Cl to remove water soluble and loosely bound P as well as exchangeable Ca,
- 2. 0.5 N NH<sub>4</sub>F for extracting P linked with Al (Al-P),
- 3. 0.1 N NaOH for removing P linked with Fe (Fe-P),
- 4. Calcium phosphates are extracted with 0.5 N  $H_2SO_4$ , and
- Occluded P in Fe and Al is extracted with a 0.3 M sodium citrate plus Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and neutral NH<sub>4</sub>F respectively (Chang and Jackson, 1957).

According to Stevenson and Cole (1999), subsequent studies on P fractionation showed that chemical extractants used in the Chang and Jackson scheme were not as specific as they were intended. Principally it was observed that in calcareous soils the calcium phosphates were readsorbed after the extraction with NH<sub>4</sub>F and that there is no differentiation between P linked to Al or Fe oxides (Machold, 1963; Williams et al., 1969). The extraction method presented by Chang and Jackson (1957) has been modified several times in other investigations, but the changes proposed by Hedley et al. (1982) represented a new way to interpret the role of P in soil.

The fractionation proposed by Hedley et al. (1982) is based on biological availability of soil P. The soil P is separated in discreet fractions and differentiating among inorganic P ( $P_i$ ) and organic P ( $P_o$ ). The strength of the extractant solutions increase (it is based on the type of solution and its concentration) and thus, the subsequent P fractions become less available (Hedley et al., 1982; Stevenson and Cole, 1999).

Fig. 1.7 shows the sequential extraction developed by Hedley et al. (1982). The P extracted with anion exchange resin represents the P<sub>i</sub> which is biologically available (Hedley et al., 1982) or isotopically exchangeable, also called labile-pool (Saggar et al., 1990).



Fig. 1.7. Sequential extraction scheme according to Hedley et al. (1982).

According to Hedley et al. (1982) the next extraction with 0.5 M NaHCO<sub>3</sub> removes labile  $P_i$ and  $P_o$  sorbed on the soil surface and small amounts of microbial P. This procedure additionally allows the calculation of microbial P in the soil. In a parallel sample and after the extraction with anion exchange resins, the sample can be treated with chloroform (CHCl<sub>3</sub>) and then extracted with 0.5 M NaHCO<sub>3</sub>, the difference between the P of parallel samples represents the amount of microbial P, and can constitute up to 40% of the microbial P in a soil (Hedley and Stewart, 1982; Hedley et al., 1982).

The NaHCO<sub>3</sub> is followed by a 0.1 M NaOH extraction. According to Hedley et al. (1982) in this step  $P_i$  and  $P_o$  linked strongly to Al and Fe are extracted. The nature of the link between Fe and Al-P has been described as a chemisorption (McLaughlin et al., 1977; Ryden et al., 1977). In a next step, the soil sample is subject to sonification in presence of 0.1 M NaOH to facilitate the release of phosphates ( $P_i$  and  $P_o$ ) linked to internal soil surfaces. Phosphorus which is held as Ca-P is extracted with 1 M HCl and finally the more resistant P compounds in

the soil are extracted with a digestion in presence of  $H_2SO_4$  and  $H_2O_2$  in order to dissolve any residual P (Hedley et al., 1982).

This process determines the amount of organic P present in NaHCO<sub>3</sub> extraction and in the two NaOH extractions by calculating the difference between  $P_i$  and total P ( $P_t$ ) (Hedley et al., 1982).

A modification in the procedure to extract sequentially P was proposed by Tiessen and Moir (1993), where the sonicate-NaOH extraction was replaced with 1 M HCl followed by hot 11.3 M HCl addition.

The changes to the fractionation scheme proposed by Hedley et al. (1982) were intended to determine  $P_o$  that would otherwise remain undetermined, with an amount of 20 to 60% unextracted P<sub>o</sub> (Tiessen and Moir, 1993). In general terms, this sequential extraction can be understood only as an approximation to the biological functions of each fraction. For the first extraction, the phosphorus is extracted with anion exchange resins and it can be interpreted as free exchangeable P<sub>i</sub>, because anion exchange resins do not modify the chemical composition of soil solution (Tiessen and Moir, 1993). Sodium bicarbonate extracts P<sub>i</sub> and P<sub>o</sub> fractions that are easily plant available (Tiessen and Moir, 1993). The NaHCO<sub>3</sub>-P is not comparable to the so called P-Olsen test although the extractant solution is exactly the same, since P-Olsen soil fertility test has a different ratio of soil to solution (1:20) and the shaking time takes only 30 minutes (Olsen and Sommers, 1982). Furthermore, the method prevents the interference of organic matter in the measurement of P by adding carbon black (Hedley and Stewart, 1982; Olsen and Sommers, 1982). In the fractionation scheme, P extracted with sodium bicarbonate is obtained after the extraction with anion exchange resins (Tiessen and Moir, 1993). Anion exchange resins and bicarbonate extractable P<sub>i</sub> are the labile phosphorus forms obtained by this procedure, which are believed to be adsorbed on surfaces of crystalline P compounds, sesquioxides and carbonates (Mattingly, 1975; Tiessen et al., 1984) and  $P_0$  which can readily be converted into inorganic available form to the plants (Bowman and Cole, 1978; Tiessen et al., 1984).

The extraction with NaOH determines Al-P and Fe-P, but there are no distinctions between the chemical forms the extracted P originates (Tiessen and Moir, 1993). It is thought that hydroxide extractable P<sub>i</sub> has a lower availability for plants and is associated with amorphous and crystalline Al and Fe-P (Tiessen et al., 1984). Hydroxide extracted organic P forms are more stable and are involved in the long term transformations of  $P_o$ , possibly chemiadsorbed to surfaces of Al and Fe oxides as well as carbonates (Cross and Schlesinger, 1995; Tiessen et al., 1984). The other important point is that in the schemes of Hedley et al. (1982) and Tiessen and Moir (1993) the extractions with NaHCO<sub>3</sub> and NaOH represent a continuum of phosphates associated with Al and Fe (Tiessen and Moir, 1993).

Phosphorus linked to carbonates are extracted by two solutions, 1 M HCl and hot concentrate HCl (11.3 M) and the residual phosphates are removed by  $H_2SO_4$  and  $H_2O_2$  respectively (Tiessen and Moir, 1993). According to Mehta et al. (1954), the hot HCl extraction is useful to determine  $P_i$  and  $P_o$  in weathered soils and seems to extract most of the organic and inorganic residual P (Tiessen and Moir, 1993).

#### 1.5 Methods to evaluate the phosphorus availability to plants

#### 1.5.1 Chemical extractants

Since plants take up the nutrients from the soil liquid phase and the replenishment depends on the soil solid phase, the description of this two pools is necessary to evaluate the soil fertility (Stevenson and Cole, 1999). While the intensity of a nutrient (i.e. the concentration in soil solution) is the instant indicator of availability, it is more important to take into account the ability of the soil to maintain the intensity for a long period of time or for the growth season of a crop (Beegle, 2005; Mengel and Kirkby, 1987). It is the so called soil buffer power which depends on exchangeable nutrients on the soil solid phase (i.e. quantity). Thus a soil test must be able to characterize the specific P fraction which is in exchange with the soil solution P (Beegle, 2005). In order to evaluate the amount of plant available P several soil tests have been developed over the years, however no single soil test is suitable for all soils (Schüller, 1969; Stevenson and Cole, 1999). Some of these tests are as simple as the P determination in soil solution (Adams, 1974), but as it was mentioned above, the intensity of Phosphorus is only the immediate available source and does not reflect the amount of exchangeable P. Other methods are as simple as P extracted with water which has a good correlation with the P uptake by plants (Sissingh, 1971; Stevenson and Cole, 1999; van der Paauw, 1971). Phosphorus extracted with water attempts to simulate the P concentration in soil solution, but there are several problems since the water disperse the clay particles and it is necessary to use a salt to flocculate them (i.e. CaCl<sub>2</sub>). The method

seems to be more suitable for acid sandy soils, where the conversion to insoluble forms is not important and the dispersion of clay particles is not relevant (Stevenson and Cole, 1999). As described previously (1.4.5), the major available P fractions for plants are Al-P, Fe-P and Ca-P (Beegle, 2005) thus, it seems to be obvious that a soil test must extract plant available P from those P pools. A high correlation between the plant uptake and the P extracted by a soil test is expected. This relation is not necessarily equal to the amount of a nutrient taken up by a crop, but it must be closely related to it (Havlin et al., 2005). Another important point is that the P extracted by a chemical method is only an index of nutrient availability and it represents in no case the exact amount of a nutrient available for plants (Black, 1993; Havlin et al., 2005). Therefore many authors argue better to use the term "extractable P" than "available P" (Beegle, 2005).

A widely used soil test to evaluate the plant available P in Germany was developed by Schüller (1969) for Austrian soils, the so called calcium-acetate-lactate method (CAL-P), an acid extractant (pH 4.1) originally designed for soils that were not alkaline (Schüller, 1969). This method correlates with the exchangeable P extracted with 1 M NH<sub>4</sub>Cl from Chang and Jackson (1957) scheme, which only extracts water soluble P and loosely bound P (Schüller, 1969).

Another soil test used worldwide was developed by Olsen et al. (1954). The procedure involves extracting soil with 0.5 M NaHCO<sub>3</sub> at 8.5 pH in a relation of 1:20 soil/solution, and it has been successfully applicable both in alkaline as in acid soils (Olsen et al., 1954; Stevenson and Cole, 1999). In alkaline soils the HCO<sub>3</sub><sup>-</sup> decreases the Ca<sup>2+</sup> concentration in soil solution by causing precipitation of CaCO<sub>3</sub>, as a result the P concentration in soil solution increases (Olsen and Sommers, 1982; Olsen et al., 1954; Stevenson and Cole, 1999). In acid soils the P concentration in soil solution increases by replacing HPO<sub>4</sub><sup>2-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup> by HCO<sub>3</sub><sup>-</sup> and probably the change of pH in the solution raises the P solubility. Olsen et al. (1954) showed that the NaHCO<sub>3</sub>-P correlates closely with the isotopically exchangeable <sup>32</sup>P. Other methods are available (e.g. Bray, Mehlich-3 and resin-P) but will not be discussed here because they are beyond the scope of this research.
#### 1.5.2 Isotopic exchange of phosphorus in soils

Plants take up P from soil solution producing a decrease of P concentration and a desorption of it from the soil solid phase (Wild, 1988). A portion of P in soil solid phase is in equilibrium with P in solution (Olsen and Sommers, 1982; Stevenson and Cole, 1999) and this fraction seems to be available for plants (Wild, 1988). This fraction has been defined as isotopically exchangeable P and it can be measured equilibrating the soil with a P-labelled phosphate (H<sub>3</sub><sup>32</sup>PO<sub>4</sub> or H<sub>3</sub><sup>33</sup>PO<sub>4</sub>), assuming that ions of isotope <sup>32</sup>P or <sup>33</sup>P have the same fate in the soil system (Frossard and Sinaj, 1998; Morel and Plenchette, 1994; Olsen and Sommers, 1982; Stevenson and Cole, 1999; White, 1976).

The following reaction represents the theoretical isotopic reaction of P in the exchangeable pool:

Eq. 3. 
$${}^{31}P \text{ solid} + {}^{32}P \text{ solution} \rightleftharpoons {}^{32}P \text{ solid} + {}^{31}P \text{ solution}$$

once the balance has been reached, the equation can be written as follows and it is possible to calculate the amount of isotopically exchangeable P (Wild, 1988):

Eq. 4.

$$^{31}P \ solid = \frac{^{32}P \ solid}{^{32}P \ solution} \times ^{31}P \ solution$$

Isotopic methods have been used since 1948 to determine the exchangeable isotopic P with <sup>32</sup>PO<sub>4</sub> ions introduced in the soil solution (Frossard and Sinaj, 1998). By means of isotope methods it has been possible to establish the availability of different P fractions. For example, Machold (1962; 1963) performed sequential extractions according to Chang and Jackson's procedure in different soils previously labeled with <sup>32</sup>P, showing that P extracted by NH<sub>4</sub>Cl and NH<sub>4</sub>F correlates with the exchangeable isotopic P more than that P extracted by NaOH, H<sub>2</sub>SO<sub>4</sub> and Na-citrat-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solutions (Machold, 1963). The method also has been used to determine the rate of mineralization of organic P (Frossard et al., 1996) and to

evaluate the effectiveness of P fertilizers (Casanova et al., 2002; Randhawa et al., 2005; Randhawa et al., 2006).

#### 1.6 Objectives of the study

Phosphorus recycling has become an important topic since P resources are decreasing. Furthermore, the increase of world population and the current demand for food and water quality have encouraged policies to recycle P from different sources. The German Government has promoted the P recycling through a national project where several partner institutions have collaborated in the different instances to obtain and prove the effectiveness of the P recycling processes.

The recycled P products have different chemical composition depending on the process by which they were obtained (i.e. chemical precipitation or thermal process). Thus, the effectiveness as P fertilizer depends on chemical form of P as well as the soil properties in which it is applied. Furthermore, recycled P fertilizers, can affect the P pools of soils and their plant availability in different ways because of their chemical composition.

The objective of the first part of this study (chapter 2) was to evaluate the agronomic effectiveness of recycled P fertilizers in field conditions using three different soils of low P availability. The questions were, to which extent recycled P fertilizers are as effective as a water soluble P fertilizer and how soil properties affect this effectiveness under field conditions. Grain yield and P uptake were taken as parameters to assess the effectiveness of recycled P fertilizers as well as P concentration in soil solution and P extracted by calcium-acetate-lactate (CAL-P).

In a second part (chapter 3), a pot experiment was carried out to evaluate the effectiveness of recycled P fertilizers in comparison to reference P fertilizers applied to the soil. The questions were to which extent recycled P products are as effective as water soluble fertilizer under stressful conditions (i.e. high root density). Furthermore (chapter 4), for a better understanding of P dynamics in soils, P fractions extracted by a sequential procedure and the isotopically exchangeable P were evaluated in the pot experiment.

By these field and pot experiments as well as laboratory research it is expected to obtain a better understanding of P fertilizers from P recycling.

# Chapter Two: Effectiveness of P fertilizers from P recycling in field experiments

# 2.1 Introduction

Phosphorus (P) as an essential nutrient has no substitute for animals and plants, and without its presence the growth of any organism is not possible (Berg and Schaum, 2005). Phosphorus supply is a major constraint to produce food in quantity and quality. However, P resources are limited and therefore it is necessary to reduce the dependence on industrial fertilizers by recovering and reusing the nutrients from the food production and consumption chain (Cordell et al., 2009). This recovery can be achieved by recycling nutrients from human excreta as well as animal wastes. However, the direct application of wastewaters or sewage sludge on agricultural land has several problems. Among the more relevant concerns against the direct application of sewage sludge are the high levels of heavy metals they contain and hazardous organic compounds of anthropogenic origin like antibiotics, hormones and other pharmaceuticals or human pathogens (Adam et al., 2009a; Balmer, 2004; Dentel, 2004). Thus, as a way to prevent chemical and biological contamination of agricultural soils, and to reduce the reliance on industrial fertilizers, some European governments have been promoting new technologies to recycle P from wastewaters and sewage sludge (SCOPE, 2003).

Phosphorus in wastewaters and sewage sludge can be recovered by many different processes i.e. chemical processes such as magnesium-ammonium-phosphate and Ca-P precipitation, or through thermochemical processes (Adam et al., 2009a; Ehbrecht et al., 2009; Phan et al., 2009). Phosphorus recovery by the processes mentioned, varies in its P content and in its availability to the plants depending on its final chemical composition. Limited information about the effectiveness of these recycled products on agronomical trials is available in the literature. Only few examples of agronomic experiments can be found, the works of Römer and Samie (2002), Johnston and Richards (2003), Plaza et al. (2007), Massey et al. (2009) and Adam et al. (2009a) are among the more relevant, however all works were carried out on pot experiments. One advantage of conducting pot experiments is the control on the variables affecting the plant growth. Furthermore, root system reaches a high density, allowing that the whole soil volume and so most soil nutrients are exploited.

However, this does not represent the real conditions for the growth in the field. A crop under field conditions is not subject to inter-root competition for P since the depletion zone of P is not wider than 2 mm and the half distance between roots is normally not smaller than 2 mm in the first 30 cm of soil (Jungk, 2002). Thus, the plant roots cannot explore the total volume of soil containing P. Therefore, it is not possible to extrapolate results of P fertilizers effectiveness tested in pot experiments to field conditions.

The objective of this study was to evaluate the agronomic effectiveness of P recycled products of different recycling processes in long-term field experiments.

#### Hypothesis:

- Phosphorus products from P recycling processes vary in their effectiveness in comparison to soluble fertilizers depending on their chemical composition and the process to obtain them.
- The effectiveness of P recycled products obtained by chemical processes will be similar to the water soluble fertilizer triple superphosphate (TSP), independent of the soil pH value, whereas products obtained by thermal processes will be more effective on acid soils similar to rock phosphate (RP).
- The effectiveness of recycled P products of low solubility will increase with time due to a slow dissolution and release of P compounds.

To test these hypotheses field experiments in three different locations were carried out during three years. The P fertilizers effectiveness was evaluated using dry matter yield (DMY), P uptake and the effect on soil parameters such as P concentration in soil solution and CAL-P.

#### 2.2 Materials and methods

#### 2.2.1 Products from P recycling as P fertilizers

Four different materials were tested with regard to their effectiveness as P fertilizers in field experiments on three different soils. Additionally, two commercial fertilizers with different P availability, i.e. triple-superphosphate (TSP) and rock phosphate (RP) were taken as references. The materials used were: two magnesium-ammonium-phosphates (MAP) of different sewage treatment plants (MAP-Sb and MAP-Gf), a heavy metal depleted sewage sludge ash (SI-ash), and an alkali sinter phosphate made from meat-and-bone meal (Sinter-P). Tab. 2.1 shows the P concentration and water soluble P in the materials. All products were finely ground before fertilization.

Material	Description	Total P	Proportion of total P soluble in		
Wateria	Description	concentration	*Water	+2% citric acid	
Reference fert	ilizers		- % -		
Triple super	phosphate (TSP) -	20.1	90	-	
Rock phosp	hate (RP) -	11.8	<0.01	17.0	
Obtained by ch	nemical processes				
MAP-Sb	Precipitated as MgNH <sub>4</sub> PO <sub>4</sub>	11.0	1.1	51.0	
MAP-Gf	$Precipitated as MgNH_4PO_4$	9.6	0.8	47.0	
Obtained by th	ermal processes				
Sinter-P	Meat and Bone meal sintered over 1000°C	11.3	0.3	34.5	
SI-ash	Sewage sludge burned over 1000°C	7.8	6.4	31.4	

Tab. 2.1. Description of the reference P fertilizers and P fertilizers from P recycling.

\*5 g of material were extracted with 250 mL of water. †2.5 g of material were extracted with 250 mL of 2% citric acid.

#### 2.2.2 Description of the experimental location

Field experiments were carried out on three farms with different crop rotations and during 3 years. The places are located in Lower Saxony, Germany. Lower Saxony has a transitional climate between maritime and continental, with an average annual temperature of 8.7°C, being the average temperature in August of 22.5°C and an average temperature of -2.2°C in January. The mean annual rainfall in Göttingen is 644.9 mm, with February as driest month and June as rainiest (39.1 and 81.3 mm respectively). One experiment was established in a silt loam soil near to Sattenhausen with a distance of 7.3 km in Southeast direction to

Göttingen. A second experiment was realized on a silt loam soil at Gieboldehausen 20 km Northeast of Göttingen. A last field experiment was carried out on a silty clay soil at Lutterbeck 22 km Northwest of Göttingen. The criterion for deciding to carry out the field experiments on these soils was the low phosphorus availability determined with the calcium-acetate-lactate extractable P (CAL-P) method (Schüller, 1969) and differences in pH, clay and organic matter content. The main soil characteristics of the sites used in the field experiment are shown in Tab. 2.2.

Tab. 2.2. Main characteristics of the soils used in the experiments of fertilization with recycled phosphorus materials.

Location	Clay Silt		Sand	Organic matter	pH in $CaCl_2$	CAL-P	
		%			(relation 1:2.5)	mg P kg $^{-1}$	
Gieboldehausen	25.0	65.5	9.5	2.8	6.8	21.0	
Sattenhausen	11.4	86.9	1.7	1.7	5.6	19.0	
Lutterbeck	50.0	47.0	3.0	3.3	7.1	18.0	

The phosphate fertilization took place as a top dressing into the crop in March 2007 for a whole period of a three-year crop rotation with an amount of 60 kg P ha<sup>-1</sup> for each fertilizer. This is a suboptimal rate in order to be able to differentiate the P available to the plants from the P fertilizers. A well fertilized (100 kg P ha<sup>-1</sup> as triple superphosphate, TSP-100) and unfertilized controls were also established. All treatments were conducted in plots of 24 m<sup>2</sup> size. The crop management was done like it is usually performed by the farmers. Crop rotations used in the experiments are displayed in Tab. 2.3.

Tab. 2.3. Crop rotations used in the field experiment.

Location	Crop rotations
Location	Years 2007 - 2008 - 2009
Gieboldehausen	Winter wheat - winter wheat - rapeseed
Lutterbeck	Winter barley - rapeseed - winter wheat
Sattenhausen	Rapeseed - winter wheat - winter wheat

#### 2.2.3 Soil and plant material sampling

Soil samples were collected from the upper 30 cm soil depth before fertilization and at harvest during three years (2007-2008-2009). Eight sub samples were taken for each plot and mixed to form a representative sample of the plot. The samples were air dried and sieved to 2 mm. Plant samples were taken from 6 m<sup>2</sup> in the middle of the experimental plots for cereals and from 1 m<sup>2</sup> for plots with rapeseed. Unfortunately, the farmer of Gieboldehausen harvested the whole field before samples were taken in the first year.

#### 2.2.4 Analytical procedure

The available P was determined by extraction with calcium-acetate-lactate (Schüller, 1969). Soil solution was obtained according to the displacement method described by Adams (1974). The P concentration in both methods was measured colorimetrically by the method of Murphy and Riley (1962). Plants were dried at 65°C to constant weight before grain and shoot yield were determined. Subsamples of plant dry matter were digested in concentrated HNO<sub>3</sub> at 180°C and the P concentration herein was measured colorimetrically by the molybdenum-vanadate method (Scheffer and Pajenkamp, 1952). Total P uptake was calculated from shoot dry matter and shoot P concentration.

#### 2.2.5 Data analysis and experimental design

Statistical analysis was performed using Statistica 9.0 (StatSoft, Inc. Tulsa, USA.). The experimental design for field experiments was in a complete randomized block design, with 8 treatments and 4 blocks. The fertilizers were considered as main factors, according to the following model:

Eq. 5. 
$$y_{ij} = \mu + \alpha_i + \beta_j + \varepsilon_{ij}$$

being y the dependent variable,  $\alpha$  the treatment (different sources of P fertilizer),  $\beta$  the block factor,  $\mu$  the mean of the overall population and  $\varepsilon$  the random effect (Quinn and Keough, 2002). The ANOVA test was followed by a Tukey test at the 0.05 level of significance to separate the means or by a Dunnet test at the 0.05 level of significance to compare the

treatments in relation to the control. Outliers were detected and removed for samples of P in soil solution according to the Hampel's test (Linsinger et al., 1998).

#### 2.3 Results

#### 2.3.1 Crop yield and P uptake

In the following section results of the three field experiments carried out to test the effectiveness of P fertilizers from different sources of P recycling are presented.

#### 2.3.1.1 Gieboldehausen soil



Fig. 2.1. Effect of different recycled P products tested as P fertilizers in field experiments at Gieboldehausen soil. The data represent the A) grain yield and B) total P uptake for 2 years for winter wheat and rapeseed respectively. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. Treatments were applied in a dose of 60 kg P ha<sup>-1</sup>. Data are means of 4 replicates and error bars represent the standard error of means. n.s. means no significant difference among treatments at the 0.05 level of significance.

Fig. 2.1 shows the grain yield for wheat and rapeseed cultivated on Gieboldehausen soil (21.0 mg P kg<sup>-1</sup> and pH 6.8) for 2 years (2008 and 2009). The data for 2007 are not presented because no samples of plant material were taken. However, in 2008 and 2009 there was no response to P fertilization, neither in grain yield nor P uptake and so no differences among any fertilizer or the control could be determined. Note that the production of rapeseed is lower than the production obtained by wheat but nevertheless P uptake was higher by rapeseed mainly because the concentration of P in rapeseed was higher than in wheat. Values for wheat production ranged from 6116 to 6844 kg of grain ha<sup>-1</sup> for TSP-60 and Sinter-P. The phosphorus removal by wheat ranged from 23 to 28 kg P ha<sup>-1</sup> for TSP-60 and Sinter-P respectively. Grain yield and P uptake by rapeseed range from 4081 to 4812 kg of seed ha<sup>-1</sup> and 30 to 38 kg P ha<sup>-1</sup> for MAP-Gf and TSP-100 respectively (Fig. 2.1).

#### 2.3.1.2 Lutterbeck soil

The Fig. 2.2 shows the grain yield and P uptake of 3 years on Lutterbeck soil. As in Gieboldehausen no fertilizer effects were observed for the grain yield of the 3 crops. Concerning the barley production (year 2007), the data ranged from 5508 and 6557 kg grain ha<sup>-1</sup> for TSP-100 and MAP-Sb, respectively. In 2008, the rapeseed yield was lower than that of cereal crops with a yield of 3497 (control unfertilized) to 4482 kg ha<sup>-1</sup> (MAP-Gf) (Fig. 2.2A). The yield obtained for wheat in the year 2009 showed no statistical differences between treatments with the lowest production of 7260 kg ha<sup>-1</sup> obtained in unfertilized control and the highest production of 8095 kg ha<sup>-1</sup> for MAP-Gf treatment. As can be seen in Fig. 2.2B, data for the P uptake range from 23 to 33 kg P ha<sup>-1</sup> for RP and MAP-Sb respectively for the year 2007; however most of treatments were similar in their P uptake and show no statistical differences, except treatment MAP-Sb which showed a significantly higher P uptake than the control, the reference RP, the thermal fertilizers (Sinter-P and SI-ash) and MAP-Gf. The P uptake obtained with the treatments for the second and third year of the experiment on the Lutterbeck soil did not show statistical differences; nevertheless, in tendency the treatment with MAP-Gf together with the water soluble TSP reached the higher P uptake. For the second year, the treatment with MAP-Gf (31 kg P ha<sup>-1</sup>) was the highest and unfertilized control the lowest (22 kg P ha<sup>-1</sup>).



Fig. 2.2. Effect of different recycled P products tested as P fertilizers in field experiments at Lutterbeck soil. The data represent the A) grain yield and B) total P uptake for 3 years for winter barley, rapeseed and winter wheat respectively. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. Treatments were applied in a dose of 60 kg P ha<sup>-1</sup>. Data are means of 4 replicates and error bars represent the standard error of means. Different letters mean significant difference among treatments and n.s. means no significant difference among treatments at the 0.05 level of significance.

In the third year (2009) 24 kg P ha<sup>-1</sup> were taken up by the plants from the soil treated with MAP-Gf being again the highest P uptake and 19 kg P ha<sup>-1</sup> for the thermal treated SI-ash the lowest. It is interesting to remark that there was a trend of increasing P uptake due to P fertilization as indicated by the arrows in Fig. 2.2B.

# 2.3.1.3 Sattenhausen soil

The field experiment carried out at Sattenhausen soil (Fig. 2.3) had a rotation with rapeseed, winter wheat and winter wheat during the investigation.



Fig. 2.3. Effect of different P recycled products tested as P fertilizers in field experiments at Sattenhausen soil. The data represent the A) grain yield and B) total P uptake for 3 years for rapeseed, winter wheat and winter wheat respectively. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. Treatments were applied in a dose of 60 kg P ha<sup>-1</sup>. Data are means of 4 replicates and error bars represent the standard error of means. n.s. means no significant difference among treatments at the 0.05 level of significance.

No statistical significances were found for yield and P uptake in any year. In relation to rapeseed yield, for the year 2007 it is interesting to note that it was the lowest of the three soils tested, reaching only 3327 kg of seed ha<sup>-1</sup> for MAP-Gf treatment and a minimal yield of 2506 kg of seed ha<sup>-1</sup> for unfertilized control. The data obtained for wheat yield in the second year (2008) appeared very similar in all treatments and were around of 8000 kg of grain ha<sup>-1</sup>,

while TSP-100 treatment yielded the highest amount of 8504 kg grain ha<sup>-1</sup>. As for the previous year, the year 2009 did not show statistically significant variations for the treatments. The recorded data indicated that the highest production was achieved with the treatment Sinter-P (7049 kg ha<sup>-1</sup>) and the lowest with MAP-Gf (6361 kg ha<sup>-1</sup>). No certain pattern was observed for grain yield in the experiment on Sattenhausen soil.

The results for P uptake did not show statistically significant differences; nevertheless it is possible to recognize a trend showing increased absorption for TSP-60 and TSP-100 in comparison to unfertilized control and in the first year an increase for the MAP treatments. The amount of P taken up by rapeseed ranged between 23 and 37 kg P ha<sup>-1</sup> for unfertilized control and MAP-Sb respectively. In the second year the data showed that the treatment TSP-100 achieved a P uptake of 30 and MAP-Sb of 26 kg P ha<sup>-1</sup>. Similar values were collected in 2009 with a highest absorption for Sinter-P (28.3 kg P ha<sup>-1</sup>) and the lowest for MAP-Gf (24.7 kg P ha<sup>-1</sup>).

#### 2.3.1.4 Phosphorus concentration in plant material

Tab. 2.4 shows the P concentrations for straw and grain at the harvest of the different crops in the three different soils. The most important variations were found in the first year of the experiment, being the concentrations in straw in the range of 0.6 to 0.7 g kg<sup>-1</sup> for winter wheat (Gieboldehausen), 0.9 to 1.4 g kg<sup>-1</sup> for winter barley (Lutterbeck) and 0.9 to 1.6 g kg<sup>-1</sup> for rapeseed (Sattenhausen). The P concentration in grains was higher than in the straw, with a concentration between 3.2 and 3.9 g kg<sup>-1</sup> for winter barley and between 7.4 and 8.1 g kg<sup>-1</sup> for rapeseed. The treatment with MAP-Sb in the year 2007 had a higher P concentration than P-0 being similar to TSP-60.

In the second year, only the treatment with a dose of 100 kg ha<sup>-1</sup> of P reached statistical higher P concentrations. In the third year all treatments were statistically equal to the unfertilized control.

Tab. 2.4. Phosphorus concentration in straw and grain for different crops at harvest in three different soils after fertilization with standard P fertilizers and with P recycled products. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. Values are the mean of 4 replicates.

	Soils												
		oldehaus	en		Lutterbeck				Sattenhausen				
		g kg <sup>-1</sup>											
		Season 2007											
Treatment		Wint	ter wheat			Winter barley			Rapeseed				
	Stra	w	G	rain	Sti	aw	Gra	in	Stra	w	Gr	ain	
P-0	0.56	а		-	0.96	а	3.22	а	0.89	а	7.37	а	
TSP-60	0.64	ab		-	1.13	ab	3.75	cd	1.33	ab	7.95	b	
TSP-100	0.68	b		-	1.09	ab	3.86	d	1.59	b	8.05	b	
RP	0.59	ab		-	0.88	а	3.23	а	0.99	а	7.35	а	
MAP-Sb	0.65	ab		-	1.36	b	3.67	bcd	1.59	b	8.09	b	
MAP-Gf	0.62	ab		-	0.99	а	3.42	abc	1.12	ab	7.65	ab	
Sinter-P	0.62	ab		-	0.90	а	3.35	ab	1.16	ab	7.74	ab	
SI-ash	0.56	а		-	0.92	а	3.19	а	1.13	ab	7.66	ab	
						Sea	son 2008						
	Winter wheat				Rc	ipeseed		Winter wheat					
P-0	0.87	а	3.39	а	0.61	а	5.86	а	0.53	а	2.75	а	
TSP-60	0.92	а	3.37	а	0.66	ab	6.19	а	0.51	а	2.88	ab	
TSP-100	0.88	а	3.53	а	0.97	b	6.95	b	0.68	а	3.11	b	
RP	0.94	а	3.40	а	0.73	ab	6.07	а	0.51	а	2.77	ab	
MAP-Sb	0.89	а	3.34	а	0.66	ab	6.20	а	0.52	а	2.74	а	
MAP-Gf	0.60	а	3.35	а	0.67	ab	6.17	а	0.54	а	2.82	ab	
Sinter-P	0.98	а	3.47	а	0.77	ab	6.05	а	0.63	а	2.74	а	
SI-ash	0.92	а	3.38	а	0.74	ab	5.96	а	0.56	а	2.74	а	
		Season 2009											
		Ra	peseed			Win	ter wheat			Winte	er wheat		
P-0	0.89	а	6.28	а	0.26	а	2.52	а	0.64	а	3.45	а	
TSP-60	0.87	а	6.38	а	0.24	а	2.56	а	0.68	а	3.52	а	
TSP-100	1.05	а	6.76	а	0.27	а	2.69	а	0.71	а	3.47	а	
RP	0.95	а	6.61	а	0.22	а	2.55	а	0.65	а	3.43	а	
MAP-Sb	0.92	а	6.20	а	0.25	а	2.58	а	0.63	а	3.43	а	
MAP-Gf	0.93	а	6.37	а	0.26	а	2.47	а	0.65	а	3.44	а	
Sinter-P	0.99	а	6.53	а	0.25	а	2.53	а	0.65	а	3.56	а	
Sl-ash	0.84	а	6.28	а	0.23	а	2.40	а	0.66	а	3.36	а	

Different letters indicate a significant difference among treatments in the same soil, season and crop at P<0.05 level of significance. Treatments statistically significant to unfertilized control are highlighted in bold.

# 2.3.2 Phosphorus in soil solution and plant available phosphorus extracted by calcium-acetate-lactate (CAL-P)

#### 2.3.2.1 Gieboldehausen

The Fig. 2.4 shows the results obtained for P in soil solution and calcium-acetate-lactate extractable P (CAL-P) in Gieboldehausen. The data are expressed as  $\mu$ M for P in soil solution and mg of P kg<sup>-1</sup> of soil for CAL-P.

The P concentration in soil solution increased in summer 2007 after fertilization only in the reference fertilizer TSP-100. In the next year (spring 2008), TSP-100 and MAP-Gf showed a significant difference in relation to the P-0, and for the next dates only TSP-100 was statistically different from P-0. To increase data reliability for the first sampling (Summer 2007) outliers were eliminated by the Hampel's test (1 sample was removed for the control TSP-60).



Fig. 2.4. Phosphorus in soil solution and CAL-P after application of P recycled products in Gieboldehausen soil pH 6.8. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. The symbol \* indicates a significant difference between the treatments and the unfertilized control (P-0) (Dunnett test). Values are means of 4 replicates.

As it can be seen in Fig. 2.4, the levels for CAL-P at the beginning as well as during the experiment were in the ranges defined as very low (0-20 mg P kg<sup>-1</sup>) and low (30-40 mg P kg<sup>-1</sup>) according to the German classification for P levels in soil. All treatments receiving recycled P products were equal in each sampling, no differences were found in relation to the

unfertilized treatment (P-0). Slight trends over time were found for the reference fertilizer TSP-100 to be increased concerning CAL-P.

#### 2.3.2.2 Lutterbeck

The concentration of P in soil solution found in Lutterbeck was higher in comparison to Gieboldehausen (Fig. 2.5). Fertilizers were applied in spring as a top dressing after the emergence of plants (Spring 2007). At crop harvest in 2007, P concentration in soil solution fertilized with TSP-100 and TSP-60 was significantly higher than the unfertilized control which was not the case for the recycled P products. At the next sampling dates, the P in soil solution of the TSP-100 treatment was up to 10 times increased in relation to the unfertilized control (P-0). Note that P concentration in soil solution shows a slight trend to decline over time. For the first sampling date outliers were discarded for the statistical analysis by the Humpel's test (1 sample was removed from P-0 and TSP-100).



Fig. 2.5. Phosphorus in soil solution and CAL-P after application of P recycled products in Lutterbeck soil. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. The symbol \* indicates a significant difference between the treatments and the unfertilized control (P-0) (Dunnett test). Values are means of 4 replicates.

Phosphorus extracted by CAL is shown in Fig. 2.5 for Lutterbeck soil. The data of CAL-P were in the range of very low to low level and after fertilization no significant changes were recorded in relation to the unfertilized control (P-0), only in summer 2008 and spring 2009

TSP-100 showed a difference in relation to the control P-0. On the other hand CAL-P increased over time; however the unfertilized control showed a similar trend.

#### 2.3.2.3 Sattenhausen

Comparison of fertilizer effects on soil solution P and CAL-P over the whole experimental period in Sattenhausen can be seen in Fig. 2.6. The P concentration in soil solution in this location was the highest compared to the other places. No statistical differences were found for treatments with P recycled products in comparison to the unfertilized control. Only TSP-100 was different in three of five sampling dates, and TSP-60 was different once in summer 2008. Like in Lutterbeck soil, a trend of declined P concentration in soil solution could be observed.

For the CAL-P no statistical differences were recorded at any sampling date, only TSP-100 was different to the control P-0 in summer 2008 and 2009 as well as in spring 2009. The P extracted by CAL was similar over time. The values of CAL-P were in the range of very low to low like in the others locations.



Fig. 2.6. Phosphorus in soil solution and CAL-P after application of P recycled products in Sattenhausen soil. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. The symbol \* indicates a significant difference between the treatments and the unfertilized control (P-0) (Dunnett test). Values are means of 4 replicates.

2.3.2.4 Variation of the soil P level after fertilization with P recycled fertilizers as a measure of long-term dynamics of P in the soil

Fig. 2.7 shows the levels of P extracted with calcium-acetate-lactate (CAL-P) before fertilization with recycled P products and after 2.5 years respectively (season 2007 and 2009 in Fig. 2.7).



Fig. 2.7. Phosphorus extracted by CAL (CAL-P) before fertilization (spring 2007) and 2.5 years after fertilization with P reference fertilizers and recycled P fertilizers to indicate the long term effect of the P fertilizers. P-0=unfertilized; TSP-60= Triple superphosphate (60 kg ha<sup>-1</sup>); TSP-100= Triple superphosphate (100 kg ha<sup>-1</sup>); RP= Rock phosphate; MAP-Sb= Magnesium-ammonium-phosphate (MAP) Seaborne; MAP-Gf= MAP Gifhorn; Sinter-P= Sinter phosphate; SI-ash= Sewage sludge ash. \* indicates statistical differences between CAL-P before and after fertilization within a same treatment at 0.05 level of significance (Dunnett test). Values are means of 4 replicates.

Data for the three soils were around 20 mg P kg<sup>-1</sup> of soil at the beginning as well as at the end of the field experiment. In general, there was no statistical significant trend in increasing CAL-P over time in any soil of the unfertilized control (P-0) and with recycled P fertilizers with the exception of MAP-Gf and Sinter-P which obtained a significant increase in CAL-P in Lutterbeck soil. However, because the amount of P applied in the treatment TSP-100 (100 kg P ha<sup>-1</sup>) was enough to find differences in comparison to the unfertilized control (P-0), the change in the three soils was significant between the beginning and the end of the experiment.

#### 2.4 Discussion

#### 2.4.1 Yield and P uptake

According to Barrow (1985), there are two possible situations when comparing P fertilizers. The first is that the chemical form of P in the product is similar but the dilution is different and the second possibility is that the chemical composition is different. In our study, and according to the data from Tab. 2.1, the P fertilizers differ in their P water solubility i.e. chemical composition, and a differentiation between products of P recycling was expected. If P fertilizers were effective, changes in different parameters such as the yield and P uptake should be observable. Nevertheless, the effect of the fertilizers from recycled P on the dry matter yield (DMY) did not show differences in comparison to the unfertilized control and to the water soluble fertilizer (TSP). Moreover, it was expected that the treatments with recycled P products and with water soluble fertilizers would increase the DMY in relation to the unfertilized control, because the three soils were characterized as low P available according to the German classification for P in soils (Schachtschabel et al., 1989), but it was only possible to observe some tendencies for increased DMY, as in the case of TSP-100.

A possible reason for the absence of differences was the high DMY reached in the unfertilized control, which might indicate that there was enough P available for the crop in the non fertilized plot and the agronomic potential in the system was reached. Moreover, it is possible to argue that cereals and rapeseed are very efficient to take up P, owing to the large root system in cereals in comparison to the other crops (Barber, 1995). In the case of rapeseed, the exudation of organic acids such as malic or citric acid can represent a strategy to improve the availability of soil P (Marschner, 1995). Thus, plants in field are not restricted by limitations like rooting soil volume as in pot experiments and a higher plasticity may be expected to adverse conditions such as low P availability. In the literature there are contradictory results about P fertilization and yield response. For example, Bolland et al. (1989) evaluated in the field the response of several crops to P fertilization and they found that wheat and rapeseed increased the yield as a function of P applied. However, Römer et al. (2005) in a 20 year field experiment with cereals found no correlation between the plant available P extracted with CAL and the yield. Similar results were found in 16 field experiments by Schachtschabel and Köster (1985). According to the results it seems to be that only at very low P concentrations in soil a response to the P fertilization can be

expected and it seems also that CAL-P shows a very low correlation with the yield. Hence, the results obtained in the present field experiment are similar to other ones conducted in Germany where the yield was not clearly affected by P fertilization or the differentiation between treatments was not sensitive.

In those cases where the DMY is not a responsive parameter it is possible to compare other ones, such as P uptake and P concentration (Barrow, 1985; Batten, 1992). Concerning the P uptake, only the field experiment carried out in Lutterbeck soil showed a statistical difference among treatments for the first year (Fig. 2.2). The treatment that resulted in a higher P uptake was the MAP-Sb. This finding is supported by several authors who indicated that magnesium-ammonium-phosphate is equally available than water soluble fertilizers and that these products are able to increase the yield and the P uptake (Johnston and Richards, 2003; Plaza et al., 2007). However, in the other field trials there was no differentiation among the products tested. While it was expected that the second year would have a greater differentiation among treatments, because of the slow solubility of some fertilizers applied, it was only the first year which showed more variations among treatments. This seems to be more obvious in the Lutterbeck soil, although for Sattenhausen soil a similar trend was observed, however lacking statistical significance.

Phosphorus concentration in the plant and grain yield is the result of P uptake, the latter can obscure differentiations among treatments and some important information might be lost. The P concentration in the first year for the treatments with TSP-100 was higher than the unfertilized control in the three soils. In winter barley and rapeseed the P concentration in grain and in straw for MAP-Sb treatment was higher than the unfertilized control in the first year. For the second year the results indicated that P concentration in rapeseed and winter wheat for TSP-100 was higher than the unfertilized control. In some cases, it was also possible to observe a higher P content in grain as well as in straw for TSP-60. Nevertheless, the results are statistically different only until the second year (Tab. 2.4). The lack of differentiation among treatments could be explained by the normal P concentration obtained in plants growing in the unfertilized control (P-0). In Gieboldehausen the P concentration for plants grown in P-0 was of 0.34 and 0.64% for wheat grain and rapeseed respectively. These values are in the optimal P concentration range which is 0.3 to 0.5% for wheat and 0.65 to 0.85% for rapeseed (Havlin et al., 2005). A similar situation was registered

for barley grown on Lutterbeck soil. This implies that the plants grown in the plots with recycled P fertilizers were not under P deficiency and the differentiation was only possible in the treatment where more P was added (TSP-100).

#### 2.4.2 Phosphorus in the soil solution and CAL-P

In the present study, the main changes for P in soil solution were observed in the first year. After an initial increment of the P in soil solution the P concentration decreased over time. According to Barber (1995) after a P fertilization the concentration in the soil solution raises. However, this gain was not permanent and at the following sampling dates the P concentration decreased (Fig. 2.4, Fig. 2.5 and Fig. 2.6), because P undergoes fixation processes and uptake by plants. Only TSP-100 was able to maintain a high P concentration over a long period of time, which indicates that the solubility and the amount of P contained in the fertilizer determines the P in soil solution. It was not possible to differentiate between the P concentration in soil solution within the treatments with recycled P fertilizers and the unfertilized control. Some tendencies were observable and the following order is suggested according to the effectiveness of the fertilizers: TSP > MAP > = SI-ash = Sinter-P = RP. This order is related to the water solubility of the compounds (Tab. 2.1), where MAP-Sb has a solubility of 1% and RP of <0.01%. Although, SI-ash has more water soluble P than MAP products (6.4%), there was no increment neither in P in soil solution nor CAL-P.

For the treatments with recycled P products and RP an increase in the P soil solution for the soil with a low pH value (Sattenhausen) was expected, however no differentiation was observed in relation to the unfertilized control (Fig. 2.6). Thus, the pH of the soils seems to have no effect on the recycled P products, nevertheless, it cannot be concluded that pH did not play a role on the P products solubility, since P adsorption and precipitation in the soil are also related to pH value (Havlin et al., 2005). The differentiation of these processes is difficult, because dissolution and fixation of P in the soil are concomitant. Other possible effects on the P products solubility can be attributed to the organic matter, the clay content and mineralogy. However, in the present experiment soil organic matter was not analyzed for its chemical nature. On the other hand, the clay content cannot be related to the P fixation, because its mineralogy is the determining factor rather than its amount (Havlin et al., 2005). As a way to characterize the effect of soil properties on the effectiveness of

#### <u>Chapter Two – Field experiment</u>

fertilizers the buffer power can be used (Barber, 1995). The buffer power, *b*, after the fertilization with 60 and 100 kg ha<sup>-1</sup> of TSP was: 580 and 420, 160 and 300 and 126 and 70 for Gieboldehausen, Lutterbeck and Sattenhausen soils, respectively. The buffer power was calculated by dividing the amount of P applied as TSP,  $\Delta P$ , by the change of P concentration in soil solution after fertilization,  $\Delta C_L$  ( $\Delta P$  applied/ $\Delta C_L$ ). These data support the idea of a low effect of P fertilizers in Gieboldehausen soil, which showed the higher buffer capacity (Fig. 2.4). Otherwise, a higher effect of the P fertilizers was found in Sattenhausen soil, which had the lowest buffer capacity (Fig. 2.6).

Despite the differences in the buffer power among soils, the P concentration in soil solution was always enough to sustain an optimal growth of the plants. The P concentration was not lower than 0.5  $\mu$ M and for the most treatments it was higher than 1  $\mu$ M. Even at harvest the P concentrations in soil solution were above 0.5  $\mu$ M. These data are supported by Kovar and Claassen (2009) who worked with three different grass species in solution culture and found that the maximal growth was reached at 1  $\mu$ M of P. Similar data have been registered by Bhadoria et al. (2004) working with maize and groundnut and Buhse (1992) working with sugar beet and rapeseed. Also it is important to remark, that the P concentration in the unfertilized soil was sufficient to maintain plant growth, in consequence, the P concentration in the field experiments.

Even though changes concerning P extracted with CAL were expected no statistical effect of recycled P fertilizers was found. This means that P applied is readily adsorbed on soil surface in different fractions which seems to be not extractable by CAL. We can also speculate that P fertilizers were not solubilized, as apparently it is the case for rock phosphate. This means that the amount of P extracted by CAL depends on the characteristics of the fertilizer applied. Thus, CAL does not seem to be able to extract P from some products as might be the case of SI-ash and Sinter-P which consit of P associated to Ca. According to Schüller (1969) CAL method correlates strongly with the isotopically exchangeable P and less with Ca-P, that means that CAL solution can not differentiate Ca-P despite its acid pH (4.1). The results in the present experiment do not allow to clarify if CAL-P represents the amount of plant available P. Similar results were found by Schachtschabel and Köster (1985) in field experiments with several crops, where the optimal amount of CAL-P could not be

established clearly, being a value of 20 mg kg<sup>-1</sup> CAL-P which is enough to reach the maximal yield. Thus, these results support the idea that in our field experiment, CAL-P was in the range of sufficiency for the crops and that the CAL method is not able to differentiate the available P after fertilization with 60 kg of P ha<sup>-1</sup>.

Concerning the variation of CAL-P after the fertilization with P recycled products, no changes were registered in Gieboldehausen and Sattenhausen soils. The treatment with a dose of 100 kg of P ha<sup>-1</sup> was highest at the end of the experiment for the three soils. For the soil Lutterbeck the treatments with MAP-Gf and Sinter-P increased the CAL-P after the fertilization significantly. However, with these results it is difficult to conclude that P recycled fertilizers have an improving effect on P fertility in field conditions. Moreover, CAL method does not allow to distinguish small changes in soil P and previous experiments furthermore showed that it has a high temporal variation (Römer et al., 2005).

#### 2.5 Conclusions

The effectiveness of recycled P fertilizers could not be differentiated clearly and it was only possible to estimate a general trend. According to this trend, P fertilizers can be ranked as follows: TSP > MAP > SI-ash = Sinter-P > RP.

No effects were observed for the chemically estimated plant availability of P in soil over a long term. However, the evidence does not allow confirm the central hypothesis that the recycled P fertilizers are as effective as P water soluble fertilizers.

# Chapter Three: Effectiveness of P fertilizers from P recycling in pot experiments

#### 3.1 Introduction

The effectiveness of recycled P products obtained by chemical and thermal processes was tested in a field experiment in comparison to reference P fertilizers. However, due to the lack of P response it was not posible to confirm the hypothesis that recycled P fertilizers are as effective as P water soluble fertilizers. The high variability of replicates may in part have obscured possible differences among treatments. Thus, a pot experiment was set up to have a more accurate assessment of possible differences among recycled P products under controlled conditions.

In Germany, several processes have been implemented to recover P, among the more important are the precipitation as magnesium-ammonium-phosphate (MgNH<sub>4</sub>PO<sub>4</sub>) (Phan et al., 2009), calcium-phosphate (Ca-P) (Ehbrecht et al., 2009) and the recovery by thermochemical processes (Adam et al., 2009b; Scheidig et al., 2009). Recycled P products obtained by chemical and thermal processes vary within their P content and their water solubility, thus the amount of plant available P depends on the final chemical composition. With the exception of MgNH<sub>4</sub>PO<sub>4</sub> these products have not been tested in agronomic trials to evaluate their effectiveness as P fertilizers. Magnesium-ammonium-phosphates (MAP) have been already tested by different work groups in greenhouse studies. Johnston and Richards (2003) worked with synthetic struvite and struvite from sewage sludge found that these products were as effective as monocalcium phosphate in soils with neutral to slightly acid pH value. In an experiment with ryegrass, Plaza et al. (2007) indicated that struvite from sewage sludge reached similar efficiency in comparison to triple superphosphate (TSP) in an acid soil (pH 5.7). Massey et al. (2009) tested three different recycled products, dittmarite, struvite and a heterogeneous P recovered product and found that Mg phosphate products were equivalent to TSP in alkaline and slightly acid conditions. Regarding to P recovered as a calcium phosphate (Ca-P), only few experiments concerning P plant availability have been conducted, among the more relevant are the experiments of Johnston and Richards (2003), Römer (2006) and Bauer et al. (2007). In the work from Bauer et al. (2007), they indicated that Ca-P from liquid swine manure has a high P availability to plants when the size of

granules is below 1 mm, however it was not so effective as TSP, despite the acid soil pH value. In relation to P recovered by thermal processes limited information is available. Adam et al. (2009b) carried out a pot experiment with a thermal P recycled product finding that P uptake by maize plants was similar to soluble commercial fertilizers.

Phosphorus fertilizers will be effective in soil if the P products that they contain have larger solubility than P products present already in soil (Hedley and McLaughlin, 2005). Water soluble fertilizers applied to soils react immediately increasing the P in soil solution and which subsequently decreases due to adsorption and precipitation processes (Havlin et al., 2005). The initial solubilization of P products depends on the soil water content and its diffusion inward the granule of P products (Havlin et al., 2005; Hedley and McLaughlin, 2005; Lindsay, 1979). The dissolution of water soluble P fertilizer (i.e.  $Ca(H_2PO_4)_2$ ) lowers the pH value to 1.5 in the soil around the P granules due to the release of  $H_3PO_4$  (Havlin et al., 2005). The acidification of the soil around the P granule facilitates the dissolution of Al, Fe and Mn in acid soils and CaCO<sub>3</sub> in calcareous soils. Subsequently, the pH of the soil solution increases as a consequence of  $H_3PO_4$  neutralization and P precipitates as colloidal metal phosphates (Fe-P or Al-P) and DCP (CaHPO<sub>4</sub>·2H<sub>2</sub>O) (Hedley and McLaughlin, 2005; Sample et al., 1980). Furthermore, adsorption processes are expected in the surrounding of P-soil reaction zone (Barber, 1995; Havlin et al., 2005; Sample et al., 1980).

Regarding MAP products, it is expected that they react in a similar way as diammonium phosphates (DAP). The reactions of DAP depend on soil pH, soil cations and organic matter (Hedley and McLaughlin, 2005). Formation of struvite (MAP) after the application of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was observed by Lindsay et al. (1962) in a calcareous soil high in exchangeable Mg. Therefore, struvite is considered as an insoluble or little soluble secondary product from dissolution of MoAP or DAP. In spite of this first reaction, Bell and Black (1970), found that it was dissolved to form Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and after 48 weeks struvite disappeared. Regarding MAP solubility in alkaline soils Massey et al. (2009) argued that there is no evidence about which factors addressed the effectiveness of MAP products in alkaline or calcareous soils, suggesting that MAP products are as effective as P fertilizers in those soils with high Ca concentration; mainly because Ca would not inhibit the P dissolution.

Unlike water soluble P fertilizers, rock phosphates are sparingly soluble in soil solution and their equilibrium concentration is very low (Hedley and McLaughlin, 2005). The effectiveness

of P fertilizers containing Ca-P is close related to soil pH value and Ca activity. A high Ca concentration in soil solution favors the P precipitation and harms Ca solubility of a product, thus a low P dissolution is expected in compounds rich in calcium phosphates (Mackay and Syers, 1986). In the same way, an acid soil contains low Ca concentration which favor Ca-P solubilization (Chien and Menon, 1995). On the other hand, P recovered with thermal processes, which can also contain Fe and Al, would be more soluble in neutral and slightly acid soils mainly due to that the solubility product of Fe-and Al-P increase at high pH values (Havlin et al., 2005; Lindsay, 1979).

Some of the products mentioned above were tested in a field experiment for three years. Nevertheless, evaluating effectiveness of P fertilizers in field trials has several issues, mainly because P in agricultural soils is not uniformly distributed in the field and these soils are frequently under P fertilization. Thus, it would be desirable to measure differences between P sources in an agricultural soil with a low amount of plant available P (Crozier et al., 2009). Moreover, because soils in field conditions have a high spatial variability and crops use different strategies to take up P, the crop response to P fertilization can be difficult to identify. Some advantages can be obtained in pot experiments, since soils used in these trials can previously be well homogenized with the P fertilizer, pots can be irrigated to maintain constant water content and a high root density might be reached, which allows a high exploitation of the fertilizers applied. Thus, under these conditions it is possible to obtain a better differentiation of tested P fertilizers.

Hypothesis:

- 1. Recycled P products obtained by chemical processes are similar to the water soluble fertilizer triple superphosphate (TSP) i.e. effective at a wide range of pH values.
- 2. Recycled P products obtained by thermal processes are more soluble at low pH values (acid soils) and are similar to rock phosphate.

#### 3.2 Materials and methods

A pot experiment was carried out in three soils to assess the effectiveness of P products from P recycling applied as P fertilizers. The main characteristics of recycled P products and some relevant properties of the soils used will be described in the following sections.

# 3.2.1 Products from P recycling as P fertilizers

Eight different materials were tested with regard to their effectiveness as P fertilizers in a pot experiment on three different soils during two years. Additionally, two commercial fertilizers with different P availability, triple-superphosphate (TSP) and rock phosphate (RP) were taken as reference fertilizers. The materials used were: three Magnesium-ammonium-phosphates (MAP) of different sewage treatment plants (MAP-Sb, MAP-Gf and MAP-St), a precipitated apatite from sewage sludge (Ca-P), an alkali sinter phosphate made from meat-and-bone meal (Sinter-P), a heavy metal depleted sewage sludge ash (SI-ash), a cupola furnace slag (Cupola slag) made from sewage sludge and a meat-and-bone meal ash (MB meal ash).

#### 3.2.1.1 Description of recycled P fertilizers

#### 3.2.1.1.1 Phosphorus precipitated as magnesium-ammonium-phosphate (MAP)

The phosphorus recovery as magnesium-ammonium phosphate (MAP) is realized from the sewage sludge. In a first step, sewage sludge is anaerobically stabilized and then this digested stabilized sludge is acidified with  $H_2SO_4$ . It is possible that not all solids are dissolved in this process which are decanted and then incinerated. The ashes can return to the acidification. After acidification processes sodium sulphide (Na<sub>2</sub>S) is added to precipitate heavy metals which are separated from the process flow. From this flow N and P are precipitated by the addition of NaOH and Mg(OH)<sub>2</sub> increasing the pH up to 9. Finally, MAP is separated from the flow by a decanter. The recovery effectiveness is about 50% of the total P present in the digested sewage. The final product contains MgNH<sub>4</sub>PO<sub>4</sub> ·  $6H_2O$  but also phosphate salts of Ca and Fe (Scheidig et al., 2009). Phosphorus precipitated as MAP could vary depending on the sewage sludge chemical composition and on other technical parameters of the process.

#### 3.2.1.1.2 Phosphorus precipitated as calcium phosphate (Ca-P)

The recycled product Ca-P is obtained by crystallization of P from sewage sludge. Phosphorus is recovered by fixation with tobermorite  $(Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O)$  which is a calcium silicate hydrate mineral (CSH). This calcium silicate hydrate (CSH) is a by-product from the building industry which triggers a kinetically inhibited calciumphosphate (Ca-P) precipitation onto its surface. The P precipitation is achieved by the addition of CSH to the waste activated sludge (WAS). The Ca-P precipitation depends on the P concentration and on the pH value of the WAS. This method can recover up to 36% of the total P present in WAS (Ehbrecht et al., 2009; Petzet and Cornel, 2009).

#### 3.2.1.1.3 Phosphorus recovery by sintering of animal by-products (Sinter-P)

This product is made by calcination of a mixture of meat-and-bone meal as a source of P, sodium carbonate and silica in a rotary furnace at over 1000°C. Sodium carbonate produces CaNaPO<sub>4</sub> and silica produces Ca<sub>2</sub>SiO<sub>4</sub>. The P contained in this product is nearly soluble in neutral or alkaline ammonium citrate solution (United Nations Industrial Development Organization, 1998). Sinter-P might be comparable to the earlier Rhenania phosphate fertilizer.

# 3.2.1.1.4 Phosphorus recovery by burning of sewage sludge (SI-ash)

The P of this product is recovered from sewage sludge by thermal treatment. Through a mono-incineration of the sludge the organic pollutants present are destroyed. The ashes obtained in this first step contain a high amount of P and heavy metals which are above the limits allowed for European countries. In the next step, heavy metals are volatilized from the ashes by adding a chlorine donor (usually magnesium or calcium chloride) and water at high temperatures (1000°C) in a rotary furnace. Water is added for pelleting the ashes. After heavy metal volatilization a raw P material is obtained which contains the P mainly as  $Ca_4Mg_5(PO_4)_6$  and  $Ca_5(PO_4)_3Cl_{1-x}(OH)_x$  (Adam et al., 2009b).

## 3.2.1.1.5 Phosphorus recovery by smelting of sewage sludge (Cupola slag)

Cupola slag is a P containing product made by smelting a mixture of sewage sludge and filter dust from animal meal. In a first step, sewage sludge is mechanically dried to reach 25% dry

matter and then mixed with filter dust from animal meal mono-incineration and cement. This mixture is agglomerated by mechanical pressuring. This material is smelted in a shaft furnace using limestone or dolomite for the slag formation. The energy for the smelting process is given by metallurgical coke that is burned at 2000°C, thus a liquid slag is produced and a small metal phase. The latter is separated from the liquid slag containing P. The basic slag contains P mainly as calcium phosphate (Scheidig et al., 2009). Cupola slag might be comparable to the Thomas phosphate fertilizer.

3.2.1.1.6 Phosphorus recovery by mono-incineration of animal by-products (MB meal ash) Phosphorus can be recovered directly by mono-incineration of animal by-products. In this process a mixture of meat-and-bone meal and water is agglomerated by mechanical pressure forming a pellet. The pellet is incinerated in a rotator furnace at 1000°C.

Tab. 3.1 shows the P concentration and P water solubility of the materials. All products were finely ground before fertilization.

Material	Description	Total P	Proportion of total P soluble in		
Wateria	Description	concentration	*Water	+2% citric acid	
Reference fertilize	rs		- % -		
Triple superpho	sphate (TSP) -	20.1	90	-	
Rock phosphate	e (RP) -	11.8	11.8 <0.01		
Obtained by chem					
Ca-P	Precipitated as Ca-P	11.1	4.1	48.6	
MAP-Sb	$\label{eq:precipitated} Precipitated as \ MgNH_4PO_4$	11.0	1.1	51.0	
MAP-Gf	$\label{eq:precipitated} Precipitated as \ MgNH_4PO_4$	9.6	0.8	47.0	
MAP-St	Precipitated as MgNH <sub>4</sub> PO <sub>4</sub>	11.8	1.9	43.6	
Obtained by therm	al processes				
Sinter-P	Meat and Bone meal sintered over 1000°C	11.3	0.3	34.5	
SI-ash	Sewage sludge burned over 1000°C	7.8	6.4	31.4	
Cupola slag	Sewage sludge burned over 1000°C	2.9	-	-	
MB meal ash	Animal ashes	16.4	0.1	23.8	

Tab. 3.1. Description of the reference P fertilizers and P fertilizers from P recycling.

\*5 g of material was extracted with 250 mL of water. †2.5 g of material was extracted with 250 mL of 2% citric acid.

#### 3.2.2 Description of the experiment

The pot experiment was performed with 5.5 kg of soil in 6 L pots with maize plants during two years. The soils were taken from two sites of the field experiments (Sattenhausen and Gieboldehausen) described in chapter 2. Additionally, an acid sandy soil (Düshorn) was also used in the pot experiment, which was not in agricultural use (Tab. 3.2). Phosphate was given at a suboptimal rate of 60 mg of P kg<sup>-1</sup> soil for each fertilizer, plus unfertilized and well fertilized (200 mg P kg<sup>-1</sup>, TSP-200) controls. Furthermore, the pots were fertilized with 1 g K (K<sub>2</sub>SO<sub>4</sub>), 0.2 g Mg (MgSO<sub>4</sub>·7 H<sub>2</sub>O) and 0.5 g N (NH<sub>4</sub>NO<sub>3</sub>) per pot. Two further applications of N were realized as Ca(NO<sub>3</sub>)<sub>2</sub> in doses of 0.3 g per pot each time in the first and second year. After 3 weeks of incubation without plants, maize (*Zea mais* L., cv. Atletico) was sown (4 plants per pot). In the second year no P fertilizer but Mg and N was added to the pots. Each pot was irrigated daily with demineralized water during the experiment to maintain constant water content at 75% water holding capacity. For all treatments one pot was kept moist but without plants.

Location	Clay	Silt	Organic Sand matter		$pH$ in $CaCl_2$	CAL-P	
		%	,		(relation 1:2.5)	mg P kg <sup>-1</sup>	
Gieboldehausen	25.0	65.5	9.5	2.8	6.8	21.0	
Sattenhausen	11.4	86.9	1.7	1.7	5.6	19.0	
Düshorn	2.1	5.3	92.6	5.3	4.4	24.2	

Tab. 3.2. Main characteristics of the soils used in the experiments of fertilization with recycled phosphorus materials.

#### 3.2.3 Soil and plant material sampling

Soil samples were collected from the total soil volume twice in each growing season, before sowing and after harvesting. The samples were air dried and sieved to 2 mm. The plants were harvested at beginning of flowering at the 80th and 70th day after the sowing for the first and second year, respectively. At harvest, aboveground biomass and P concentration were determined.

#### 3.2.4 Analytical procedure

Soil samples were extracted with calcium-acetate-lactate to determine the plant available P (CAL-P) (Schüller, 1969). Soil solution was obtained according to the displacement method described by Adams (1974). The P concentration in both methods was measured colorimetrically by the method of Murphy and Riley (1962). Plants were dried at 65°C to constant weight before the dry matter was determined. Subsamples of plant dry matter were digested in concentrated HNO<sub>3</sub> at 180°C and the P concentration herein was measured colorimetrically by the molybdenum-vanadate method (Scheffer and Pajenkamp, 1952). Total P uptake was calculated from shoot dry matter and shoot P concentration.

#### 3.2.5 Data analysis and experimental design

Statistical analysis was performed using Statistica 9.0 (StatSoft, Inc. Tulsa, USA.). The experimental design was in a complete randomized design, with 11 treatments and four replicates. The fertilizers were considered as main factors, according to the following model:

Eq. 6. 
$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij}$$

being y the dependent variable,  $\alpha$  the treatment (different sources of P fertilizer),  $\mu$  the mean of the overall population and  $\varepsilon$  the random effect (Quinn and Keough, 2002). The ANOVA test was followed by a Newman-Keul test at the 0.05 level of significance to separate the means or by a Dunnet test at the 0.05 level of significance to compare the treatments in relation to the control. The relationship between P uptake and P soil solution concentration as well as CAL-P was described by a linear regression with the following form:

Eq. 7. 
$$y_i = \beta_0 + \beta_1 X_i + \varepsilon_i$$

being  $y_i$  the value of Y when the predictor variable X=  $x_i$ ,  $\beta_0$  the intercept when X is zero,  $\beta_1$  is the slope and measures the change in Y per unit change in X, finally  $\varepsilon_i$  is the random and unexplained error (Quinn and Keough, 2002).

# 3.2.5.1 Relative fertilizer efficiency (RFE)

The relative fertilizer efficiency (RFE) was taken as a parameter to rank the P sources with respect to TSP. The RFE is the comparison between the difference of P uptake (PU) of a specific fertilizer and the PU of unfertilized control in relation to a standard water soluble P fertilizer, and is expressed as:

Eq. 8

$$RFE(\%) = \frac{PU_{treatment} - PU_{control}}{PU_{TSP} - PU_{control}} \times 100$$

being,  $PU_{treatment}$  the PU obtained by a especific P fertilizer,  $PU_{control}$  the PU of the unfertilized control and  $PU_{TSP}$  the PU obtained by the standard water P soluble fertilizer triple superphosphate.

#### 3.3 Results

#### 3.3.1 Phosphorus uptake and dry matter yield

In the acid soil Düshorn (pH 4.4) phosphorus uptake (PU) and dry matter yield (DMY) by triple superphosphate (TSP-60) were twice as high as from the unfertilized control (Fig. 3.1). Furthermore, the PU obtained by the supra optimal control TSP-200 was higher than TSP-60 indicating that at 60 mg P kg<sup>-1</sup> maximum yield was not reached yet. The PU and DMY observed for maize grown on rock phosphate (RP) treatment were not different from unfertilized control (P-0). All treatments with recycled P products obtained by chemical processes, i.e. MAP products as well as Ca-P were similar to TSP-60 either for PU or for DMY (Fig. 3.1). On the other hand, recycled P products obtained by thermal processes were similar to RP and no effect on PU and DMY was observed, with the exception of treatment with Sinter-P.

The P uptake by maize from Düshorn soil in the first year ranged between 13 and 27 mg P kg<sup>-1</sup> soil for P-0 and MAP-Sb respectively (Fig. 3.1). Furthermore, plant P uptake was higher with MAP-St than with other MAP products. Within the thermal products, Sinter-P was similar to TSP-60 reaching a PU of 20 mg P kg<sup>-1</sup> soil.

For the second year both PU and DMY decreased and only some treatments were higher than the unfertilized control. Of the recycled P products by chemical processes, Ca-P, MAP-Gf and MAP-St reached a maximal P uptake of 18 mg P kg<sup>-1</sup> soil, being equivalent to TSP-60. The lowest value of PU was 13 mg P kg<sup>-1</sup> soil in the treatment fertilized with MB meal ash.

Regarding DMY, similar trends like for P uptake were observed. For the two years of experiment MAP's products and Sinter-P were similar to TSP-60. However, the second year showed a general reduction in the amount of P taken up by the maize plants.

In the soil of neutral reaction Gieboldehausen the response of the reference fertilizer TSP was similar as in the acid soil Düshorn but there was a clear different effect of the recycled P products (Fig. 3.2). The soil fertilized with RP did neither increase the amount of PU by maize nor the DMY. The MAP products were similar to TSP-60 in the increase of PU and in the DMY. Maize plants growing on Ca-P treatment did not increase the PU nor the DMY being similar to RP.

For the thermal fertilizers Sinter-P and Cupola slag, PU and DMY were comparable to TSP-60. The products SI-ash and MB meal ash were in an intermediate situation being higher than P-0 but lower than TSP-60.

In the second year, in contrast to the results of Düshorn soil, the P uptake of maize from Gieboldehausen soil showed greater differentiation and the trend was similar to that of the first year (Fig. 3.2). The reference fertilizer TSP-60 obtained a similar value for PU as in the first year. Products from MAP were similar to TSP-60 and Ca-P was higher than RP. The thermal product Cupola slag was higher than TSP-60.



Fig. 3.1. Phosphorus uptake (PU) expressed per kg of soil and dry matter yield (DMY) of maize on Düshorn soil (pH<sub>caCl<sub>2</sub></sub> 4.4), as response to different reference and recycled P fertilizers during a two year pot experiment. Treatments were applied in a dose of 60 mg P kg<sup>-1</sup> soil. Data are means of 4 replicates and error bars represent the standard error of the means. Different letters indicate a significant difference between treatments at the 0.05 level of significance.



Fig. 3.2. Phosphorus uptake (PU) expressed per kg of soil and dry matter yield (DMY) of maize on Gieboldehausen soil (pHcaCl<sub>2</sub> 6.8), as response to different reference and recycled P fertilizers during a two year pot experiment. Treatments were applied in a dose of 60 mg P kg<sup>-1</sup> soil. Data are means of 4 replicates and error bars represent the standard error of the means. Different letters indicate a significant difference between treatments at the 0.05 level of significance.

Dry matter yield (DMY) showed a similar trend as P uptake (Fig. 3.2). The MAP products, Sinter-P and Cupola slag were similar to TSP-60 in the resulting DMY of maize plants. Rock phosphate (RP) and Ca-P gave markedly inferior maize DMY to the other treatments being similar to P-0. Thermal products SI-ash and MB meal ash were higher than the unfertilized control (P-0) but lower than TSP-60 like for PU. The DMY in the second year was lower than in the first year (Fig. 3.2). All treatments decreased the amount of dry matter produced, despite the P uptake was similar to TSP-60. However, in this soil the thermal products obtained a
higher PU and DMY than in the acid soil Düshorn and the RP and Ca-P were ineffective to increase these plant parameters.

In the acid soil Sattenhausen (Fig. 3.3) the increase of PU in the soil fertilized with TSP-60 was higher than in the other soils.



Fig. 3.3. Phosphorus uptake (PU) expressed per kg of soil and dry matter yield (DMY) of maize on Sattenhausen soil (pHcacl<sub>2</sub> 5.6), as response to different reference and recycled P fertilizers during a two year pot experiment. Treatments were applied in a dose of 60 mg P kg<sup>-1</sup> soil. Data are means of 4 replicates and error bars represent the standard error of the means. Different letters indicate a significant difference between treatments at the 0.05 level of significance.

As it was observed for Düshorn and Gieboldehausen soils, maize fertilized with MAP products had similar P uptake to that of TSP-60 treatment. The reference fertilizer RP did not increase the amount of P taken up by maize plants. The product Ca-P was similar to RP.

Among the thermal products only Sinter-P was higher than P-0, SI-ash and MB meal ash did not increase the PU in comparison to P-0 being similar to RP.

In the second year treatments with recycled P products did not increase the PU, with exception of the MAP-Sb, Sinter-P and MB meal ash (Fig. 3.3).

The pattern of fertilizer effect on DMY for Sattenhausen soil was similar to that of the other soils. As in Düshorn soil a high yield was reached by maize fertilized with Ca-P although the P uptake was not high. The treatments P-O, RP and MB meal ash yielded the lowest amount of DM. In the second year the amount of DMY of maize plants was decreased for all treatments gaining similar weight like in the worst case observed in the first year for MB meal ash (Fig. 3.3).

## 3.3.2 Phosphorus soil solution concentration and CAL-P

Plants take up nutrients from soil solution which represents the immediate available P pool. Fig. 3.4 shows the P concentration in soil solution before and after maize growth in two seasons in the soils used in pot experiments. The P concentration in soil solution increased after fertilization with the reference P fertilizer TSP-60 in all soils (Fig. 3.4, May 2007). The reference fertilizer RP did not increase the P concentration in soil solution in any of the soils in comparison to the unfertilized control (P-0).

The MAP products were able to increase the P in soil solution in all soils being higher than P-0. The Ca-P product increased the P concentration in soil solution only in the acid soils i.e. Düshorn and Sattenhausen. Only all thermal products were able to increase the P in soil solution in comparison to P-0 in Sattenhausen soil. While, Sinter-P increased the P concentration in soil solution in the three soils, the Cupola slag was effective in Gieboldehausen soil but no in Düshorn soil.

Soil samples were taken in May 2007 after 3 weeks of incubation and before maize plant sowing. Fig. 3.4A, B and C show the P soil solution concentration in Düshorn soil. The unfertilized control (P-0), and treatments RP, SI-ash, Cupola slag and MB meal ash reached the lowest P concentration in soil solution ( $\approx 2 \mu$ M) (May 2007). In an intermediate group were treatments with Ca-P, MAP-Gf and Sinter-P ( $\approx 4 \mu$ M) and the highest P concentrations in soil solution were registered for TSP-60, MAP-Sb and MAP-St treatments ( $\approx 6-7 \mu$ M). Phosphorus in soil solution was in general lower in the second year, with a decrease by 2.6 times (May 2008). In the two years of experiment a decrease of P in soil solution after maize growth was observed.



Fig. 3.4. Phosphorus concentration in soil solution after fertilization with reference fertilizers (TSP and RP) and P recycled products in pot experiments. Values indicate the P concentration before and after maize growth in two seasons (2007 and 2008). \* indicates a statistical difference in comparison to the unfertilized control (P-0) within the same growing season (Dunnett test).

The data for Gieboldehausen soil are shown in Fig. 3.4D, E and F. Phosphorus concentration in soil solution by TSP-60 was the highest (14.8  $\mu$ M), while the lowest was found in the

unfertilized control (P-0, 0.62  $\mu$ M) (Fig. 3.4D). The treatments MAP-Sb and MAP-St reached a higher P in soil solution although this was slightly lower than TSP-60. Treatments with MAP-Gf, Cupola slag and Sinter-P can be summarized to a third group, which increased P soil solution concentration between 3 and 4  $\mu$ M. The other treatments were not different to P-0 and ranged from 0.6 to 2.3  $\mu$ M (Fig. 3.4D, E and F). In the second year P in soil solution before maize sowing was markedly inferior to the first year (May 2008).

Phosphorus concentration in soil solution in Sattenhausen soil was generally higher than in the other soils (Fig. 3.4G, H and I). The treatments with MAP-St and MAP-Sb obtained a high P in soil solution (27.7 and 24.7  $\mu$ M respectively), followed by MAP-Gf (12.4  $\mu$ M) (Fig. 3.4H). MAP-Gf, Ca-P, SI-ash and Sinter-P gained a similar concentration of P in soil solution. The treatments with RP and MB meal ash were unable to increase the P concentration and were equivalent to P-0. As in the other soils a similar and decreasing trend was observed for P soil solution concentration after growth of maize plants.

Phosphorus extracted by calcium-acetate-lactate (CAL-P) is shown in Fig. 3.5. Soils fertilized with the reference fertilizer TSP increased the CAL-P in the three soils in comparison to P-0. The reference fertilizer RP only increased the amount of CAL-P in the acid soil Düshorn. In those soils amended with MAP products the CAL-P increased and were comparable to the increase obtained by TSP-60. The recycled P product Ca-P increased the CAL-P in all soils being comparable to TSP.

In relation to the thermal products, Sinter-P and Cupola slag were as effective to increase CAL-P as TSP in Düshorn and Gieboldehausen soils. In Sattenhausen Sinter-P was also comparable to TSP, Cupola slag was not tested on this soil. The other thermal products, SI-ash and MB meal ash were comparable to RP in the acid soil Düshorn and they were unable to increase the CAL-P in the other soils.

In general, CAL could extract similar P levels after TSP-60 and MAP products treatments in all soils (Fig. 3.5B, E and H). Phosphorus of thermal products in soils was less extractable by CAL and only Sinter-P and Cupola slag were similar to TSP-60. A decrease of CAL-P values was observed in all treatments after maize growth and the P availability in the second year (May 2008) was lower than in the first one.



Fig. 3.5. Calcium-acetate-lactate extractable P (CAL-P) after fertilization with reference fertilizers (TSP and RP) and P recycled products in pot experiments. Values indicate the P concentration before and after maize growth in two seasons (2007 and 2008). \* indicates a statistical difference in comparison to the unfertilized control (P-0) within the same growing season (Dunnett test).

For the first year in Düshorn soil CAL-P determination shows that Ca-P, MAP-Gf, MAP-Sb, MAP-St, Sinter-P and Cupola slag obtained similar amount of CAL-P as TSP-60 which reached the maximal CAL-P value (May 2007). In a second group RP, SI-ash and MB meal ash

increased the CAL-P in comparison to unfertilized control (P-0) but did not obtain the levels of TSP-60. A similar situation was observed for CAL-P in the second year where the values of CAL-P declined and the range between unfertilized control (P-0) and TSP-60 was smaller than that of the first year (Fig. 3.5A, B and C, May 2008). Treatments with RP, SI-ash and MB meal ash increased CAL-P, however the values obtained by these treatments were lower than TSP-60 (Fig. 3.5C).

In Gieboldehausen soil CAL was able to extract similar amounts of P for TSP-60 as for almost all other treatments; only RP, SI-ash and MB meal ash were in a chemical way not extractable by CAL and were equal to the CAL-P amounts of unfertilized treatment (Fig. 3.5D, E and F). After the growth of maize plants a decrease was registered for CAL-P values in all variants in the first year and subsequently a stronger decrease in the second year.

Regarding Sattenhausen soil, fertilization with MAP products increased significantly the CAL-P in comparison to unfertilized treatment (P-0) (Fig. 3.5G, H and I). Note that the maximal value for CAL-P was reached by Ca-P being higher than TSP-60. Within products obtained by thermal processes only Sinter-P was similar to TSP-60. SI-ash and MB meal ash did not increase CAL-P.

To get information about P dynamics, the soils were fertilized with standard P fertilizers (TSP and RP) and P recycled products and kept without planting. Fig. 3.6 and Fig. 3.7 show P concentration in soil solution and CAL-P for the overall experiment without plants. The values were divided in groups of reference P fertilizers, recycled P products obtained by chemical processes and recycled P products obtained by thermal processes, besides there is a differentiation between growing seasons.

Soil samples were taken after 3 weeks of incubation. The concentration of P in soil solution increased with the reference P fertilizer TSP in the three soils used in this study (Fig. 3.6). Rock phosphate was unable to increase the P concentration in soil solution and it was similar to the unfertilized control.



Fig. 3.6. Phosphorus concentration in soil solution in soils fertilized with reference P fertilizers and P recycled products without maize plants. A, D and G) Control and reference fertilizers (TSP and RP), B, E and H) Products from chemical processes and C, F and I) Products from thermal processes.

All soils treated with MAP products increased the P in soil solution above the concentration of unfertilized control (P-0). In the three soils and during the overall experiment, the recycled P products of MAP maintained a higher P concentration than P-0 (Fig. 3.6B, E and H).

In general, treatments with recycled P products from thermal processes had the same level than P-0 (Fig. 3.6C, F and I). Only Sinter-P was higher than P-0 in Düshorn soil and Cupola slag in Gieboldehausen soil.

Because P concentration in soil solution is buffered in soils, CAL-P represents the pool that replenishes the soil solution and it is interesting to know its dynamics. The reference fertilizer TSP increased the CAL-P in the three soils, while RP increased only the P extracted by CAL in the acid soil Düshorn in comparison to P-0. Products obtained by chemical processes (MAP and Ca-P) increased CAL-P above the concentration of the unfertilized control P-0 during the overall experiment in the three soils (Fig. 3.7 B, E, H).



Fig. 3.7. Calcium-acetate-lactate P extractable (CAL-P) in soils fertilized with reference P fertilizers and P recycled products and used as controls without maize plants. A, D and G) Control and reference fertilizers, B, E and H) Products from chemical processes and C, F and I) Products from thermal processes.

Products of P recycling from thermal processes were especially effective in the acid sandy soil Düshorn, but in the slightly acid soil Sattenhausen and in the neutral soil Gieboldehausen only Sinter-P and Cupola slag reached higher CAL-P than P-O and similar to that resulting from the reference TSP-60 (Fig. 3.7 C, F, I). In general, CAL-P concentrations were stable over the whole experimental period.

#### 3.3.3 Phosphorus uptake as related by P soil solution concentration and CAL-P

Because plants take up P direct from soil solution and in turn soil solution is buffered by the exchangeable P in bulk soil, P uptake depends on P concentration in soil solution and CAL-P. In Düshorn soil, the first year showed a higher correlation for P in soil solution and P uptake than for CAL-P and P uptake (Fig. 3.8).



Fig. 3.8. Phosphorus uptake of maize in relation to P in soil solution and CAL-P after fertilization with recycled P fertilizers in a two year pot experiment on Düshorn soil (pH<sub>CaCl2</sub> 4.4). Concentration of P in soil solution and CAL-P are values from the beginning of the respective growing period. \*/\*\*/\*\*\* indicate a significant correlation at P<0.05, 0.01 and 0.001 respectively.

For the second year the dependency of P uptake on P in soil solution and CAL-P was not strong and the two parameters gave similar coefficient of determination (Fig. 3.8B and D). As can be seen in Fig. 3.8 A and C, some products were able to increase CAL-P but the concentration of P in soil solution was not affected and a lower P uptake was reached, that was especially true for Cupola slag (in Fig. 3.8, treatment number 10).

In Gieboldehausen soil a similar trend was observed like that found in Düshorn soil, P uptake showed a closer relation with P concentration in soil solution than CAL-P (Fig. 3.9). Furthermore, in the second year this relationship was stronger. In this soil, treatment with Ca-P reached a similar CAL-P value than TSP-60, nevertheless no increase in P in soil solution was registered.



Fig. 3.9. Phosphorus uptake of maize in relation to P in soil solution and CAL-P after fertilization with recycled P fertilizers in a 2 years pot experiment on Gieboldehausen soil ( $pH_{CaCl_2}$  6.8). Concentration of P in soil solution and CAL-P are values from the beginning of the respective growing period. \*/\*\*/\*\*\* indicate a significant correlation at P<0.05, 0.01 and 0.001 respectively.

At intermediate pH value in Sattenhausen soil (pH 5.6), P uptake and P in soil solution showed a significant correlation (Fig. 3.10). No correlation with CAL-P was observed and in the second year neither P in soil solution nor CAL-P correlated with P uptake. As in the other soils, treatments fertilized with some of the recycled products increased CAL-P. However, this gain was not observable in P concentration in soil solution (i.e. Ca-P, treatment number 4).



Fig. 3.10. Phosphorus uptake of maize in relation to P in soil solution and CAL-P after fertilization with recycled P fertilizers in a two year pot experiment on Sattenhausen soil ( $pH_{CaCl_2}$  5.6). Concentration of P in soil solution and CAL-P are values from the beginning of the respective growing period. \*/\*\*/\*\*\* indicate a significant correlation at P<0.05, 0.01 and 0.001 respectively.

# 3.3.4 Relative fertilizer efficiency (RFE)

The plant availability can be assessed by calculating the relative fertilizer efficiency. The difference between P uptake of a specific fertilizer treatment and the unfertilized control

reveals the amount of P that is provided by the fertilizer. This is compared with the fertilizer effect of a readily available fertilizer, i.e. the TSP-60 treatment, which is set to 100% (Eq. 8). In Düshorn soil the products obtained by a chemical process i.e. MAP and Ca-P reached more than 70% of the RFE as achieved by TSP-60 and MAP-Sb even reached a RFE of 139%. The recycled P products reached a lower RFE being lower than RP, with the exception of Sinter-P which achieved more than 70% (Fig. 3.11).



Fig. 3.11. Relative fertilizer efficiency for P recycled fertilizers and RP relative to TSP used in pot experiment the first year.

In Gieboldehausen soil, the RFE value for the reference fertilizer RP was negative and for Ca-P was of about 13%. The MAP products reached a value near to 100% being similar to TSP. In relation to thermal products, Cupola slag reached more than 100% and Sinter-P a RFE value of 70%. In relation to SI-ash and MB meal ash achieved a lower RFE than 70% but were more effective than RP and Ca-P.

## 3.4 Discussion

### 3.4.1 Phosphorus uptake and dry matter yield

The pot experiment allowed to distinguish the effectiveness of recycled P fertilizers. Phosphorus uptake (PU) and DMY by maize as well as P concentration in soil solution and CAL-P were affected by the fertilization. The higher distinctiveness between products for P uptake by maize was found in the first year. Treatments with magnesium-ammoniumphosphate (MAP) products were similar to TSP-60 showing the high P plant availability (Fig. 3.1, Fig. 3.2 and Fig. 3.3). These results are consistent with those found by Massey et al. (2009) who worked with recovered MAP in neutral and slightly alkaline soils. According to Plaza et al. (2007) the P uptake obtained by ryegrass fertilized with struvite (MAP) in greenhouse conditions was similar to that reached with a water soluble fertilizer (super phosphate). Similar results were found by Johnston and Richards (2003), who tested the effectiveness of struvite recovered from sewage sludge in comparison to monocalcium phosphate (MCP) and they found that P uptake by ryegrass fertilized with struvite was equivalent to that for MCP. It is often said that struvite has not water soluble P but actually its  $pK_{sp}$  is 13.26 (Ohlinger et al., 1998) which indicates that the maximal concentration that can be reached is about 38  $\mu$ M. In the present study the P concentration in soil solution showed values of 1-5  $\mu$ M, which was enough to obtain an optimal plant growth.

Phosphorus precipitated by Ca (Ca-P) was only as effective as TSP-60 in the acid sandy soil Düshorn. Several authors have argued that low soil pH is an important factor that influences apatite reactivity (Chien and Menon, 1995; Kanabo and Gilkes, 1987). Because low pH soils are poor in Ca ions a gradient is generated that allows the Ca-P dissolution. Thus, it is expected that apatite dissolution will be higher in acid soils (Chien and Menon, 1995). In the present study Ca-P was compared with rock phosphate (RP) in the three soils. In neutral pH soil from Gieboldehausen and acid soil from Sattenhausen no distinction was observable for P uptake in the first year among Ca-P and RP. However, in acid soil Düshorn Ca-P was higher than RP, which means that the solubility of Ca-P was higher than for RP in acid soil conditions.

The maize plants also responded to the fertilization with products obtained by thermal processes. However, only Sinter-P was similar to TSP-60 in Düshorn and Gieboldehausen soils with a tendency to be slightly lower. Products SI-ash, Cupola slag and MB meal ash were

equivalent to P-0 in Düshorn soil (pH 4.4). Furthermore, MB meal ash was in the three soils not different than P-0. Interestingly, the P uptake obtained by maize fertilized with Cupola slag in acid soil Düshorn was higher in tendency than TSP-60.

In relation to SI-ash which had an intermediate availability in comparison to TSP-60, Adam et al. (2009b) found a better performance being comparable with the DMY obtained by a commercial PK fertilizer. The authors conducted a pot experiment with maize plant fertilized with a product similar to SI-ash used in the present study, and they reported that the water solubility of SI-ash was very low (about 1% of total P) although the solubility in citric acid could be up to 100%. In the present study the water solubility of this product was about 6.4% and in citric acid it was about 31.4% of the total P. This solubility could explain the discrepancy between the two pot experiments. Furthermore, it was expected that in acid soils SI-ash had a better P availability, however in the acid soil Düshorn it was the lowest P uptake found among the three soils. The high amount of Fe and AI found in SI-ash reported by Adam et al. (2009b), might be solubilized and might react in the soil solution to precipitate the P contained in the product, this hypothesis can explain the low P plant availability reached in the acid soil. Thus, a better P availability should be found in a slightly acid or neutral soil, as in the present experiment.

Maize plants fertilized with Cupola slag had taken up different amounts of P depending on the soil where they were growing. After fertilization with Cupola slag, the uptake in acid soil Düshorn (pH 4.4) was equivalent to unfertilized control (P-0), in neutral soil Gieboldehausen (pH 6.8) it was similar to TSP-60 and in Sattenhausen soil (pH 5.6) it reached an intermediate value. Although Cupola slag is a product containing Ca, it seems to be that its availability, also depends on the Al content. This could explain the low availability in acid soils and a high solubility in neutral ones. Then, for Cupola slag it can be argued, that low pH favors a solubility of metals present in the products applied facilitating the P complexation as Al-P. A high concentration of Al in Cupola slag was reported by Scheidig et al. (2009). No information about experiments of plant availability of P for Cupola slag is available.

In general, P uptake and DMY by maize plants after fertilization with MB meal ash was equivalent to P-0, being only in Gieboldehausen slightly higher but not significantly different. Phosphorus uptake and DMY were affected by Sinter-P treatment, which reached a similar level as TSP-60 being inferior in Sattenhausen soil. This product can be compared with the commercial fertilizer sinter-phosphate Rhenania used in Germany which is sintered with sodium carbonate and silica at high temperature (Bolan et al., 1993) and is soluble in ammonium citrate (Finck, 1992; Mengel and Kirkby, 1987). According to the description above, Sinter-P should be more effective in slightly acid soils. However, in the present study it was effective in all soils at different pH values.

#### 3.4.2 Phosphorus soil solution concentration and CAL-P

Plants take up P from soil solution and this represents the immediate available P pool which is buffered by exchangeable P from the bulk soil (Mengel and Kirkby, 1987). In the present pot experiment P concentration in soil solution was affected by the different recycled P products applied to the soil. In general, all treatments increased P in soil solution, this was especially remarkable for treatments with MAP products. After a first increment of P in soil solution a decrease was observed in all treatments with P recycled fertilizers. This decrease in P soil solution concentration was mainly due to P uptake and P adsorption processes (Fig. 3.4 and Fig. 3.6). A decrease in P soil solution concentration three months after of application of recycled P fertilizers in soils without plants was observed in some treatments, which was remarkable in Sattenhausen soil (Fig. 3.6), this could be attributed to a biological immobilization after P was applied and a following increment in the concentration resulting from the new equilibrium reached. However, in the other soils only for some treatments the same tendency was observed. Thus, a decrease for treatments where plants were grown was mainly attributable to plant P uptake.

The treatments with RP and Ca-P were able to increase the P in soil solution only in acid soils, which is consistent with several works which indicated that rock phosphate is more available at low soil pH values (Casanova et al., 2002; Casanova, 1995; Chien and Menon, 1995; Havlin et al., 2005; Kanabo and Gilkes, 1987). Products obtained by thermal processes were less available than MAP products and in some cases similar to the unfertilized control (P-0), it seems to be that the Fe and Al content in the thermal products can influence the P solubility, which can be critical in acid soils. These findings are concordant with the theoretical behavior of strengite and variscite which are low soluble in acid soils (Havlin et al., 2005; Lindsay, 1979), and according to Prochnow et al. (2003), who evaluated rock

phosphates with different Fe contents, these products improve their effectiveness as soil pH increases.

Almost all fertilizers from P recycling increased the CAL-P (Fig. 3.5 and Fig. 3.7). Treatments with MAP products were more effective than thermal products. Among the thermal products, only Sinter-P increased CAL-P in all soils. Because CAL method can extract P in alkaline soils due to its low pH (4.1) and in acid soils due that acetate and lactate anions can compete with phosphates adsorbed to Fe and Al compounds, it was expected a similar P extractable by CAL in all soils used in the present experiment. Thus, acid soil Düshorn treated with products from thermal processes (i.e. Sinter-P, SI-ash, Cupola slag and MB meal ash) increased the CAL-P although the amount of P in soil solution was similar than in unfertilized control (P-0).

# 3.4.3 Phosphorus uptake as a function of P availability

Phosphorus in solution is buffered by exchangeable P from the bulk soil, that means that P solubility and the strength of its retention in soil determine the amount of P in soil solution which is immediately plant available (Holford, 1997). The process can be represented by the relationship between P uptake and P in soil solution and between P uptake and exchangeable P (in the present study CAL-P, although it does not necessarily represent exchangeable P). Fig. 3.8, Fig. 3.9 and Fig. 3.10 show the relationships between P uptake by maize plants and P in soil solution as well as CAL-P. The order of products on the regression line represents the plant availability of fertilizer P. As it can be seen in Fig. 3.8, for Düshorn soil P soil solution concentration explains more satisfactorily the P availability of the products than CAL-P ( $R^2$ =0.7 and  $R^2$ = 0.48 respectively). Some products increased CAL-P which did neither mean an increment in P concentration in soil solution nor in P uptake by maize (i.e. Cupola slag). These findings are supported by the results of Torres-Dorante et al. (2006) who found that P in soil solution was a better indicator than CAL-P. Thus, Sl-ash, Cupola slag and MB meal ash besides RP increased CAL-P in to some degree but it did not reflect a gain on P uptake by maize plants being similar to P-0. In Gieboldehausen soil a similar trend was observed, but in this soil CAL-P value was reached by Cupola slag which meant an increase of P in soil solution concentration (Fig. 3.2 and Fig. 3.9). A close correlation was calculated for the second year for P uptake and P in soil solution in

Gieboldehausen soil, which might be due to a high P retention in this soil which contains more clay minerals (Tab. 3.2), allowing a replenishment of the soil solution for a long time in comparison to Düshorn soil. Treatments with MAP products were remarkable different to the other treatments on Sattenhausen soil. The relationship between P uptake and P soil solution concentration was significant; however CAL-P was not able to extract P related to P uptake in this soil. Herein, it is important to clarify that no simple chemical method can extract exactly the plant available P. As in Gieboldehausen soil, CAL-P for Ca-P treatment was similar to that for TSP-60, although the increase of P in soil solution was not in the same range (Fig. 3.10).

## 3.4.4 Relative fertilizer efficiency (RFE)

Depending on soil and fertilizer the RFE (relative fertilizer efficiency) ranged from -11% (RP, Gieboldehausen) up to 139.4% (MAP-Sb, Düshorn). A RFE close to the control TSP-60, i.e. more than 70%, was achieved by Ca-P, MAP-Sb, MAP-Gf, MAP-St and Sinter-P in Düshorn soil, MAP products, Sinter-P and Cupola slag in Gieboldehausen soil and MAP-Sb and MAP-St in Sattenhausen soil (Fig. 3.11).

The RFE is related to the P concentration in the soil solution (Fig. 3.4). In those soils where MAP products increase the P in soil solution up to similar values as does TSP-60 the RFE was near 100%. Thus, in Düshorn soil with MAP products and with Ca-P the P in soil solution was higher than 3  $\mu$ M in the first year. In the same soil, only Sinter-P showed similar values of P in soil solution, which confirms that the higher RFE was reached by this product in comparison to the other thermal products.

In Gieboldehausen soil, P in soil solution obtained by MAP products was similar to that of TSP. The thermal product Cupola slag increased the P in soil solution in a similar amount to TSP, which is reflected in the RFE achieved (more than 100%). In the case of SI-ash, this product showed a lower P concentration in soil solution than TSP but higher than P-0 and its RFE was about 70%. The thermal products SI-ash and MB meal ash were similar in increasing the P in soil solution, and a comparable RFE was observed. Calcium phosphate was not able to increase the P in soil solution in this soil being comparable to RP, both obtained a low RFE. The MAP products MAP-Sb and MAP-St achieved a similar P concentration in soil solution, which was reflected in a similar RFE in Sattenhausen soil (more than 70%). While the other

recycled P products could increase the P in soil solution of about 5  $\mu$ M, the amount increased for TSP was of about 25  $\mu$ M, which could explain the low RFE shown by thermal products as well as by Ca-P.

In the literature there is limited information about the effectiveness of recycled P products which is related exclusively to MAP products. For example, Johnston and Richards (2003), working with a pot experiment with ryegrass in two soils (pH 6.6 and 7.1 respectively), obtained RFE between 121% and 158% for two struvite of municipal wastewater in comparison to monocalcium phosphate and 48% for Ca-P in the slightly acid soil. The same authors, reported that Ca-P was ineffective in the neutral soil (-15%). Plaza et al. (2007), also working with ryegrass in a sandy soil of pH 5.7, found a RFE of about 100% for struvite in comparison to super phosphate.

In relation to phosphorus extracted by calcium-acetate-lactate (CAL-P), in Düshorn soil MAP products as well as Ca-P increased the CAL-P and were similar to TSP, which is consistent with the RFE obtained by these products. However, for the fertilizers obtained by thermal products, CAL solution extract similar amounts of P for Sinter-P and for Cupola slag and only Sinter-P could achieve a RFE similar to TSP. Furthermore, the thermal products SI-ash and MB meal ash showed an intermediate value of CAL-P which was higher than for P-0, however did not increase the PU and the RFE was about 10%.

In Gieboldehausen soil CAL-P increased by the treatments MAP and Ca-P to a similar amount as TSP, however only MAP products obtained a similar RFE as TSP, being Ca-P of about 13%. Regarding the thermal products, only Sinter-P and Cupola slag increased CAL-P, which is consistent with the RFE achieved by these products.

In Sattenhausen soil the CAL-P for MAP products and Ca-P was similar to the value obtained by TSP, but the RFE achieved by these products was only similar to TSP in the case of MAP-St. Among the thermal products only Sinter-P increased the CAL-P value which was similar to TSP, however, the RFE was lower than TSP.

It seems to be that CAL-P is not related to all P fractions that are plant available. In chapter 4, information about the P dynamics after the application of reference P fertilizers and recycled P products will be examined.

# **3.5 Conclusions**

The recycled MAP fertilizers were as effective as TSP in increasing the P concentration in soil solution, CAL-P and as consequence the phosphorus uptake and the dry matter yield in all soils tested in the present study. Also Ca-P obtained by chemical process, was only effective in the acid soil Düshorn.

Recycled P products obtained by thermal processes were in general of lower effectiveness than TSP and more similar to RP. Sinter-P and Cupola slag were as effective as TSP in the acid soil Düshorn and in the neutral soil Gieboldehausen respectively. The products SI-ash and MB meal ash were ineffective to increase the P in soil solution nor the CAL-P and as a consequence the PU of maize plants.

The effectiveness of the recycled P products and of the reference fertilizers is more related to their capacity to increase the P in soil solution. The P extracted by CAL was not always related to the phosphorus uptake, indicating that this extractant can take P from fractions that are actually not plant available.

# Chapter Four: Dynamics of P in soil from P compounds of the P recycling in comparison to standard fertilizers as evidenced by soil P fractionation, isotopically exchangeable P and P uptake by maize (*Zea mais* L.)

# 4.1 Introduction

The results of the pot experiment showed that the effectiveness to supply P to plants varied among reference as well as recycled P fertilizers depending furthermore on the soil used. In this chapter possible reasons for the different effectiveness will be investigated.

Phosphorus applied to soils is subjected to precipitation and adsorption processes which decrease plant available P (Sample et al., 1980). Thus, P from fertilizers is accumulated in different P fractions in soils or remains unaltered due to its low equilibrium concentration (e.g. rock phosphate). These P fractions have been recognized to be of different plant availability depending on soil type and plant abilities (Hedley et al., 1994; Lambers et al., 2008; Saleque et al., 2004). The evaluation of P fractions is achieved by chemical sequential extraction procedures based on the assumption that stronger acid or alkali extract less available P (Cross and Schlesinger, 1995; Schmidt et al., 1996; Sui et al., 1999). One of the more widely used P-fractionation procedure was developed by Hedley et al. (1982) which was later modified by Tiessen and Moir (1993). This approach distinguishes among P exchangeable by resins, P extracted by NaHCO<sub>3</sub>, P extracted by NaOH, P linked to Ca extracted by HCl and finally residual P (H<sub>2</sub>SO<sub>4</sub> P extractable) (Tiessen and Moir, 1993). From NaHCO<sub>3</sub>, NaOH and HCl extractions, organic P is evaluated which can be defined as labile and stable organic P respectively (Sui et al., 1999). According to Tiessen and Moir (1993) some role can be assigned to each P fractions under different conditions of incubation, cultivation, root activity or soil development. Phosphorus extracted by anion exchange resins is considered to be in equilibrium with soil solution and is biologically available (Hedley et al., 1982). Labile P extracted by NaHCO<sub>3</sub> is considered to be adsorbed on soil surfaces (Mattingly, 1975) and is likely plant available (Tiessen and Moir, 1993). Hydroxide-extractable P<sub>i</sub> is chemisorbed on Al and Fe oxides and is assumed to be moderately labile P (Guo et al., 2000; Ryden et al., 1977; Schmidt et al., 1996). However, this assumption is unlikely since Ca-P can be extracted as well with NaOH (Williams et al., 1971). Phosphorus soluble in acids is linked to calcium phosphates and carbonates (Cross and

Schlesinger, 2001) since Al- or Fe-P that remain unextracted by NaOH is insoluble in acid (Tiessen and Moir, 1993). The HCl-P<sub>i</sub> is considered of low availability to plants (Guo et al., 2000). In the following fraction P is assessed by hot acid which extracts very stable inorganic and organic P (P<sub>i</sub> and P<sub>o</sub> respectively). This organic P can be easily bioavailable (Tiessen and Moir, 1993). Residual P is normally accepted to be recalcitrant P (Short et al., 2007).

Phosphorus fractions are interconnected through the soil solution with a dynamic equilibrium. For that reason, it is not possible to visualize P as discrete pools containing available and unavailable P forms. This is especially true for bicarbonate and hydroxide extractable P<sub>i</sub> (Tiessen and Moir, 1993). In contrast, it is postulated that exists a continuum between P present in soil solution and P forms present in the solid phase that are slowly available as well as precipitated P (Frossard et al., 2000). The idea of Frossard et al. (2000) is supported by previous studies on the processes of P sorption and desorption described by Barrow (1980; Barrow, 1983). That means that after application of P products in soils a rearrangement of P fractions is expected, which is based on P compounds solubility, soil properties and the effect of plants. Thus, application of mineral P fertilizer (TSP) during 10 years under barley monoculture contributed significantly to increase Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub> although the more available organic P pool decreased (Zheng et al., 2004). Saleque et al. (2004) in a long term field experiment with rice, showed that mineral P fertilizers mixed with cow dung accumulated in NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub> fractions more than in acid P fractions. In soils fertilized with TSP and rock phosphate (RP), Rivaie et al. (2008) found that NaOH-P<sub>i</sub> was highest when TSP was applied, while H<sub>2</sub>SO<sub>4</sub>-P<sub>i</sub> was highest in soil fertilized with RP, no changes were registered for NaOH-P<sub>o</sub>. The same authors indicated that NaOH-P<sub>i</sub> was higher in Allophonic soil than in Pumice soil, which support the idea that NaOH extracted P that is bound to Al (Guo et al., 2000; Rivaie et al., 2008). In other study with soils from Eucalyptus forest in Australia, applications of mono-calcium phosphate (water soluble P) was converted rapidly (4 weeks) to forms of low availability associated with Al and Fe oxides  $(NaOH-P_i)$  (Short et al., 2007).

Several investigations with P radioisotopes (usually <sup>33</sup>P or <sup>32</sup>P) have shown that the main source of P available to plants is the isotopically exchangeable P<sub>i</sub> (Frossard et al., 1994; Frossard et al., 2000; Morel and Plenchette, 1994). Furthermore, the time of exchange with P isotopes determines the amount of P available to plants over time. Thus, a kinetic study of isotopic exchange during 100 min represents the P<sub>i</sub> availability within 3 months and the quantity of P<sub>i</sub> exchangeable during 1 min is considered to be totally and immediately plant available (Frossard et al., 2000). Therefore, P isotopically exchangeable depends on the reactivity of P products and soil conditions. Owusu-Bennoah et al. (2002) showed that direct application of Togo rock phosphate on acid soils from Ghana did not increase the isotopically exchangeable P in comparison to unfertilized control despite of low soil pH value (lower than 5.0). However, applications of TSP increased the P concentration in soil solution as well as isotopically exchangeable P.

The objective of this study was to compare the fate and effectiveness of different P recycled products as compared with standard fertilizers applied to two soils varying in pH value, texture and organic matter content under maize growth in a pot experiment. To this purpose, it was distinguished between the P fractions in soils after maize growth and in soils incubated without plants. To evaluate the amount of isotopically exchangeable P, incubation with <sup>33</sup>P isotope was conducted in the same soils used above.

The hypotheses of the present work were:

- 1. For water soluble P fertilizers: P will be extracted mainly by resins and NaHCO<sub>3</sub>.
- The sum of the isotopically exchangeable P of the planted soil plus the P taken up by plants is equal to the isotopically exchangeable P of soils without plants.
- 3. For the standard and recycled P fertilizers of low solubility: P will remain in the soil unaltered.
- 4. Plants may accelerate the dissolution of the P fertilizer (either by decreasing the concentration of P in soil solution or exuding P mobilizing compounds), and then the sum of isotopically exchangeable P after plant growth plus P uptake by plants will be larger than the isotopically exchangeable P in soils without plants.

## 4.2 Materials and methods

Soil samples from a pot experiment conducted on two soils under maize growth were collected to assess the fate of P from recycled P products. Eight different compounds from P recycling were tested as P fertilizers. Additionally, two commercial fertilizers with different P availability, i.e. triple superphosphate (TSP) and rock phosphate (RP) were taken as control. The materials used were: three Magnesium-ammonium-phosphates (MAP) of different sewage treatment plants (MAP-Sb, MAP-Gf and MAP-St), a precipitated apatite of municipal sewage sludge (Ca-P), an alkali sinter phosphate made from meat-and-bone meal (Sinter-P), a heavy metal depleted sewage sludge ash (SI-ash), a cupola furnace slag (Mephrec procedure, Cupola slag) made from sewage sludge and a meat-and-bone meal ash (MB meal ash). The same treatments were applied to soils without plant growth. For detailed information about products applied to the soils and experimental setting see chapter 3.

# 4.2.1 Soil characteristics and P uptake by maize plants

Soil samples were collected from the total soil volume at the end of the experiment from soil under maize growth and soils without plants. Samples were taken two years after fertilizer application, either without plants or planted twice to maize. Soil samples from treatments without plants were used as incubation experiment to assess the fate of recycled P fertilizers isolated from plant effects. Samples were air dried, sieved to 2 mm and posterior stored in paper bags. Tab. 4.1 shows the main properties of the soils.

Phosphorus uptake of maize plants during the overall experimental time (two years) was used to correlate with P fractions and isotopically exchangeable P. Detailed information about P uptake by maize plants in this experiment was presented in chapter 3.

isotopically exchangeable P applied to soils in a pot experiment.	Tab. 4.1. Main characteristics of the soils used to evaluate the fate of recycled P fertilizers and the
	isotopically exchangeable P applied to soils in a pot experiment.

Location	Clay	Silt	Sand	Organic matter	pH in $CaCl_2$	CAL-P
		%	)		(relation 1:2.5)	mg P kg⁻¹
Gieboldehausen	25.0	65.5	9.5	2.8	6.8	21.0
Düshorn	2.1	5.3	92.6	5.3	4.4	24.2

## 4.2.2 Analytical procedure

#### 4.2.2.1 Phosphorus fractionation procedure

The characterization of P fractions in the soil was performed using the Hedley et al. (1982) sequential-fractionation procedure modified by Tiessen and Moir (1993) (Fig. 4.1). Air dried soil samples were finely ground to pass a 500 µm sieve. Then, 0.5 g of soil was weighed in a 50 mL centrifuge tube. Two anion exchange resin strips converted to bicarbonate form (9 x 62 mm, anion resin PC Acid 35, PCA Company, Germany) plus 30 mL distilled water were added to the tubes. The samples were shaken overnight during 16 h. After shaking, anion exchange resin strips were washed with distilled water to remove soil particles and were placed into clean 50 mL centrifuge tubes and added 20 mL 0.5 M HCl. Samples were shaken again for 16 h. Inorganic P in the HCl solution was determined colorimetrically according to Murphy and Riley (1962). The soil suspension was centrifuged at 12,000 rpm for 10 min at 0°C. Supernatant was filtered through a 0.45 µm acetate cellulose filter and discarded. Soil sample was shaken overnight (16 h) with 30 mL 0.5 M NaHCO<sub>3</sub>. After shaking, soil suspension was centrifuged and filtered as described above. Inorganic and organic P was determined in the filtered extract. To determine P<sub>i</sub>, an aliquot of 5 mL was taken and acidified with 3 mL 0.9 M  $H_2SO_4$  and refrigerated for 30 min to precipitate organic matter (OM). The acidified NaHCO<sub>3</sub> samples were centrifuged as was described previously and P<sub>i</sub> was determined colorimetrically. From the same NaHCO<sub>3</sub> extract an aliquot was taken to determine total P ( $P_T$ ) for which organic matter was digested in presence of 0.25 g ammonium persulfate plus 5 mL 0.9 M H<sub>2</sub>SO<sub>4</sub> in a 25 mL volumetric flask. The samples were autoclaved for 60 min at 120°C. Total P was colorimetrically measured in the extract. Organic P ( $P_o$ ) was calculated by the difference between  $P_T$  and  $P_i$ . The following extraction was conducted with 1 M NaOH. The procedure was essentially the same as performed with NaHCO<sub>3</sub>. Unlike the NaHCO<sub>3</sub> extraction, OM was precipitated with 0.8 mL 0.9 M H<sub>2</sub>SO<sub>4</sub> and P<sub>T</sub> was digested with 0.3 g ammonium persulfate and autoclaved during 90 min at 120°C.

The next P fraction was extracted with 30 mL 1 M HCl. The samples were shaken during 16 h, centrifuged and filtered as described above. An aliquot from this solution was taken and  $P_i$  was colorimetrically determined but no  $P_T$  was determined in this step. The soil sample was then heated with 10 mL concentrated HCl (11.3 M) at 80°C for 10 min in a water bath. The samples were mixed with a vortex each 15 min during 1 h. The solution was centrifuged and

decanted into a 50 mL volumetric flask and the volume was completed with distilled water. Inorganic P was measured directly from this solution and P<sub>T</sub> was determined digesting an aliquot of the solution with 0.2 g ammonium persulfate and 5 mL distilled water in the same way as was already described for NaHCO<sub>3</sub> extract. Organic P was calculated by the difference between P<sub>T</sub> and P<sub>i</sub>. Residual P corresponds to the last fraction in this sequence. It was determined by digestion of the residual soil sample with 5 mL concentrate H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> at 360°C in a digestion block until an uncoloured solution was reached. Inorganic P (P<sub>i</sub>) was colorimetrically measured in this fraction (for more details see Tiessen and Moir (1993)).



Fig. 4.1. The procedure for sequential P extraction (P<sub>t</sub>=Total P, P<sub>i</sub>= inorganic P).

Total P concentration without fractionation was determined using a digestion with an acid solution which contains nitric, perchloric and sulfuric acid in a proportion of 7:2:1 respectively plus 2 mL concentrated H<sub>2</sub>SO<sub>4</sub>. A soil sample of 1 g was placed into 100 mL glass tube and heated up slowly in a digestion block to 230°C. The samples were digested during 3 h. Phosphorus was colorimetrically measured in the extract (Hoffmann, 1991).

Before colorimetric measurement of P, pH value of all samples was adjusted to 7 with 4 M NaOH and 0.25 M  $H_2SO_4$  using *p*-nitrophenol as indicator. All P fractions as well as total P extraction were conducted in triplicate.

#### 4.2.2.2 Isotopically exchangeable phosphorus (IEP)

Soil samples from pot experiments with maize plants and from soils without plants used in the incubation experiment were taken for the determination of the isotopically exchangeable P. In 50 mL plastic tubes 2 g of air dried soil sieved to pass 500 µm were weighed. To each of these tubes 8 mL distilled water and 7 mL of carrier-free solution  $H_3^{33}PO_4$  having a radioactivity of about 0.04 to 0.06 MBq were added. The samples were shaken for 5 d. After shaking time, samples were centrifuged at 4,000 rpm. In the supernatant solution the ratio of <sup>33</sup>P and <sup>31</sup>P has to be determined, but the <sup>31</sup>P concentration is often very low and its determination would be very insecure. For this reason the solution was concentrated by using an anion exchange resin. The procedure consisted in that 10 mL aliquots of supernatant were placed in 13 mL tubes with a anion exchange resin strip (9 x 15.5 mm, anion resin PC Acid 35, PCA Company, Germany) and shaken 24 h. Then, the resin strips were taken carefully and placed in clean tubes with 2 mL 0.5 M HCl and shaken for 2 h. From this solution <sup>31</sup>P and <sup>33</sup>P were determined. Non radioactive P concentration was colorimetrically measured, after neutralizing the HCl, according to Murphy and Riley (1962). Radioactivity of P in the HCl extract was measured with a liquid scintillation analyzer (Perkin Elmer TRI-CARB 2800 TR). Isotopically exchangeable P was calculated based on the theoretical relationship:

Eq. 9

$$IEP = \frac{C_L}{r_t}R$$

where, *IEP* is the isotopically exchangeable P in mg kg<sup>-1</sup> of soil,  $C_L/r_t$  is is the ratio of P concentration in solution ( $C_L$ , mg L<sup>-1</sup>) over the radioactivity in solution ( $r_t$ , Bq L<sup>-1</sup>) and R is the total radioactivity introduced in Bq kg<sup>-1</sup> soil (Owusu-Bennoah et al., 2002). The method is based on the assumption that <sup>31</sup>P and <sup>33</sup>P have the same chemical behavior and that the relationship between <sup>31</sup>P and <sup>33</sup>P is maintained in anion exchange resin strips as it was found in soil solution.

## 4.2.3 Data analysis and experimental design

Statistical analysis was performed using Statistica 9.0 (StatSoft, Inc. Tulsa, USA.). The experimental design was a complete randomized design, with 11 treatments. The fertilizers were considered as main factors, according to the following model:

Eq. 10. 
$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij}$$

being y the dependent variable,  $\alpha$  the treatment (different sources of P fertilizer),  $\mu$  the mean of the overall population and  $\varepsilon$  the random effect (Quinn and Keough, 2002). The ANOVA test was followed by a Newman-Keuls test at the 0.05 level of significance to separate the means.

The relationships between P uptake, P fractions and isotopically exchangeable P were described by Pearson's correlations and linear regressions with the following formula:

Eq. 11. 
$$y_i = \beta_0 + \beta_1 X_i + \varepsilon_i$$

being  $y_i$  the value of Y when the predictor variable X=  $x_i$ ,  $\beta_0$  the intercept when X is zero,  $\beta_1$  is the slope and measures the change in Y per unit change in X, finally  $\varepsilon_i$  is the random and unexplained error (Quinn and Keough, 2002).

#### 4.3 Results

## 4.3.1 Fate of P from fertilizers applied to Düshorn soil

To study the dynamics and transformations of P fertilizers added to the soil a sequential fractionation was carried out. In general, in Düshorn soil without maize plants (Fig. 4.2), the addition of water soluble fertilizer (TSP) and insoluble (RP) reference P fertilizers and P recycled fertilizers increased the Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub> fractions in relation to the unfertilized soil (P-0). Recycled P fertilizers obtained by chemical processes showed a similar increase of the level of P extracted by anion exchange resins as the reference fertilizer triple superphosphate (TSP-60), among them MAP-Sb reached in tendency the highest value (Fig. 4.2A). Recycled P fertilizers from thermal processes were unable to increase significantly the P extracted by anion exchange resins and were lower than the reference fertilizer RP. Fig. 4.2B and Fig. 4.2C show the P extracted by alkaline extractants. The reference fertilizers TSP and RP increased the NaHCO<sub>3</sub>-P<sub>i</sub> significantly. Among the chemical products, only MAP-St was different than P-0.

Thermal P products did not increase the level of NaHCO<sub>3</sub>-P<sub>i</sub> except the Sinter-P which was similar to the reference fertilizer TSP-60. The change of P extracted by NaOH was generally lower than the change of P extracted by anion exchange resins and NaHCO<sub>3</sub> (Fig. 4.2C). Of the reference fertilizers only TSP caused a significant increase of the NaOH-P<sub>i</sub>. The increase caused by fertilizers obtained by chemical processes was significant for the MAP products but not for Ca-P. And of the fertilizers from thermal processes only the Cupola slag caused a significant increase in NaOH-P<sub>i</sub> (Fig. 4.2C).

Fig. 4.3 shows the effect of the fertilizers on P extracted by acids. Fig. 4.3A shows that the reference fertilizer TSP had no effect on HCl 1M-P<sub>i</sub> which for the case of RP the acid still dissolved almost 1/3 of the fertilizer applied even in this very acid soil. Phosphorus extracted by HCl showed to be higher in treatments fertilized with recycled P products from thermal processes. For these products, the amount of HCl 1M-P<sub>i</sub>, was similar than the reference fertilizer RP, of which SI-ash was the highest. Treatments fertilized with recycled P products obtained by chemicals processes did not show a significant increase in relation to the original P level in the unfertilized soil (P-0). Small changes were registered in the P fraction extracted by concentrated HCl and no differences were observed in the residual P (Fig. 4.3B and Fig. 4.3C).



Fig. 4.2. Changes of different P fractions in Düshorn soil (pH<sub>CaCl2</sub> 4.4), two years after the application of reference and recycled P fertilizers. The P fractions were determined in a sequential fractionation procedure. The figure shows the first three fractions. A) Anion exchange resins (Resin-P<sub>i</sub>), B) sodium bicarbonate (NaHCO<sub>3</sub>-P<sub>i</sub>) and C) sodium hydroxide (NaOH-P<sub>i</sub>). Different letters mean a significant difference among treatments at the P<0.05 (Newman-Keuls test). Open bars= Reference fertilizers, gray bars= recycled P products obtained by chemical processes and black bars= recycled P products obtained by thermal processes.



Fig. 4.3. Changes of different P fractions in Düshorn soil (pH<sub>CaCl2</sub> 4.4), two years after the application of reference and recycled P fertilizers. The P fractions were determined in a sequential fractionation procedure. The figure shows the next three fractions. A) 1M hydrochloric acid (HCl 1M-P<sub>i</sub>), B) concentrated hydrochloric acid (HCl conc.-P<sub>i</sub>) and C) residual P. Different letters mean a significant difference among treatments at the P<0.05 (Newman-Keuls test). Open bars= Reference fertilizers, gray bars= recycled P products obtained by chemical processes and black bars= recycled P products obtained by thermal processes.

#### 4.3.2 Fate of P from fertilizers applied to Gieboldehausen soil

In the neutral (pH 6.8) soil Gieboldehausen in contrast to the acid soil Düshorn of the reference fertilizer only the TSP increased the Resin-P<sub>i</sub> while the RP had no effect. Similar to the RP the Ca-P and the thermal SI-ash and MB meal ash had no effect on the Resin-P<sub>i</sub>. The remaining fertilizers from chemical processes (MAPs) and from thermal processes (Sinter-P and Cupola slag) increased the Resin-P<sub>i</sub> (Fig. 4.4A).

Phosphorus extracted by NaHCO<sub>3</sub> was increased in all treatments with recycled P and reference P fertilizer. Almost all products from P recycling were similar than TSP-60 in increasing P extracted by NaHCO<sub>3</sub> with the exception of the thermal product MB meal ash (Fig. 4.4B). For P extracted by NaOH, the reference fertilizer TSP reached similar values as for NaHCO<sub>3</sub>, and no changes were registered for RP and Ca-P. A high performance was observed for the recycled P products obtained by precipitation as magnesium-ammonium-phosphate (Fig. 4.4C). No effect was observed for P extracted by NaOH from soils fertilized with Sinter-P and MB meal ash.

The change in concentration of P extracted by 1M HCl was high for rock phosphate (RP) and Ca-P. Furthermore, P products obtained by thermal processes increased significantly the level of P to a similar amount than that obtained by RP treatment (Fig. 4.5A). In the case of MAP products no changes were observed in P extracted by 1M HCl. Phosphorus extracted by concentrated HCl showed a decrease in some treatments (Ca-P, MAP-St, Cupola slag and MB meal ash), however the magnitude of the changes were small in comparison to those observed for P extracted by 1M HCl.



Fig. 4.4. Changes of different P fractions in Gieboldehausen soil (pHcad2 6.8), two years after the application of reference and recycled P fertilizers. The P fractions were determined in a sequential fractionation procedure. The figure shows the first three fractions. A) Anion exchange resins (Resin-P<sub>i</sub>), B) sodium bicarbonate (NaHCO<sub>3</sub>-P<sub>i</sub>) and C) sodium hydroxide (NaOH-P<sub>i</sub>). Different letters mean a significant difference among treatments at the P<0.05 (Newman-Keuls test). Open bars= Reference fertilizers, gray bars= recycled P products obtained by chemical processes and black bars= recycled P products obtained by thermal processes.



Fig. 4.5. Changes of different P fractions in Gieboldehausen soil ( $pH_{CaCl_2}$  6.8), two years after the application of reference and recycled P fertilizers. The P fractions were determined in a sequential fractionation procedure. The figure shows the next three fractions. A) 1M hydrochloric acid (HCl 1M-P<sub>i</sub>), B) concentrated hydrochloric acid (HCl conc.-P<sub>i</sub>) and C) residual P. Different letters mean a significant difference among treatments at the P<0.05 (Newman-Keuls test). Open bars= Reference fertilizers, gray bars= recycled P products obtained by chemical processes and black bars= recycled P products obtained by thermal processes.

#### 4.3.3 Changes of P fractions as affected by maize growth in Düshorn soil

After growing maize during two seasons (2007-2008) P fractions were affected significantly by plant uptake. In Düshorn soil, the change in P extracted by anion resins due to plant P uptake was higher than 40% for treatments with recycled P products of MAP which was similar to the reference fertilizer TSP-60 (Fig. 4.6A). On the other hand, the depletion of P as affected by maize plants in treatments with recycled P fertilizers obtained by thermal processes was lower than those observed for the reference fertilizers TSP and RP with exception MB meal ash. In the unfertilized control plant uptake decreased the amount of available P in about 50% in relation to the original value. The decrease due to P uptake was significant in almost all treatments. After plant P uptake, only the treatment with MB meal ash decreased to the same level than the unfertilized control (P-0).

The amount of P extracted by NaHCO<sub>3</sub> was higher than that extracted by anion resins and the amount of P uptake from this fraction was also higher for the reference fertilizers RP and TSP-60 (Fig. 4.6B). A significant decrease caused by P uptake of maize plants was only registered for treatments MAP-Gf, MAP-St and Sinter-P which were similar to that of TSP-60 and RP. No effect of plants was observed in treatments with Ca-P and with thermal products (SI-ash, Cupola slag and MB meal ash). Concerning to the fraction extracted by NaOH only small changes were recorded (Fig. 4.6C).

An accumulation of P in the fraction extracted by 1M HCl was observed in Düshorn soil after maize plant growth. In some cases, the increase was very pronounced as in treatments SI-ash and Mb meal ash which reached a similar amount of P in the fraction extracted by 1M HCl compared with the reference fertilizer RP (Fig. 4.7A). In the other treatments as well as in the unfertilized control and the reference fertilizer TSP-60 there were changes but the magnitude was small. Small changes were found in the P fraction extracted by concentrated HCl and for the residual P although an accumulation was observed in soils fertilized with thermal products (Fig. 4.7C).



Fig. 4.6. The figure compares the P concentration in different P fractions of unplanted and planted Düshorn soil ( $pH_{caCl_2}$  4.4). The soil had been fertilized with reference and recycled P fertilizers two years before the sequential analysis of different P fractions. The figure shows the first three P fractions of the sequential extraction procedure. A) Anion exchange resins (Resin-P<sub>i</sub>), B) sodium bicarbonate (NaHCO<sub>3</sub>-P<sub>i</sub>) and C) sodium hydroxide (NaOH-P<sub>i</sub>). Different capital letters mean a significant difference among treatments of unplanted and lower case letters among planted soil at the P<0.05 (Newman-Keuls test) and \* means a significant changes between unplanted and planted in a same treatment at P<0.05.


Fig. 4.7. The figure compares the P concentration in different P fractions of unplanted and planted Düshorn soil ( $pH_{caCl_2}$  4.4). The soil had been fertilized with reference and recycled P fertilizers two years before the sequential analysis of different P fractions. The figure shows the next three P fractions of the sequential extraction procedure. A) 1M hydrochloric acid (HCl 1M-P<sub>i</sub>), B) concentrated hydrochloric acid (HCl conc.-P<sub>i</sub>) and C) residual P. Different capital letters mean a significant difference among treatments of unplanted and lower case letters among planted soil at the P<0.05 (Newman-Keuls test) and \* means a significant changes between unplanted and planted in a same treatment at P<0.05.

#### 4.3.4 Changes of P fractions as affected by maize growth in Gieboldehausen soil

After growing of maize in Gieboldehausen soil, the P extracted by anion resins decreased in most treatments (Fig. 4.8A). The depletion caused by P uptake was higher in the soil treated with the reference fertilizer TSP but was not significantly different for RP. Soils fertilized with recycled P products showed a decrease of P extracted by anion resins although Ca-P, SI-ash and MB meal ash were lower in comparison to the other products. A high P depletion was observed in soils fertilized with MAP products, Sinter-P and Cupola slag. The decrease was about 50% in relation to the P content in the unplanted soil and in the case of Sinter-P and Cupola slag the P decrease reached a similar level to that in the unfertilized control (Fig. 4.8A).

The analysis of P extracted by NaHCO<sub>3</sub> showed that all P recycled fertilizers increased the P and that the plants had taken up P present in this fraction (Fig. 4.8B). The amount of P found in this fraction was higher in comparison to the P amount registered in the Resin-P<sub>i</sub>. In all treatments and in soils treated with reference fertilizers P depletion was significant. No differentiation was observed between P recycled products from chemical processes and thermal ones, although the P depletion caused by maize plants in the treatment with MB meal ash was lower than in the other treatments and comparable to that observed for RP. In relation to P extracted by NaOH, this fraction was higher than NaHCO<sub>3</sub>-P<sub>i</sub>. The depletion caused by P uptake of maize plants was observed in almost all treatments fertilized with recycled P fertilizers and TSP (Fig. 4.8C). No significant P decrease was observed for RP and for the thermal fertilizer Sinter-P.

Phosphorus extracted by 1M HCl in Gieboldehausen soil was considerably higher in comparison to that found in Düshorn soil (Fig. 4.9A). As in the other P fractions, P was depleted by maize plants in most cases. The P extracted by concentrated HCl showed a trend to decrease. The unfertilized control, RP, MAP-Gf, MAP-St, Sinter-P and Sl-ash decreased the amount of P extracted by concentrated HCl (Fig. 4.9B). No important variations were observed in the P dynamics of Residual P.



Fig. 4.8. The figure compares the P concentration in different P fractions of unplanted and planted Gieboldehausen soil ( $pH_{CaCl_2}$  6.8). The soil had been fertilized with reference and recycled P fertilizers two years before the sequential analysis of different P fractions. The figure shows the first three P fractions of the sequential extraction procedure. A) Anion exchange resins (Resin-P<sub>i</sub>), B) sodium bicarbonate (NaHCO<sub>3</sub>-P<sub>i</sub>) and C) sodium hydroxide (NaOH-P<sub>i</sub>). Different capital letters mean a significant difference among treatments of unplanted and lower case letters among planted soil at the P<0.05 (Newman-Keuls test) and \* means a significant changes between unplanted and planted in a same treatment at P<0.05.



Fig. 4.9. The figure compares the P concentration in different P fractions of unplanted and planted Gieboldehausen soil ( $pH_{caCl_2}$  6.8). The soil had been fertilized with reference and recycled P fertilizers two years before the sequential analysis of different P fractions. The figure shows the next three P fractions of the sequential extraction procedure. A) 1M hydrochloric acid (HCl 1M-P<sub>i</sub>), B) concentrated hydrochloric acid (HCl conc.-P<sub>i</sub>) and C) residual P. Different capital letters mean a significant difference among treatments of unplanted and lower case letters among planted soil at the P<0.05 (Newman-Keuls test) and \* means a significant changes between unplanted and planted in a same treatment at P<0.05.

# 4.3.5 Isotopically exchangeable P in soils fertilized with P recycled fertilizers and affected by maize growth

The amount of isotopically exchangeable P (IEP) in Düshorn soil is shown in Fig. 4.10A. The unplanted unfertilized control soil reached about 50 mg P kg<sup>-1</sup> of soil of IEP and the soil fertilized with the reference fertilizer TSP reached about twice that amount. Phosphorus recycled products obtained by chemical processes were able to increase the IEP in a similar way than the reference fertilizer TSP. On the other hand, P recycled products obtained by thermals processes were not different to the unfertilized control (P-0), although Sinter-P was equally efficient to increase the IEP than TSP. Rock phosphate increased the IEP as well as Ca-P. After the maize growth, all treatments with recycled P fertilizers and P fertilizers used as a reference showed a P depletion caused by P uptake of maize plants. Due to the high variation the treatment with SI-ash this did not show a significant P reduction, but only in tendency. The amount of P depleted by maize plants reached in some cases the half of the IEP in the unplanted soil.

In Gieboldehausen soil (Fig. 4.10B) a similar trend was observed as in Düshorn soil. The amount of IEP found in the soils fertilized with P recycled products from chemical processes were similar and in the case of MAP-St the IEP was higher than the IEP found in soil fertilized with TSP. The product calcium phosphate (Ca-P), showed a similar amount of IEP as RP. Among the thermal products, Sinter-P and Cupola slag were similar to TSP, whereas, SI-ash and MB meal ash were comparable to RP regarding the IEP. Phosphorus depletion caused by P uptake of maize plants was observed in the overall experiment in Gieboldehausen soil, although the soils treated with MAP products, Sinter-P and Cupola slag, showed a P change comparable with the reference fertilizer TSP. Otherwise, the changes of IEP for Ca-P, SI-ash and MB meal ash were more similar to the change registered for RP.

### 4.3.6 Phosphorus fractions compared with the isotopically exchangeable P

Phosphorus fractions extracted by anion exchange resins, NaHCO<sub>3</sub> and NaOH were compared with the isotopically exchangeable P (IEP), the results of this comparison are shown in Fig. 4.11 and Fig. 4.12. The data of P fractions as well the IEP were taken from unplanted soil. In Düshorn soil, the isotopically exchangeable P corresponds almost with the sum of P extracted by anion exchange resins and NaHCO<sub>3</sub>. In some cases, the amount of IEP

is lower than the sum of the two fractions mentioned above. The correspondence of these three P fractions and IEP for Düshorn soil was selected by the Pearson correlation found among the variables which are shown in the appendix of this chapter (Tab. 4.3). Isotopically exchangeable P correlated with Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and with NaOH-P<sub>i</sub> these were taken as causality assuming that the more readily P fractions participate in the isotopic exchange process. However, NaOH-P<sub>i</sub> was discarded because of the low correlation coefficient.



Fig. 4.10. The isotopically exchangeable P (IEP) unplanted and planted twice with maize plants A) Düshorn soil ( $pH_{CaCl_2}$  4.4) and B) Gieboldehausen soil ( $pH_{CaCl_2}$  6.8). The soils had been fertilized with reference and recycled P fertilizers two years before the analysis. Different capital letters mean a significant difference among treatments of unplanted and lower case letters among planted soil at the P<0.05 (Newman-Keuls test) and \* means a significant changes between unplanted and planted in a same treatment at P<0.05.

In Gieboldehausen soil, the sum of P extracted by anion exchange resins, NaHCO<sub>3</sub> and NaOH was higher than the IEP (Fig. 4.12). In general for Gieboldehausen soil, in all treatments with recycled P fertilizers and P fertilizers used as a reference the IEP was higher than the sum of the first two P fractions. In contrast to the Düshorn soil, some part of P extracted with NaOH apparently participates in the isotopic exchange. The Pearson correlations for IEP and P fractions in Gieboldehausen soil are showed in the appendix of this chapter (Tab. 4.4).



Fig. 4.11. Comparison of the isotopically exchangeable P (IEP), of the unplanted Düshorn soil (pHcacl<sub>2</sub> 4.4) with the first three fraction extracted in a sequential P fractionation procedure. The soil had been fertilized with reference and recycled P fertilizers two years before the analysis.

### 4.3.7 Comparison among P fractions, isotopically exchangeable P and phosphorus uptake

To understand the relationships among P fractions, isotopically exchangeable P (IEP) and phosphorus uptake (PU) data from the unplanted soil were correlated. Fig. 4.13 shows the correlations between PU of maize plants with the different fractions extracted in Düshorn soil and with the IEP. Positive and significant correlations were found for PU with IEP, Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub>. A negative correlation between P uptake and HCl 1M-P<sub>i</sub> was observed, while no correlations for the others fractions were registered.



Fig. 4.12. Comparison of the isotopically exchangeable P (IEP), of the unplanted Gieboldehausen soil (pHcaCl<sub>2</sub> 6.8) with the first three fraction extracted in a sequential P fractionation procedure. The soil had been fertilized with reference and recycled P fertilizers two years before the analysis.

As Düshorn soil, Gieboldehausen showed a positive and significant correlation among P uptake and IEP, Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub>, furthermore P uptake correlated with NaOH-P<sub>i</sub> indicating that more fractions are available in this soil (Fig. 4.14). On the other hand, no correlations were registered for P uptake and the other P fractions.

Tab. 4.2 shows the isotopically exchangeable P (IEP) as affected by fertilization and plant growth. The highest amount of IEP in Düshorn soil was obtained with TSP (104 mg P kg<sup>-1</sup>). The lowest value of IEP was reached by the unfertilized control (P-0). The recycled P products obtained by chemical processes were similar to the reference fertilizer RP (ca. 90 mg P kg<sup>-1</sup>) with the exception of MAP-St which was similar to TSP. The thermal products were lower than RP being Sinter-P equal to RP.

In Gieboldehausen soil the amount of IEP was higher after the addition of the TSP. Magnesium-ammonium-phosphates and the thermal products Sinter-P and Cupola slag were similar to TSP. Products as Ca-P, SI-ash and MB meal ash were comparable with the reference fertilizer RP.



Fig. 4.13. Correlation between P uptake per kg of soil and different P fractions in Düshorn soil two growing seasons after P fertilization. The fertilizers used came from P recycling either by chemical processes (MAP-Sb, MAP-Gf, MAP-St and Ca-P) or by thermal processes (Sinter-P, Sl-ash, Cupola slag and MB meal ash) and as reference fertilizers TSP and RP were used. The equation shows the parameters of the linear model and R<sup>2</sup> indicated the coefficient correlation, \* means the significance of the correlation at P<0.05 level.



Fig. 4.14. Correlation between P uptake per kg of soil and different P fractions in Gieboldehausen soil two growing seasons after P fertilization. The fertilizers used came from P recycling either by chemical processes (MAP-Sb, MAP-Gf, MAP-St and Ca-P) or by thermal processes (Sinter-P, Sl-ash, Cupola slag and MB meal ash) and as reference fertilizers TSP and RP were used. The equation shows the parameters of the linear model and R<sup>2</sup> indicated the coefficient correlation, \* means the significance of the correlation at P<0.05 level.

		Düshorn		(	Gieboldehausen	
Treatments	Unplanted	†∆FertP-0	Planted	Unplanted	†∆FertP-0	Planted
			IEP, mg P k	g <sup>-1</sup> of soil ——–		
P-0	50.6	0.0	26.2	57.5	0.0	42.2
*TSP-60	103.7	53.1	57.0	99.0	41.5	62.7
*RP	88.1	37.5	40.0	68.4	10.9	45.1
Recycled products of	btained by che	mical processes				
Ca-P	90.8	40.2	55.0	62.7	5.2	50.4
MAP-Sb	87.3	36.7	61.6	101.8	44.4	61.3
MAP-Gf	87.6	37.0	59.2	83.6	26.2	60.5
MAP-St	102.3	51.7	52.4	92.6	35.1	63.2
Recycled products of	btained by the	rmal processes				
Sinter-P	89.5	38.9	55.2	86.0	28.5	55.2
SI-ash	73.1	22.5	38.3	66.8	9.3	49.7
Cupola slag	70.4	19.7	56.5	90.4	33.0	59.9
MB meal ash	64.1	13.5	37.4	65.3	7.8	49.7

Tab. 4.2. Change of the isotopically exchangeable phosphorus (IEP) as affected by plant uptake in
the soils Düshorn and Gieboldehausen amended with reference fertilizers TSP and RP and with P
recycled products.

\*Were used as reference. <sup>†</sup> Change of IEP in the unplanted treatments in relation to P-0.

In Fig. 4.15 the IEP of the unplanted soil is compared with the sum of IEP of the planted soil plus the P extracted by the plants from that soil. In Düshorn soil fertilized with the reference product TSP shows a similar amount of IEP in unplanted soil as the sum of planted soil IEP and PU. In general the balance of P in Düshorn soil was in the same order of magnitude with some small variations. In the case of RP the amount of IEP in the planted soil plus PU was lower that the amount of IEP in the unplanted soil. The same situation was observed in the treatment with MAP-St. In the case of MAP-Sb, MAP-Gf and Cupola slag the sum of IEP in planted soil plus PU was higher than the IEP in the unplanted soil. In Gieboldehausen soil there was a tendency for the sum of IEP plus PU to be higher than the IEP of the unplanted soil. This was the case for P-0, TSP-60, Ca-P, MAP-St and for the thermal products SI-ash and MB meal ash. In the remaining treatments the balance was close to zero.



Fig. 4.15. Comparison of the isotopically exchangeable P (IEP), of the unplanted soil with IEP of the planted soil plus the P taken up by maize. A) Düshorn soil (pH<sub>CaCl2</sub> 4.4) and B) Gieboldehausen soil (pH<sub>CaCl2</sub> 6.8). The soil had been fertilized with reference and recycled P fertilizers two years before the analysis. \* means a significant changes between unplanted and planted in a same treatment at P<0.05.

#### 4.4 Discussion

# 4.4.1 Fate of P from different fertilizers applied to the soil

In this study soil P fractions and the isotopically exchangeable P (IEP) after fertilization with P recycled products and P standard fertilizers were analyzed. Furthermore, the effect of P uptake by maize plants on soil P fractions and on IEP was evaluated.

# 4.4.1.1 Phosphorus extracted by anion exchange resins (Resin-P<sub>i</sub>)

Phosphorus extracted by anion exchange resins is considered to be exchangeable P in equilibrium with the soil solution since anion exchange resins do not chemically modify the soil solution (Tiessen and Moir, 1993). Phosphorus applied in Düshorn soil (pH 4.4) not always increased Resin-P<sub>i</sub> (Fig. 4.2). The recycled P products obtained by chemical precipitation were as effective as TSP (i.e. Ca-P, MAP-Sb, MAP-Gf and MAP-St). The increase of Resin-P<sub>i</sub> in soils fertilized with P recycled products obtained by thermal processes (i.e. Sinter-P, Sl-ash, Cupola slag and MB meal ash) were statistically not different to unfertilized control (P-0) (Fig. 4.2A).

In Gieboldehausen soil (pH 6.8), MAP products increased the Resin-P<sub>i</sub>, however the values were lower than after fertilization with TSP-60. On the one hand, Ca-P was similar to RP which did not increase Resin-P<sub>i</sub> in relation to P-0 (Fig. 4.4). Of the thermal products i.e. Sinter-P and Cupola slag were similar to MAP products. The other two thermal products did not increase the Resin-P<sub>i</sub> and therefore being similar to RP.

In both soils, P recycled products obtained by a chemical process were more efficient in increasing the Resin-P<sub>i</sub> than the thermal products. Other reports indicate that Resin-P<sub>i</sub> increased after fertilization with TSP, which was explained by the high solubility in water (Boschetti et al., 2009; Rivaie et al., 2008). The increase of Resin-P<sub>i</sub> after application of RP and Ca-P in Düshorn soil can be explained by the lower pH value (4.4) of the soil. Rivaie at al. (2008) working with TSP and RP under *Pinus radiata* plantations found that RP increased Resin-P<sub>i</sub> in soils under pH value of 5.7, but in a soil with pH of 5.1 the increase of Resin-P<sub>i</sub> was higher. According to Hedley and McLaughlin (2005), the dissolution of RP depends on the concentration of free Ca<sup>+2</sup> and P in soil solution and on P buffer power. Furthermore, under acid soil conditions Al<sup>+3</sup> and Fe<sup>+3</sup> concentration in soil solution is increased and they can

precipitate P, facilitating P adsorption on soil particle surfaces (Havlin et al., 2005) which in turn can improve the dissolution of RP generating a concentration gradient from the soil solution to the RP granule. Thus, the increased Resin-Pi in the acid soil Düshorn after RP as well as Ca-P treatment from P recycling can be explained by the low concentration of Ca in solution, the high concentration of  $H^{+}$  and the lower P in soil solution (see Chapter 3). The increase in Resin-Pi in treatments with RP and Ca-P observed in Düshorn soil was not registered in Gieboldehausen soil which may be related to the higher pH value of this soil (pH 6.8) (Fig. 4.4). Whether anion exchange resins extract P from exchangeable P bound to soil particles or bound to the original P product is not entirely clear. Rivaie et al. (2008) and Perrot et al. (1993) suggested that exchange resins extract the exchangeable adsorbed P in soils treated with TSP while in soils fertilized with RP, exchange resins extract a part of exchangeable P adsorbed on soil particles and a part of P bound to the original RP (residual RP). In the present study, soil P fractions were extracted 2 years after fertilization and it is probable that Resin-Pi was extracted from the exchangeable P adsorbed on soil particle surfaces more than from original RP granules, because of the long term of P to react with the soil. In the present study, the reaction of magnesium-ammonium-phosphate (MAP) products in the acid soil Düshorn can be compared with that of TSP-60 (Fig. 4.2A). While that in neutral soil Gieboldehausen these products were lower than TSP-60 (Fig. 4.4A).

No information about soil P fractions in soils fertilized with MAP products is available. However, several studies had shown that MAP is an efficient source of P for plants which is comparable to a water soluble P fertilizer (Ghosh et al., 1996; Johnston and Richards, 2003; Massey et al., 2009; Plaza et al., 2007). In the literature it was indicated that MAP or struvite do not contain water soluble P (Johnston and Richards, 2003). In the present study a P water solubility of 1-2% of the total P was registered for MAP (Chapter 3, Tab. 3.1). Despite of the low P water solubility, MAP was as effective as TSP in increasing the Resin-P<sub>i</sub>. It might be caused by the difference of P concentration in soil solution and the solubility product of MAP. Ohlinger et al. (1998) published a solubility product ( $pK_{sp}$ ) for MAP of 13.26, which means a concentration of 38  $\mu$ M of P in solution. Furthermore, the P concentration in soil solution was of 0.5 to 2  $\mu$ M in the unfertilized control soil, which implies a gradient that facilitates the MAP dissolution. Also, P adsorption/precipitation processes could reduce the gradient favoring the MAP dissolution. Therefore all the 60 mg P from MAP should be dissolved and result in similar Resin- $P_i$  as TSP.

In relation to the thermal products, only Sinter-P and Cupola slag in Gieboldehausen were effective in increasing the Resin-P<sub>i</sub>. The reaction of Sinter-P can be compared with that of Rhenania phosphate because of the similar processes to obtain them. Judel et al. (1985) working with different fertilizer types found that Rhenania phosphate increase the P extracted by the electro ultrafiltration method (EUF) and that it was similar to that obtained by TSP. The study performed by Judel et al. (1985) was carried out in a sandy loam soil with a pH value of 7.1. The evidence presented by the authors supports the idea that the thermal fertilizer Sinter-P can increase the Resin-P<sub>i</sub> under alkaline conditions. However, in the present study, Sinter-P under acid conditions (Düshorn soil) did not increase Resin-P<sub>i</sub> in comparison to P-0. It is probable that the amounts of Fe and Al (1 and 3% respectively)<sup>2</sup> that Sinter-P contains play a role in the performance of this product in acid soil conditions. These results do not agree with those found by Chien (1978), who reported that Rhenania phosphate was effective in increasing the water soluble P in an acid soil (pH 4.5). It is likely that Al and Fe contained in Sinter-P complex.

In relation to the product Cupola slag, which can be compared with Thomas phosphate (a basic slag), was effective only in the neutral soil in increasing Resin-P<sub>i</sub>. This lower efficiency to increase Resin-P<sub>i</sub> of Cupola slag in the acid soil from Düshorn could be caused by the high content of Al<sub>2</sub>O<sub>3</sub>. Scheidig et al. (2009) found up to 17% of Al of the total weight of Cupola slag. The P recycled products SI-ash and MB meal ash were unable to increase the Resin-P<sub>i</sub> in both soils. According to Adam et al. (2009a) SI-ash contains between 6 to 15% of Al and 3 to 22% of Fe, and it seems to be that the concentration of these metals bound to P reduces the amount of plant available P. About MB meal ash, no information is available, however since ashes are mainly cation oxides, it is possible that the amount of Al and Fe as well as Ca could influence the performance of this material in both soils.

<sup>&</sup>lt;sup>2</sup> The data about mineral content for Sinter-P were facilitated by Ms. Christine Waida, University of Giessen.

4.4.1.2 Inorganic P extracted by 0.5 M sodium bicarbonate (NaHCO<sub>3</sub>-P<sub>i</sub>)

Phosphorus extracted by sodium bicarbonate is considered to be slightly chemiadsorbed on soil particle surfaces with Al and Fe as well as with Ca. This NaHCO<sub>3</sub>-P<sub>i</sub> is well correlated with plant P uptake (Guo et al., 2000).

In Düshorn soil (Fig. 4.2B), the high variability in some treatments did not allow a differentiation in relation to the unfertilized control (P-0). Despite this problem, a trend was observed to increase the level of NaHCO<sub>3</sub>- $P_i$  and in the case of MAP-St the result was similar to the TSP-60. It was expected that recycled P products from chemical processes increase NaHCO<sub>3</sub>-P<sub>i</sub> because these products seem to be more similar in behavior to TSP. The reference P fertilizers (TSP and RP) showed an increase of up to 30 mg P kg<sup>-1</sup> of soil (Fig. 4.2B) and a similar amount was reached only by MAP-Sb and by the thermal product Sinter-P. Other recycled products of thermal processes did not increase the amount of NaHCO<sub>3</sub>-P<sub>i</sub> in Düshorn soil. The higher amount of NaHCO<sub>3</sub>-P<sub>i</sub> in the soil treated with Sinter-P might indicate that the P is bound to Al and Fe which can be dissolved by bicarbonate in an alkaline pH. The alkaline solution of sodium bicarbonate (pH 8.5) and the activity of the anion HCO3<sup>-</sup> which can compete with phosphate may explain the increase of NaHCO3-Pi for Sinter-P. Phosphorus in thermal products can be bound to Ca that despite of the low pH of Düshorn soil was not released from the product. This could explain why the recycled P products SI-ash and MB meal ash were mainly extracted by HCl solution in the following extraction step (Fig. 4.3A). Thus, it seems to be that recycled P products SI-ash and MB meal ash from thermal processes have a similar dissolution as RP. This is consistent with the results obtained in the pot experiment for SI-ash and MB meal ash which did not increase the P concentration in soil solution (Chapter 3, Fig. 3.4). In the case of SI-ash it is reported that it contains a significant amount of Ca (between 12-19%) (Scheidig et al., 2009).

In Gieboldehausen soil (Fig. 4.4B), P recycled fertilizers obtained by chemical and thermal processes both increased the amount of NaHCO<sub>3</sub>-P<sub>i</sub>. The treatments were similar to the reference fertilizer TSP (MAP-Sb and Cupola slag). Due to the neutral reaction of Gieboldehausen soil (pH 6.8) a lower increment of the NaHCO<sub>3</sub>-P<sub>i</sub> for RP, Ca-P and MB meal ash was expected. However, it seems to be that bicarbonate can extract part of P bound to Ca which can explain the increase of NaHCO<sub>3</sub>-P<sub>i</sub> observed for these products, as explained by

the classical work of Olsen et al. (1954) who observed that the Ca concentration as well as carbonate decreased markedly with the addition of 0.5 M sodium bicarbonate.

The thermal products showed a higher RFE in Gieboldehausen than in Düshorn soil. According to Schmehl and Brenes (1953) working with alkaline soils with Rhenania phosphate, found that this thermal fertilizer was similar to TSP in increasing the plant available P (Rhenania phosphate is obtained by similar processes as Sinter-P).

In relation to Cupola slag, which is comparable with Thomas phosphate, in the literature there is evidence that Thomas phosphate, increased the NaHCO<sub>3</sub>-P<sub>i</sub> mainly by replacement of silicate for OH groups on colloids (Khanna, 1967). This is a secondary effect on P availability of products containing Si, which could reduce the bounding capacity of soil and facilitate the dissolution of P compounds.

The thermal product SI-ash contains a considerable amount of AI (Scheidig et al., 2009). The addition of this product to an alkaline soil could inhibit the AI activity by the formation of insoluble aluminum hydroxide at high pH (Brady and Weil, 2002), which would facilitate the dissolution of this product.

The thermal product MB meal ash increased the  $NaHCO_3$ -P<sub>i</sub> in a similar amount as the reference fertilizer RP. This could be caused by the basic reaction of this product that contains Ca and in the alkaline soil the dissolution of P will be reduced, also due to the possible high concentration of Ca in soil solution.

### 4.4.1.3 Inorganic P extracted by sodium hydroxide (NaOH-P<sub>i</sub>)

As the P extracted by sodium bicarbonate, NaOH extracts P associated with Al and Fe. However, P extracted by NaOH is strongly adsorbed on the soil which is extractable only by increasing the pH value. Phosphorus extracted by NaHCO<sub>3</sub> and NaOH represents a continuum of P bound to Al and Fe (Tiessen and Moir, 1993).

In the present study the treatment of Düshorn soil (pH 4.4) with TSP-60 increased the amount of NaOH-P<sub>i</sub>, while the amount of NaOH-P<sub>i</sub> recorded for the treatment with RP was similar to P-0 (Fig. 4.2C). The treatment with Ca-P increased NaOH-P<sub>i</sub> in tendency but was not statistically different to that of P-0 (Fig. 4.2C). The MAP products increased the NaOH-P<sub>i</sub> which was higher than for TSP-60. In the case of TSP it is probable that the fertilizer was solubilized and then adsorbed by Al and Fe on soil particle surfaces (Verma et al., 2005). In a

similar way MAP products increase NaOH-P<sub>i</sub> as a consequence of the solubilization of P and then it would be adsorbed on soil particle surfaces by Al and Fe mainly due to the low pH of Düshorn soil. Otherwise, the increase of NaOH-P<sub>i</sub> could also be interpreted as P that remained in the MAP product not being solubilized but linked to Al and Fe. The latter alternative is possible since MAP products are no pure compounds of MgNH<sub>4</sub>PO<sub>4</sub> and some residues of Al and Fe are present (Phan et al., 2009). In each case, if P is bound to Al/Fe soil particle surfaces or is present as Al/Fe-P in MAP product the high pH of NaOH facilitates the P dissolution since P extracted by this solution is considered to be associated with Al and Fe (Hedley et al., 1982; Tiessen and Moir, 1993).

Regarding thermal products only Cupola slag increase the NaOH-P<sub>i</sub>, this can be explained by the high amount of Al (up to 17%) present in this product (Scheidig et al., 2009), which might be bound to P. Because Cupola slag did not increase Resin-P<sub>i</sub> it is argued that P extracted by NaOH is linked to Al. Unlike Cupola slag, P in the other thermal products SI-ash and Mb meal ash was not found in Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> or in NaOH-P<sub>i</sub>. Thus, P in these products is probably linked strongly to Ca.

In Gieboldehausen soil (pH 6.8) an increase of NaOH-P<sub>i</sub> was observed in the soil treated with TSP-60. Probably, P from TSP is adsorbed on Al and Fe on soil surface particles because of the quick solubilization. On the other hand, soil fertilized with RP, Ca-P and MB meal ash did not show an increase in the quantity of NaOH-P<sub>i</sub>, being similar to P-0. This would mean that the P in these compounds is bound to Ca, which is evident in RP and Ca-P. As RP and Ca-P, MB meal ash probably contains a considerable amount of P linked to Ca. The three compounds should not be extracted by NaOH mainly due to the high pH of this solution. The recycled P products MAP-Sb, MAP-Gf and MAP-St increased the P extracted by NaOH and probably these products behave in a similar way to TSP in this soil. Due to the content of clay and silt in Gieboldehausen soil it is likely an adsorption of Al and Fe on the soil particle surfaces. However, it is also possible that NaOH could extract P associated with Ca (Guo et al., 2000; Williams et al., 1971) which might occur in Gieboldehausen soil. The product Cupola slag increased the NaOH-P<sub>i</sub> and was similar to that of TSP-60. No information about P fractions for similar products is available, despite of this lack of information Matingly (1970) reported that a phosphate slag was more soluble than rock phosphate.

# 4.4.1.4 Inorganic P extracted by 1M HCl (HCl 1M-P<sub>i</sub>)

Phosphorus extracted by 1M HCl is considered to be mainly associated to Ca (Tiessen and Moir, 1993). Thus, in the present study, in Düshorn soil (pH 4.4) no P from TSP was found with HCl, which means that P from TSP was totally dissolved and found in the more available P pools (i.e. Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub>) (Fig. 4.3A). Similar results were reported by Rivaie et al. (2008), who working in an acid soil (pH 5.1) with TSP found that the P extracted by acid (H<sub>2</sub>SO<sub>4</sub>) did not change in comparison to the unfertilized control after 2 years.

Otherwise, RP increased the HCl 1M-P<sub>i</sub>, which indicates that RP was not completely solubilized despite of the low pH value of the Düshorn soil. This finding is consistent with that reported by Rivaie et al. (2008) who found that after fertilization with RP the P associated with Ca increased despite the low pH in soil (5.1).

No increase of HCl 1M-P<sub>i</sub> was found for soils treated with Ca-P and MAP products which would mean that the P in these compounds is more soluble than P in RP. This result confirms that the P of MAP products in Düshorn soil was solubilized in a similar way than that of TSP and was then adsorbed on soil particle surfaces (Fig. 4.3A).

In relation to the soils fertilized with the thermal products SI-ash and MB meal ash the increase of HCl 1M-P<sub>i</sub> was higher than that of the other thermal fertilizers. The fact that P from these products was not found with anion exchange resins, bicarbonate or with NaOH is consistent with the idea that P of these products is linked to Ca in a similar way than in RP. The recycled P products Sinter-P and Cupola slag also increased the HCl 1M-P<sub>i</sub>, however the high amount of P from these products was found with bicarbonate and hydroxide extraction respectively.

In Gieboldehausen soil (pH 6.8), RP increased the HCl 1M-P<sub>i</sub> which was expected due to the high pH value of this soil and the low reactivity of RP. In a similar way, the product from P recycling Ca-P also was found in this fraction, which would mean that Ca-P even though it was more reactive than RP in Düshorn soil, it required pH lower than that of Gieboldehuasen for the dissolution. The reaction observed for RP and Ca-P in the neutral soil Gieboldehausen are consistent with the results reported by Kanabo and Gilkes (1987) who indicated that above pH 6.0 the solubility of RP decrease considerably.

The MAP products did not increase the HCl 1M-P<sub>i</sub> in this soil, which might be explained by the higher P solubility of these products which was found in the more available P pools. For

recycled products from thermal processes, HCl 1M-P<sub>i</sub> increased. This increase of HCl 1M-P<sub>i</sub> by the thermal products may be interpreted in a similar way as the increase by RP, a high content of P associated with Ca which was especially observed for SI-ash and MB meal ash.

4.4.1.5 Inorganic P extracted by concentrated HCl (11.3 M) and residual P (HCl conc.- $P_{\rm i}$  and residual P)

The P extracted by concentrated HCl corresponds to very stable P pools and the residual P extracted by  $H_2SO_4$  and  $H_2O_2$  is considered to be P insoluble or occluded (Hedley et al., 1982; Tiessen and Moir, 1993). In Düshorn soil a trend to reduce the amount of P extracted by concentrated acid was observed, however the magnitude of these changes was not high, and coincides with the definition given by Tiessen and Moir (1993) who considered this P fraction as very stable P pool. A similar situation was observed for residual P although there was no significant difference.

In Gieboldehausen soil the results showed some variations which are difficult to explain and the meaning is contradictory. In some cases an increase of the HCl conc.-Pi was observed (i.e. RP and Sl-ash) while in other cases a reduction was found. The accumulation of P in the more stable P pool for many recycled fertilizers in Gieboldehausen soil can be explained by the low solubility of a part of some fertilizers, as it is the case for the thermal products (Fig. 4.5C). However, a reduction is more difficult to explain since this pool would not be accessible for the plant uptake.

# 4.4.2 Changes in soil P fractions as affected by plant growth

# 4.4.2.1 Phosphorus taken up from Resin-P<sub>i</sub>

The amount of P extracted by anion exchange resin strips (Resin-P<sub>i</sub>) correlates well with P uptake by plants (Mallarino and Atia, 2005; Tiessen and Moir, 1993). The P extracted by anion exchange resins represents the amount of P that is readily available since it is in equilibrium with soil solution, which is considered exchangeable and plant available (Frossard et al., 2000).

In the present experiment, Resin-P<sub>i</sub> was decreased by maize plants in Düshorn soil. The largest P depletion was observed for the reference products TSP and RP and for products from chemical processes: Ca-P, MAP-Gf and MAP-Sb (Fig. 4.6A).

About MAP products, this P depletion is in agreement with that reported in other studies, which have shown that MAPs are as effective as a water soluble fertilizer (Johnston and Richards, 2003; Massey et al., 2009).

In relation to the thermal fertilizers, although with these products the increase was not high, plants were able to deplete P from this fraction. This was observed for plants growing on soils fertilized with SI-ash and MB meal ash. In the previous discussion about fate of fertilizers (point 4.4.1.1) it was argued that P from these products can be released if the pH of soil is low, as in the case of Düshorn soil. These findings are similar to results reported by Crozier et al. (2009) who found that a granulated manure ash was available for plants despite of the low water solubility but it was soluble in citrate.

In Gieboldehausen soil, in all treatments P was depleted from Resin-P<sub>i</sub>, with the exception of RP (Fig. 4.8A). The higher P reduction was registered in the soil fertilized with TSP-60, in soils fertilized with MAP products and in soils fertilized with Sinter-P and Cupola slag. The higher P depletion in these treatments can be explained by the better P availability (Fig. 4.4). In general, the P depletion observed in the treatments with plants in the overall experiment was due to the P uptake which has a good correlation with the P extracted by anion exchange resin strips (Fig. 4.13 and Fig. 4.14).

Due to the neutral pH of this soil, RP, Ca-P, SI-ash and MB meal ash showed a lower P availability and the amount of P depletion was lower than for TSP and similar to unfertilized control (P-0). According to Chien and Menon (1995), the factors that influence the RP solubility (i.e. calcium phosphates) are pH, exchangeable Ca, soil texture, P sorption capacity and organic matter. Then, it is likely that the effectiveness of calcium phosphate products depends greatly on soil pH in Gieboldehausen soil. It can be argued that the higher content of clay in this soil favor the exchange capacity and thus adsorb more Ca. However, it is possible that this soil has a high Ca concentration in soil solution and the exchange capacity is already saturated and no Ca from the product is depleted. This would mean that products rich in calcium phosphates in neutral or alkaline soil conditions are not readily soluble.

# 4.4.2.2 Phosphorus taken up from NaHCO<sub>3</sub>-P<sub>i</sub>

Unlike of Resin-P<sub>i</sub>, the NaHCO<sub>3</sub>-P<sub>i</sub> in Düshorn soil was only depleted from the unfertilized control, reference fertilizers (TSP and RP), from MAP products and the thermal product

Sinter-P. Furthermore, the amount of P depleted in any product was similar to the P reduced in the unfertilized control (P-0), with the exception of Sinter-P which showed a high difference between unplanted and planted variant (Fig. 4.6B). Phosphorus extracted by bicarbonate is associated mainly to Al and Fe and it is assumed to be plant available (Cross and Schlesinger, 1995; Tiessen et al., 1984; Tiessen and Moir, 1993) and it seems to be supplied directly by inorganic fertilizers. Thus, Guo et al. (2000) in a pot experiment with eight soils fertilized with Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O observed that NaHCO<sub>3</sub>-P<sub>i</sub> decreased as affected by P uptake by plants. Unfortunately, no information about soil P fractions for these specific products is available. However, in those cases where P increases the amount of NaHCO<sub>3</sub>-P<sub>i</sub> in Düshorn soil, P was significantly depleted. The low availability of some of these products (i.e. RP and MB meal ash) is likely caused by a low solubility of the calcium phosphates that they contain which despite of the low pH of Düshorn soil were not solubilized (Fig. 4.6B).

In Gieboldehausen soil, for any of the P products either for P fertilizers used as reference treatments or for recycled P products P depletion was observed (Fig. 4.8B). The amount of P taken up by maize plants was for MAP products higher than that registered for the unfertilized control. As it was mentioned above in the point 4.4.1.2, some P associated to Ca can be extracted by bicarbonate which would explain the increase of NaHCO<sub>3</sub>-P<sub>i</sub>. This increase of the P extracted by bicarbonate in the present study and the following reduction due to P uptake by plants could explain the results observed by Massey et al. (Massey et al., 2009), who found that MAP products increased the DMY in relation to the unfertilized control in alkaline soil (pH 7.6). Contrary to Düshorn soil, in Gieboldehausen soil P products from thermal processes Sinter-P, SI-ash and Cupola slag were depleted by maize plants. According to Judel et al. (1985), sintered phosphate (Rhenania phosphate) which is comparable to Sinter-P was similar to TSP in increasing the plant available P and DMY as well as P uptake by wheat plants in a neutral soil (pH 7.1). Although it has been reported that Cupola slag has an alkaline reaction (Chesworth, 2008), in Giboldehausen soil it increased the NaHCO<sub>3</sub>-P<sub>i</sub> and maize plants had taken up P from this fraction. Although thermal fertilizers seem to be of low availability in alkaline conditions, in the present study they were as effective as TSP and only MB meal ash did not contribute to the P uptake of maize plants. Because thermal products are no crystalline compounds and Al and Fe as well as Ca are present, at high pH the P bound to Fe and Al would be solubilized (Havlin et al., 2005). On the other hand, Ca-P would be of low solubility and its dissolution would depend on the Ca activity in soil solution and the P buffer power of the soil. Thus, a high P buffer power would allow a high dissolution despite of the high pH, due to the high capacity of the soil to adsorb P onto exchangeable places.

### 4.4.2.3 Phosphorus taken up by plants from NaOH-P<sub>i</sub>

Phosphorus extracted by NaOH is associated to Al and Fe and it is considered as a continuum together with NaHCO<sub>3</sub>-P<sub>i</sub> (Guo et al., 2000; Hedley et al., 1982; Tiessen and Moir, 1993). A P uptake by maize plants from this fraction in Düshorn soil was not observed which would mean that NaOH-P<sub>i</sub> was of low availability to the plants (Fig. 4.6C). Although an increase of NaOH-P<sub>i</sub> was observed after fertilization in some treatments, it seems to be that NaOH-P<sub>i</sub> is strongly adsorbed to the soil particles or maintained without transformation on the original product (i.e. as a Ca-P). According to Schmidt et al. (1996) NaOH-P<sub>i</sub> is assumed to be moderately plant available, which was not observed in our results. According to the findings reported by Guo et al. (2000), phosphorus extracted by hydroxide seems to be accumulated on Al and Fe oxides, which could be possible in Düshorn soil because of the low pH observed (4.4) and despite the low amount of clay present in this soil but with a considerable higher amount of organic matter (5.8%) (Tab. 4.1). On the other hand, a significant P reduction was observed in Gieboldehausen soil (Fig. 4.8C). Phosphorus uptake by maize plants reduced NaOH-P<sub>i</sub> fraction in all treatments with the exception of the soils fertilized with RP and Sinter-P. For the amount of P found in this fraction (in average about 60 mg P kg<sup>-1</sup> of soil) a higher P adsorption on Al and Fe oxides in this soil is assumed in comparison to Düshorn soil, despite the neutral pH. This apparent difference of P adsorption on Al and Fe may be explained by the proportion of total P that NaOH-P<sub>i</sub> represents in each soil. While in Düshorn soil, the P extracted by NaOH represents about 20% of the total P, in Gieboldehausen soil it is only about 10%. Thus, the contribution of NaOH-P<sub>i</sub> in Gieboldehausen soil to the total P is less important than in Düshorn soil. In relation to the products RP and Sinter-P, both are of alkaline reaction, this could explain the low reduction due to P uptake.

#### 4.4.2.4 Phosphorus taken up from HCl 1M-P<sub>i</sub>

The most remarkable results in Düshorn soil indicate an accumulation of HCl 1M-P<sub>i</sub> in treatments with maize plants (planted in Fig. 4.7A). This increase of HCl 1M-P<sub>i</sub> could be induced by the mass flow of Ca to the roots which could then precipitate as Ca-P in the rhizosphere. This observations are similar to those of Myint (2005) who found that P extracted by HCl increased in the rhizosphere in a short term experiment with plant growth in an acid sandy soil of low pH. However, because of the low pH value of Düshorn soil 4.4 rather a solubilization of Ca-P than a precipitation is expected.

In Gieboldehausen soil, a decrease of HCl 1M-Pi was observed in unfertilized control and soils fertilized with the reference product TSP and RP and with the products from P recycling Ca-P, MAP-Sb and the thermal products Sinter-P and Cupola slag. The depletion of P from these products could be due to the exudation of organic acids of maize plants followed by a mobilization of P, however this phenomenon was not measured in the present study. On the other hand, no correlation between HCl 1M-P<sub>i</sub> and P uptake by maize plant was observed (Fig. 4.14) which indicated that the depletion observed was a punctual situation for these treatments. In the literature it has been reported that HCl 1M-P<sub>i</sub> is of low plant availability. Zhang and McKenzie (1997) who found that HCl 1M-P<sub>i</sub> was an inert material and that plants could not take up P from this fraction in an experiment under maize production. Other authors obtained similar results (Boschetti et al., 2009; Guo et al., 2000; Selles, 1993). Otherwise, maize plants grown in pots reached a high root density, generating a high depletion zone and in such circumstances they can take up P from this fraction. That would mean that HCl 1M-P<sub>i</sub> in treatments with RP, Ca-P, MAP-Sb, Sinter-P and Cupola slag could be depleted by a high root system developed by the maize plants. The depletion of HCl 1M-P<sub>i</sub> seems also to be related to the length of time of the study. Myint (2005) found that HCl 1M-P<sub>i</sub> during a study of few weeks was not depleted in the rhizosphere, but the same soils in a field study of 20 years showed a clear depletion of this fraction. Therefore, the depletion of HCl 1M-P<sub>i</sub> seems to be a kinetic problem besides the crystallinity of the compound dissolved. Some of the recycled P fertilizers might have had a low crystallinity and could be dissolved more rapidly than others.

#### 4.4.2.5 Phosphorus taken up from HCl conc.-P<sub>i</sub> and residual P

Phosphorus extracted by concentrated HCl (HCl conc.-P<sub>i</sub>) and by sulfuric acid (Residual P) has been described as a very stable P fraction associated to Ca in the first case. Residual P is defined as a highly "recalcitrant P" (Tiessen and Moir, 1993), which does not imply a defined chemical composition of P. In Düshorn soil, although there are differences among unplanted and planted treatments no relation was observed between P uptake and HCl conc.-P<sub>i</sub> (Fig. 4.7 and Fig. 4.13). Related to Residual P, an increase was observed for soils fertilized with thermal products in the treatments planted with maize plants. A possible reason for this increase could be that P bound to root exudates was not extracted in the previous extractions and it was found in the last extraction, which can release this P due to the aggressive hot digestion (Fig. 4.1). Similar results were reported by Guo et al. (2000) who worked with highly weathered soils and found that residual P was accumulated mainly as Ca-P, which was not extracted by previous solutions in the sequential extraction. However, in the same work mentioned above, a reduction of residual P was registered after intensive plant growth. Pheav et al. (2003) reported that residual P increased and they interpreted it as a consequence of fertilizer reaction product.

In Gieboldehausen soil, HCl conc.-P<sub>i</sub> decreased in some treatments (P-0, RP, MAP-Gf, MAP-Sb, Sinter-P and Sl-ash) (Fig. 4.9). Phosphorus depletion of this fraction is not related to P uptake (Fig. 4.14). However, it seems to be that plants in soils treated with RP as well as Sl-ash and Sinter-P had taken up P from this fraction as a response to the low availability of previous P pools. As in Düshorn soil, a trend was observed to increase the residual P in treatments with plants in those soils fertilized with thermal products.

# 4.4.3 Isotopically exchangeable P (IEP) as affected by plant growth and its relation to P fractions

In the present study the amount of isotopically exchangeable P (IEP) after the addition of reference P fertilizers TSP and RP as well as P recycled products obtained by chemical and thermal processes was analyzed. The measuring of IEP was realized in the soil samples from unplanted treatments and treatments planted with maize. The results show that IEP increased after the fertilization with P products (Fig. 4.10A). In the unfertilized control of Düshorn soil, the amount of IEP was of about 50 mg P kg<sup>-1</sup> of soil and for the reference

fertilizer TSP more than 100 mg P kg<sup>-1</sup> of soil. In the treatments with MAP products the increase of IEP was significantly different to that of P-0 and similar to that of TSP. Although the reference fertilizer RP was higher than P-0 it was lower than TSP in tendency. In general, P recycled products from thermal processes were lower than TSP but higher than RP although the difference was not significant. The higher increase of the TSP was probably due to the high water solubility of the fertilizer. The lower IEP observed in soils after RP treatment and after fertilization with thermal products would mean that the P associated with Ca was less accessible to the isotopic exchange. Owusu-Bennoah et al. (2002) reported similar results from a work with 6 acid soils of different clay content. The authors found that the IEP was always higher than the IEP for RP and that RP increases the IEP as a function of pH and clay content, which means that with a lower pH value and higher clay content P from RP was more accessible to the exchange. Ca-P and MAP products obtained a similar amount of IEP which would mean that these products showed a similar behavior than TSP in acid conditions. These findings are consistent with the results reported in the section about fate of fertilizers in Düshorn soil in the current study (4.3.1). The amount of IEP registered in Düshorn soil in treatments without plants correlated with the amount of Resin-Pi and NaHCO<sub>3</sub>-P<sub>i</sub> (appendix). Plants affected significantly almost all treatments with the exception of SI-ash which was not statistically significant, but in tendency showed a decrease caused by P uptake. This depletion was particularly high in the soils fertilized with the reference fertilizer TSP (47 mg P kg<sup>-1</sup> of soil), RP (48 mg P kg<sup>-1</sup> of soil) and MAP-St (50 mg P kg<sup>-1</sup> of soil). In the soils fertilized with Ca-P, MAP-Gf, Sinter P and SI-ash IEP was of about 30 mg P kg<sup>-1</sup> of soil and the IEP from treatments with MAP-Sb, Cupola slag and MB meal ash were similar to that from P-0 with a decrease of P of about 25 mg P kg<sup>-1</sup> of soil (Fig. 4.10). If the data of isotopically exchangeable P are correlated with the P uptake it would mean that IEP is plant available, which is shown in Fig. 4.13. These results are in agreement with other works indicating that IEP is plant available (Larsen, 1952; Owusu-Bennoah et al., 2002). Although IEP is considered to be plant available it is not taken up completely by maize plants in Düshorn soil. The results show that between 37 and about 53% of the IEP is taken up by maize plants (Fig. 4.15). Why IEP is not completely taken up by plants, is not completely understood. Morel and Fardeau (1989) observed in a pot experiment with Lolium perenne that only 15% of the P taken up by plants came from fresh P applied to the soil, they argued

that the low contribution to the P uptake was caused by the high P fixation capacity of the soil. Hendriks et al. (1981), found that the 50% of the IEP in equilibrium with the P in soil solution was below 1  $\mu$ M. We argue that IEP could not be accessible for the plants in the present study, because the IEP could be below of the minimum concentration of P in soil solution (i.e. minimum concentration, is the concentration where the influx of a nutrient is equal to the efflux).

Phosphorus products that did not increase the IEP had a low contribution to the P taken up by plants (Fig. 4.15). This was especially true for the thermal fertilizers and RP, with the exception of Sinter-P. The correlation of IEP with Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub> confirms that P uptake is closely related to the more available P pools (see appendix). While, IEP correlates mathematically with NaOH-P<sub>i</sub> (r=0.36\*) it is not considered to be part of the IEP or only in a low degree. Fig. 4.11 shows the contribution of P fractions to the IEP. As it can be seen for all treatments, IEP corresponds with Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub>. These findings confirm the idea that only P fractions in a quickly equilibrium with soil solution are plant available in Düshorn soil. Thus, P stored in HCl-P<sub>i</sub> fraction can take part of the P taken up by plants in very low P soil conditions (Guo et al., 2000).

For Gieboldehausen soil, the IEP increased after the addition of P fertilizers, either with the reference fertilizers TSP and RP or with the P recycled products obtained by chemical and thermal processes, with the exception of Ca-P, SI-ash and MB meal ash (Fig. 4.10B). Note that RP reached higher IEP than P-0 but lower than TSP. The data are consistent with the idea that P products containing Ca are of low solubility in neutral soil conditions and that TSP and MAP products are effective in a wide range of pH values. In this soil the increase due to the addition of P products was not of the magnitude as the amount incorporated. In the case of Ca-P the contribution to the IEP was as low as 5 mg P kg<sup>-1</sup> of soil (Tab. 4.2). On the other hand, the contribution of MAP-Sb was higher than 40 mg P kg<sup>-1</sup> of soil. The amount of P added to the soils was 60 mg P kg<sup>-1</sup> of soil. In none of the treatments the increase of the IEP reached the amount of P applied to the soil. Despite of this, the IEP correlates well with P uptake in Gieboldehausen soil indicating that IEP represents plant available P like in Düshorn soil (Fig. 4.14).

However, both the amount of IEP increased as a result of P application and the amount of P taken up do not have a direct correspondence with each other, which means that the

efficiency of the fertilizers to increase the P in soil is limited by several soil characteristics. According to Barrow (1980) the P applied to the soil will be adsorbed on soil particle surfaces and with the time it will decrease mainly due to secondary reactions which are depending on soil temperature and P concentration which finally result in that P is more firmly held and is less plant available. The soil parameters that play a role on the P adsorption are Ca, Al and Fe concentration in soil which can be dissolved in the process of P fertilizer dissolution and the organic matter content (Barrow, 1980; Havlin et al., 2005; Mattingly, 1975). Another possible reason for the decrease of P effectiveness is that P is protected within water stable aggregates (Frossard et al., 2000). Sinaj et al. (1997) found that up to 30% of the slowly isotopically exchangeable P was more rapidly accessed after dispersion of soil particles, which suggests that P<sub>i</sub> is physically protected from rapid isotopic exchange. The possible P fractions that may contribute to IEP in Gieboldehausen soil are Resin-Pi, NaHCO3-Pi and a part of NaOH-P<sub>i</sub> (Fig. 4.12). This assumption is supported by the correlation coefficient obtained with IEP and the fractions mentioned above (see appendix). The reason to incorporate the NaOH-P<sub>i</sub> is based on the assumption that Gieboldehausen has higher clay content, thus an increase of Al/Fe-P adsorbed on soil particle surfaces is expected. This assumption is further supported by the higher amount of P extracted with NaOH in Gieboldehausen soil in comparison to Düshorn soil. These results suggest that whole NaOH-P<sub>i</sub> or at least part of it can contribute to the IEP. However, Machold (1963) working with different German soils found that P forms associated with Al and Fe were more accessible to the isotopic exchange than P associated with Ca under pH 7.0. Above this pH value the amount of P associated with Ca that was accessible to the isotopic exchange increased exponentially. The finding of Machold (1963), suggests that the amount of IEP in Düshorn soil, is more related to P associated with Al and Fe and that the IEP in Gieboldehausen soil may be associated with both P fractions, P bound with Ca and P bound with Al and Fe.

### **4.5 Conclusions**

Phosphorus applied as water soluble fertilizer (i.e. triple superphosphate) was found mainly in the more available P fractions: Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and in NaOH-P<sub>i</sub> in the acid soil as well as neutral soil, and in the neutral soil part of the soluble P fertilizer was also found in the HCl-P<sub>i</sub>.

In the planted unfertilized control soil as well as in the soil fertilized with water soluble fertilizer (TSP), the sum of isotopically exchangeable P (IEP) plus absorbed by maize was similar to the IEP of the unplanted soil. This indicated that plants removed P only from the IEP. But not all the IEP is actually plant available because even at strong P deficiency of the plants the IEP was not depleted below 50%.

Phosphorus of recycled P products obtained by chemical processes had a similar behavior to TSP and the fate of these fertilizers was mainly the Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub>. The sum of the IEP in the soil with maize plants plus P uptake for MAP products under acid and neutral soil conditions was higher or remained in a similar level than the IEP in the soil without plants. This indicates that MAP products were similar to TSP.

Thermal products remained almost unaltered in the Ca-P form, i.e. HCl soluble in both soils, and only a smaller portion appeared in the NaHCO<sub>3</sub> and NaOH fraction. In the acid soil plants were unable to increase the P availability of these products as shown by the fact that the sum of IEP in soil with plants and P uptake was similar to the IEP in the soil without plants. In the neutral soil, in the case of SI-ash and MB meal ash the sum of IEP in soils with plants and P uptake was higher than IEP in soils without plants, indicating that the plants solubilized part of the P of these products. No modifications of the P availability in this soil were observed for Sinter-P and Cupola slag.

In the acid Düshorn soil, plants took up P from the more available P fractions (i.e. Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub>), furthermore, these fractions seem to be accessible to the isotopic exchange. In Gieboldehausen plants took up P from Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> as well as from NaOH-P<sub>i</sub> and the HCl fractions. To which extent these fractions were accessible to isotopic exchange could not be shown.

# 4.6 Appendix



Fig. 4.16. Significant Pearsons correlations for isotopically exchangeable P (IEP) and P fractions for the unplanted Düshorn soil. The symbols \*, \*\* \*\*\* mean significant correlation at 0.05, 0.01 and 0.001 respectively.

mean signifi	cant correlat	ion at 0.05, 0	.01 and 0.00	1 respectively	÷					
	IEP	Resin-P <sub>i</sub>	NaHCO <sub>3</sub> -P <sub>i</sub>	NaHCO <sub>3</sub> -P <sub>o</sub>	NaOH-P <sub>i</sub>	NaOH-P <sub>o</sub>	HCI 1M-P <sub>i</sub>	HCl concP <sub>i</sub>	HCl concP <sub>o</sub>	Residual P
IEP	1									
Resin-P <sub>i</sub>	0.65***	1								
NaHCO <sub>3</sub> -P <sub>i</sub>	0.62***	0.48**	1							
NaHCO <sub>3</sub> -P <sub>o</sub>	0.17	0.28	-0.28	1						
NaOH-P <sub>i</sub>	0.36*	0.54**	0.25	0.51**	1					
NaOH-P <sub>o</sub>	0.16	0.10	0.14	0.11	0.41*	Ч				
HCI 1M-Pi	-0.29	-0.35*	-0.24	-0.31	-0.35*	-0.10	Т			
HCl concP <sub>i</sub>	-0.27	-0.37*	-0.00	-0.32	-0.58***	-0.35*	0.26	1		
HCl concP <sub>o</sub>	0.38*	0.44*	.0.60***	-0.08	0.26	-0.01	-0.19	-0.15	1	
Residual P	0.15	0.25	0.18	0.07	0.06	0.13	-0.54**	0.24	0.0.2	1
*,**,*** Signi	ficant at the 0.0	5, 0.01 and 0.00	1 levels of proba	bility.						

Tab. 4.3. Pearsons correlations for isotopically exchangeable P (IEP) and P fractions for the unplanted Düshorn soil. The symbols \*/ \*\* /\*\*\*



Fig. 4.17. Significant Pearsons correlations for isotopically exchangeable P (IEP) and P fractions for the unplanted Gieboldehausen soil. The symbols \*' \*\* '\*\*\* mean significant correlation at 0.05, 0.01 and 0.001 respectively.

	IEP	Resin-P <sub>i</sub>	NaHCO <sub>3</sub> -P <sub>i</sub>	NaHCO <sub>3</sub> -P <sub>o</sub>	NaOH-P <sub>i</sub>	NaOH-P <sub>o</sub>	HCI 1M-P <sub>i</sub>	HCl concP <sub>i</sub>	HCl concP <sub>o</sub>	Residual P
IEP	Ţ									
Resin-P <sub>i</sub>	0.86***	Ч								
NaHCO <sub>3</sub> -P <sub>i</sub>	0.71***	0.43*	Ч							
NaHCO <sub>3</sub> -P <sub>o</sub>	0.11	-0.09	0.31	Ļ						
NaOH-P <sub>i</sub>	0.86***	0.76***	0.68***	0.11	1					
NaOH-P <sub>o</sub>	0.05	0.36*	-0.39	-0.48**	0.18	1				
HCI 1M-P <sub>i</sub>	0.01	60.0	-0.08	-0.12	-0.05	0.39*	1			
HCl concP <sub>i</sub>	-0.13	-0.09	-0.22	-0.53**	0.00	0.07	0.15	1		
HCl concP <sub>o</sub>	-0.09	0.24	-0.53 **	-0.65 ***	0.02	0.83***	0.17	0.15	Ļ	
Residual P	0.04	0.03	0.11	0.63 ***	00.0-	-0.3	-0.05	-0.36*	-0.44*	Ч
*,**,*** Signi	ificant at the 0.0	)5, 0.01 and 0.00	01 levels of prob	ability.						

# Summary

Phosphorus (P) is an essential plant nutrient necessary for several metabolic processes. More or less frequently, the concentration of plant available P in the soil is low, limiting the crop growth which results in a scarce yield. Thus, the P fertilization to reach optimal crop yield is a normal practice in modern agriculture. The industry of fertilizers is dependent on the natural rock phosphate (RP) resources to produce P fertilizers. However, RP resources are not renewable and it has been forecasted its total depletion in about 100 years with the current consumption rate. Phosphorus has been recycled mainly with direct application of sewage sludge to forest and crop land. However, the direct application of sewage sludge has several concerns since it contains heavy metals, antibiotics and human pathogens which produce a reject in the public opinion. In this scenario, European countries have supported projects related to the P recovery from different waste materials.

In Germany, different technologies have been developed to recover P from wastewater and sewage sludge as well as from animal residues. These processes are, normally, focused on the efficiency to recover P and decrease the heavy metal content from the waste material. Among the different processes to recover P, it is possible to distinguish chemical and thermal processes. From chemical Ρ is recovered the processes, usually as magnesium-ammonium-phosphate (MAP) or calcium phosphate (Ca-P) and in thermal works, P is recovered through mono-incineration, sintering or smelting processes. The recycled P products obtained by these processes differ in the total P content and in the chemical form in which P is found. Therefore, these recycled P products are not necessarily similar and effective to improve the plant available soil P if they are used as a P fertilizer.

This study was done to assess the effectiveness of recycled P products as P fertilizers in comparison to standard fertilizers and to understand the P dynamics in soil after application of these P products. We hypothesized that recycled P products from chemical processes are as effective as water soluble P fertilizers and that recycled P products obtained by thermal processes are similar to the effectiveness of rock phosphate (RP). Furthermore, our hypothesis is that recycled P products from chemical processes are accessible to the isotopic exchange in a similar extent as water soluble P fertilizers and that they are extractable in the more available P forms in a sequential P extraction. On the other hand, the P of products

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from thermal processes will not be extractable in the more readily fractions and not be accessible to the isotopic exchange. To evaluate these questions field and pot experiments as well as laboratory works were conducted.

Field experiments were carried out to assess the effectiveness of recycled P fertilizers in comparison to standard P fertilizers, triple superphosphate (TSP) and rock phosphate (RP). The effectiveness was characterized by the phosphorus uptake by the crops and the grain yield. Furthermore, P in soil was characterized by the P concentration in soil solution and the extractable P with calcium-acetate-lactate (CAL-P). The recycled P products tested in this experiment were: two ammonium-magnesium-phosphates (MAP-Sb and MAP-Gf) and two thermal products, a heavy metal depleted sewage sludge ash (SI-ash) and an alkali sinter phosphate made from meat-and-bone meal. The recycled P products were compared to the standard water P soluble fertilizer TSP and with the sparingly soluble RP. The field experiment was conducted in two silt loam soils and in a silty clay soil which had a very low P content (about 20 mg P kg<sup>-1</sup> soil). The fertilization was for a whole three year crop rotation with a suboptimal amount of 60 kg P ha<sup>-1</sup> plus a well fertilized with TSP (100 kg ha<sup>-1</sup>) and an unfertilized control. The recycled P fertilizers did not increase the CAL-P or P concentration in soil solution. Phosphorus uptake and grain yield were not affected by the P fertilization and only in one soil and in the first year there was a significant effect on the P uptake (PU) with the product MAP-Sb. Therefore, it was not possible to confirm the hypothesis that recycled P products from chemical processes are as effective as TSP or confirm that recycled P products from thermal processes are similar to RP. However, the recycled P products from chemical processes were in tendency, more effective than the thermal products.

The pot experiment was carried out with two soils from the field experiment and with a third acid sandy soil, which was not under cropping. The experiment was set for two years and the soils were planted with maize. In this study 8 recycled P products were evaluated, 4 from chemical processes (3 MAP of different sewage treatment plants and a precipitated calcium phosphate [Ca-P]) and 4 from thermal products (a heavy metal depleted sewage sludge [Sl-ash], and alkali sinter phosphate [Sinter-P], a cupola furnace slag from sewage sludge [Cupola slag] and a mono-incinerated meat-and-bone meal). The products were compared with the standard fertilizers TSP and RP. The reference P fertilizers and the recycled P products were applied in a dose of 60 mg P kg<sup>-1</sup> soil. The parameters evaluated were PU, dry

matter yield (DMY), P concentration in soil solution and CAL-P. The MAP products were as effective as TSP to increase the PU and the DMY of maize plants. Calcium phosphate was only effective in the acid sandy soil which was similar to RP. Thermal products were of lower effectiveness being more similar to RP. Although the products Sinter-P and Cupola slag were as effective as TSP, the first in the acid sandy soil (Düshorn, pH 4.4) and the second in a neutral soil (Gieboldehausen, pH 6.8).

In laboratory works the fate of P applied to the soils from P fertilizers and the isotopically exchangeable P (IEP) were evaluated. Furthermore, these laboratory works had the objective to identify from which P fraction the plants take up P.

Parallel to the planted pots other pots were kept moist but without plants two years to assess the fate of P applied from P fertilizers. For this study the acid soil Düshorn and the neutral soil Gieboldehausen were used. To evaluate the different soil P fractions a sequential fractionation procedure was used. The extractants and the order used in the sequential fractionation procedure were: anion exchange resins (Resin-P<sub>i</sub>), 0.5 M NaHCO<sub>3</sub>, 1 M NaOH, 1 M HCl, concentrated HCl and concentrated H<sub>2</sub>SO<sub>4</sub> plus H<sub>2</sub>O<sub>2</sub> (Residual P). In this scheme, Resin-P<sub>i</sub> is considered P being adsorbed to soil particle surfaces in equilibrium with the soil solution, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub> as inorganic P associated to Al and Fe hydroxides, HCl 1M-P<sub>i</sub> and concentrated HCl as inorganic P bound to Ca and Residual P represents occluded P.

The results showed that P from MAP products was extracted mainly by the anion exchange resins, NaHCO<sub>3</sub> and NaOH in both soils and this was comparable to the fate of P from TSP. The P from Ca-P was found mainly in Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-Pi in the acid soil Düshorn. However, in the neutral soil Gieboldehausen, the P from Ca-P was not found in Resin-P<sub>i</sub> but in NaOH-P<sub>i</sub> and in HCl 1M-P<sub>i</sub> indicating that it is similar to RP.

The thermal products can be separated in two groups according to the extraction procedure. The P from the products Sinter-P and Cupola slag in Düshorn soil was found mainly in Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> and NaOH-P<sub>i</sub>, however the amount of P found in Resin-P<sub>i</sub> was in tendency lower than for TSP. The products SI-ash and MB meal ash are in the second group, which were similar to RP. The P from these products was mainly found in HCl 1M-P<sub>i</sub> fraction. Although in Gieboldehausen some P was found in NaHCO<sub>3</sub>-P<sub>i</sub> fraction.
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To study from which P fractions maize plants take up P, the soil from the pot experiment with plants was subjected to a sequential extraction of P. In Düshorn soil plants took up P from the more available P fractions (i.e. Resin-P<sub>i</sub> and NaHCO<sub>3</sub>-P<sub>i</sub>). On the other hand, in Gieboldehausen soil, maize plants took up P from Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> as well as from NaOH-P<sub>i</sub> and from HCl 1M-P<sub>i</sub>.

The isotopically exchangeable P (IEP) was evaluated in the soil from pot experiments amended with recycled P fertilizers and with reference P fertilizers. It was observed that MAP products increased the IEP in a similar amount than TSP in both soils. Calcium phosphate was more effective in the acid soil Düshorn being similar to the MAP products and RP. The thermal Sinter-P showed a comparable IEP as TSP in Düshorn soil and the thermal product Cupola slag was similar to TSP in both soils. The other thermal products, SI-ash and MB meal ash were ineffective to increase the IEP in both soils.

In conclusion, recycled P products from chemical processes i.e. MAP products, were similarly effective as the water soluble fertilizers i.e. TSP, in increasing the plant available P. The recycled P fertilizer calcium phosphate (Ca-P) was only effective in acid conditions (pH 4.4). From the recycled P products obtained by thermal processes, Sinter-P was more effective in the acid soil than in the neutral soil. The product Cupola slag was as effective as TSP in neutral conditions (pH 6.8). The thermal products SI-ash and MB meal ash were not effective and were comparable to RP in both soil conditions.

# Zusammenfassung

Phosphor (P) ist ein wesentlicher Pflanzennährstoff und notwendig für verschiedene Stoffwechselprozesse. Manchmal ist die Konzentration an pflanzenverfügbarem Phosphor im Boden so gering, dass das pflanzliche Wachstum limitiert wird und Erträge verringert sind. Daher ist die Düngung mit Phosphor in der modernen Landwirtschaft praxisüblich, um optimale Erträge zu garantieren. Die Düngemittelindustrie ist von den natürlichen P-Reserven (Rohphosphat) abhängig, um P-Düngemittel herzustellen. Allerdings sind die Rohphosphatreserven nicht erneuerbar und bei dem derzeitigen Verbrauch wird in 100 Jahren die Erschöpfung der wirtschaftlich abbaubaren Reserven prognostiziert. Eine Wiederverwertung des Phosphors ist hauptsächlich durch das Ausbringen von Klärschlämmen auf land- und forstwirtschaftlich genutzten Flächen möglich. Allerdings bringt das direkte Ausbringen von Klärschlamm verschiedene Probleme mit sich, da im Klärschlamm Schwermetalle, Antibiotika und menschliche Pathogene enthalten sein können. Die gesellschaftliche Akzeptanz der Klärschlammausbringung ist deshalb gering. Aus diesem Grunde unterstützen die europäischen Staaten Projekte, die sich mit Phosphor-Recycling von verschiedenen Abfallprodukten befassen.

In Deutschland wurden verschiedene Verfahren zur Wiedergewinnung aus Abwasser, Klärschlamm sowie aus tierischen Rückstanden entwickelt. Diese Prozesse konzentrieren sich darauf, die Effizienz der P-Gewinnung zu steigern und die Schwermetallrückstände zu reduzieren. Innerhalb der verschiedenen Prozesse kann man zwischen nasschemischen und thermischen Verfahren unterscheiden.

Durch die chemischen Prozesse wird P als Magnesium-Ammonium-Phosphat (MAP) oder Calciumphosphat gewonnen. Die P-Gewinnung durch thermische Prozesse geschieht durch Monoverbrennung, Sintern oder Schmelzen. Die Recycling-P-Produkte, die durch diese Prozesse gewonnen werden, unterscheiden sich im Gesamt-P-Gehalt und in der chemischen Form, in der P gebunden ist. Deshalb unterscheiden sich die Produkte hinsichtlich ihrer Pflanzenverfügbarkeit, wenn sie als P-Düngemittel verwendet werden.

Diese Studie wurde unternommen, um die Wirksamkeit von recycelten P-Produkten als P-Düngemittel im Vergleich zu herkömmlichen Düngern zu beurteilen und die P-Dynamik im Boden nach der Anwendung dieser P-Produkte zu verstehen. Die Vermutung war, dass

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P-Recycling-Produkte aus chemischen Prozessen genauso effektiv sind wie wasserlösliche P-Düngemittel und dass recycelte P-Produkte aus thermischen Prozessen eine ähnliche Wirksamkeit wie Rohphosphat besitzen. Darüber hinaus bestand die Hypothese, dass recycelte P-Produkte aus chemischen Prozessen in ähnlichem Maße im Boden isotopisch austauschbar sind wie wasserlösliche P-Düngemittel und dass sie bei einer sequentiellen P-Extraktion eher in den leicht verfügbaren Fraktionen erscheinen. Andererseits sind thermisch hergestellte P-Produkte nicht in den leichter extrahierbaren P-Fraktionen zu finden und im Boden nicht isotopisch austauschbar gebunden. Zur Beurteilung dieser Fragen wurden Feld- und Gefäßversuche sowie Laboranalysen durchgeführt.

Um die Effizienz von recycelten P-Düngemitteln im Vergleich zu den Standard-P-Düngemitteln Triple-Superphosphat (TSP) und Rohphosphat (RP) zu bewerten, wurden Feldversuche durchgeführt. Die Wirksamkeit wurde anhand der P-Aufnahme durch die Pflanzen und des Kornertrags beurteilt. Darüber hinaus wurde P im Boden durch die P-Konzentration in der Bodenlösung und das Calcium-Acetat-Lactat extrahierbare P (CAL-P) charakterisiert. Die P-Recycling-Produkte, die in diesen Versuchen getestet wurden, waren: zwei Magnesium-Ammonium-Phosphat unterschiedlicher Herkunft (MAP-Sb und MAP-Gf) und zwei thermische Produkte, eine an Schwermetallen abgereicherte Klärschlammasche (SI-ash) und ein Alkali-Sinter Phosphat aus Fleisch- und Knochenmehl. Die Feldversuche wurden auf zwei Lehm- und einem Tonboden mit jeweils sehr niedrigen P-Gehalten (ca. 20 mg P kg<sup>-1</sup>) durchgeführt. Es wurde einmalig für eine dreijährige Fruchtfolge eine suboptimalen P-Menge von 60 kg P ha<sup>-1</sup> gedüngt, zudem gab es eine hoch gedüngte Variante mit 100 kg P ha<sup>-1</sup> als TSP sowie eine ungedüngte Kontrolle. Die recycelten P-Düngemittel erhöhten den CAL löslichen Phosphor und die P-Konzentration in der Bodenlösung nicht. Generell wurden P-Aufnahme und Ertrag nicht durch die Düngemittel beeinflusst, lediglich im ersten Jahr und nur mit einem Boden wurde ein Effekt durch die Düngung mit MAP-Sb gefunden. Trotz der niedrigen P-Gehalte im Boden konnten bereits die ungedüngten Pflanzen genug P aufnehmen. Aussagen über die P-Verfügbarkeit der Produkte lassen sich deshalb in dem Feldversuch nicht machen. Es zeigte sich allenfalls eine leichte Tendenz, dass chemisch gefällte Produkte etwas wirksamer waren als thermisch gewonnene.

Für den Gefäßversuch wurden zwei Böden des Feldversuches sowie ein saurer Sandboden eines nicht bewirtschafteten Standortes verwendet. Der Versuch wurde für zwei Jahre angelegt und die Böden wurden mit Mais bepflanzt. Für den Gefäßversuch wurden insgesamt 8 recycelte P-Produkte verwendet: vier aus chemischen Prozessen (3 MAP aus verschiedenen Kläranlagen und ein gefälltes Calciumphosphat [Ca-P]) und vier Produkte aus thermischen Prozessen (ein an Schwermetallen abgereicherter Klärschlamm [Sl-ash], ein Alkali-Sinter-Phosphat [Sinter-P], eine Kupolofenschlacke aus Klärschlamm [Cupola slag] und ein Fleisch- und Knochenmehlprodukt aus Mono-Verbrennung). Die Produkte wurden ebenfalls mit den Standard-Düngemitteln TSP und RP verglichen. Die Dünge mengen für beide Jahre waren einmalig 60 mg P kg<sup>-1</sup>. Die untersuchten Parameter waren P-Aufnahme, Trockenmasse, P-Konzentration der Bodenlösung und CAL-P.

Die MAP-Produkte waren so effektiv wie TSP bezüglich der Erhöhung der P-Aufnahme und der Trockenmasse der Maispflanzen. Ca-P war genauso wie RP nur im sauren Boden (pH 4,4) und Cupola slag nur im neutralen Boden (pH 6,8) wirksam. Das Sinter-P wirkte ebenfalls auf allen drei Böden, allerdings blieben Ertrag und Aufnahme hinter TSP und MAP zurück. Die beiden Aschen konnten von den Pflanzen gar nicht genutzt werden.

Der Verbleib des applizierten P im Boden und seine Wirkung auf das isotopisch austauschbare P (IEP) wurden ebenfalls ermittelt. Darüber hinaus sollten diese Untersuchungen klären, aus welchen Fraktionen die Pflanzen P aufnehmen. Hierfür wurden parallel zu den bepflanzten Gefäßen unbepflanzte Gefäße für zwei Jahre feucht gehalten. Die verschiedenen P-Fraktionen im Boden wurden mittels einer sequentiellen P-Extraktion bestimmt. Die Reihenfolge der benutzten Extraktionsmittel war: Anionenaustauschermembranen (Resin-Pi), 0,5 M NaHCO<sub>3</sub>, 1 M NaOH, 1 M HCl, konzentrierte HCl und konzentrierte  $H_2SO_4$  mit  $H_2O_2$  (Residual P). In diesem Schema wird angenommen, dass Resin-Pi austauschbar an Bodenpartikeloberflächen adsorbiert ist und im Gleichgewicht mit der Bodenlösung steht. NaHCO<sub>3</sub>-P<sub>i</sub> und NaOH-P<sub>i</sub> ist anorganischer Phosphor, der mit Al-und Fe-Hydroxiden assoziiert. Wenig und schwer lösliche Calciumphosphate werden mit 1M HCI-P<sub>i</sub> bzw. konzentrierte HCI extrahiert und das Residual P stellt hauptsächlich das okkludierte P dar.

Die Ergebnisse zeigten, dass der P der MAP-Produkte in beiden Böden vor allem durch die Anionenaustauschermembranen, NaHCO<sub>3</sub> und NaOH extrahiert wurde. Dies war vergleichbar zum TSP. In dem sauren Boden wurde der P des Ca-P vor allem in der Resin-P<sub>i</sub>-, NaHCO<sub>3</sub>-P<sub>i</sub>- und NaOH-P<sub>i</sub>-Fraktion gefunden, was darauf hindeutet, dass das Ca-P in diesem

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Boden in Lösung gegangen war. Im neutralen Boden dagegen war das Ca-P, ähnlich wie das RP hauptsächlich in der 1M HCI-Fraktion und lag damit selbst noch zwei Jahre vermutlich noch ungelöst vor.

Die thermischen Produkte können nach der Extraktion in zwei Gruppen unterteilt werden. Der P aus den Produkten Sinter-P und Cupola Slag im sauren Boden wurde vor allem in der Resin-P<sub>i</sub>-, NaHCO<sub>3</sub>-P<sub>i</sub>- und NaOH-P<sub>i</sub>-Fraktion gefunden, wobei die Menge des in der Resin-P<sub>i</sub>-Fraktion gefundenen P in der Tendenz niedriger als bei TSP war. Die Produkte SI-ash und MB meal ash fallen ähnlich dem RP in die zweite Gruppe. Der P aus diesen Produkten wurde vor allem in der HCl 1M P<sub>i</sub>-Fraktion gefunden. Dennoch wurde ein Teil des P im neutralen Boden in der NaHCO<sub>3</sub>-P<sub>i</sub>-Fraktion nachgewiesen.

Um herauszufinden, welche P-Fraktionen durch die Maispflanzen beeinflusst werden, wurde der bepflanzte Boden des Gefäßversuchs ebenfalls einer sequentiellen Extraktion unterzogen. Im sauren Boden nahmen die Pflanzen P aus den leicht verfügbaren P-Fraktionen (Resin-P<sub>i</sub> und NaHCO<sub>3</sub>-P<sub>i</sub>) auf. Im neutralen Boden waren neben den Fraktionen Resin-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> aber auch die Gehalte der Fraktionen NaOH-P<sub>i</sub> und HCl 1M-P<sub>i</sub> vermindert.

Der isotopisch austauschbare P (IEP) wurde ebenfalls im unbepflanzten Boden des Gefäßversuchs untersucht. Es zeigte sich, dass die MAP-Produkte in beiden Böden den IEP um den gleichen Betrag wie TSP erhöhten. Auch die Cupola slag zeigte auf beiden Böden ein dem TSP vergleichbares Ergebnis. Ca-P, Sinter-P und RP erhöhten das IEP nur im sauren Boden, während die Aschen SI-ash und MB meal ash nicht in der Lage waren, den IEP zu erhöhen.

Abschließend kann festgehalten werden, dass die MAP ähnlich wirksam in der Erhöhung des pflanzenverfügbaren P waren wie das wasserlösliche Düngemittel TSP. Der recycelte P-Dünger Ca-P war nur unter sauren Bedingungen (pH 4,4) wirksam. Unter den recycelten P-Produkten, die durch thermische Prozesse gewonnen wurden, war Sinter-P unter sauren Bedingungen effektiver als unter neutralen Bedingungen. Das Produkt Cupola slag war unter neutralen Bedingungen (pH 6,8) ebenso wirksam wie TSP. Die thermischen Produkte SI-ash und MB meal ash waren vergleichbar dem RP in beiden Böden nicht wirksam.

### Resumen

El fósforo (P) es un nutriente esencial para las plantas, el cual es necesario para diversos procesos metabólicos. Frecuentemente, la concentración de P disponible para las plantas en el suelo es baja, limitando el crecimiento de los cultivos, lo cual conlleva a un bajo rendimiento. De esta forma, la fertilización fosforada es una práctica habitual en la agricultura moderna, la cual tiene como objetivo obtener el máximo rendimiento alcanzable en un sistema. Por otro lado, la industria de los fertilizantes fosforados depende de la producción de roca fosfórica (RF). Sin embargo, la RF es un recurso no renovable y se prevé su agotamiento en aproximadamente 100 años según la tasa de consumo actual. De esta forma, el reciclaje de P es necesario para la sustentabilidad de este recurso. El P ha sido reciclado principalmente a través de aplicaciones directas de lodos sanitarios presenta algunos problemas relacionados a la presencia de metales pesados, antibióticos y agentes patógenos humanos, lo cual provoca rechazo en la opinión pública. En este escenario, los países europeos han apoyado proyectos para la recuperación de P a partir de diferentes materiales de desecho.

En Alemania, se han desarrollado diferentes tecnologías para recuperar P de aguas servidas y lodos sanitarios, como también de residuos animales. Estos procesos están centrados, en la eficiencia de recuperación del P y la disminución del contenido de metales pesados de los materiales de desecho. Entre los diferentes procesos para recuperar P, es posible distinguir dos: químicos y térmicos. En los procesos químicos, el P es recuperado mediante la precipitación de fosfatos de magnesio y amonio (MAP) o fosfatos de calcio (Ca-P) y en los procesos térmicos, el P es recuperado a través de mono-incineración o fundición de los materiales de desecho. Los productos fosforados obtenidos por estos procesos, se diferencian en el contenido de P total y en la forma química en la cual se encuentra el P. Por esta razón, estos productos no necesariamente son similares y eficientes en aumentar el P disponible para las plantas si son utilizados como fertilizantes.

La presente investigación tuvo como objetivo evaluar la eficiencia de los productos reciclados como fertilizantes fosforados y entender la dinámica del P en el suelo después de su aplicación. Nuestra hipótesis se basa en que los productos reciclados por procesos

químicos, son tan efectivos como los fertilizantes fosforados solubles en agua (superfosfato triple, SFT) y que los productos reciclados por procesos térmicos son similares a la eficiencia de la roca fosfórica (RF). Por otra parte, nuestra hipótesis es que los productos reciclados en procesos químicos son accesibles al intercambio isotópico en una medida similar al de los fertilizantes fosforados solubles en agua. Además, el P de estos productos es extraído en formas de P disponibles en una extracción secuencial. Al contrario, el P de los productos de procesos térmicos no es extraíble en las fracciones más disponibles y no es accesible al intercambio isotópico. Para evaluar estas hipótesis, se realizaron ensayos de campo y experimentos en macetas.

Los experimentos de campo, se llevaron a cabo para evaluar la eficiencia de los fertilizantes fosforados reciclados en comparación a un fertilizante soluble en agua, superfosfato triple (SFT) y en comparación a un fertilizante poco soluble en agua, roca fosfórica (RF). La eficiencia fue caracterizada mediante la absorción de fósforo por los cultivos y el rendimiento. Además, el P del suelo fue caracterizado a través de la concentración de P en la solución del suelo y del P extraíble con acetato de calcio y lactato (CAL-P). Los productos probados en este experimento fueron: dos fosfatos de amonio y magnesio (MAP-Sb y MAP-Gf) y dos productos térmicos, cenizas de lodo sanitario con baja concentración de metales pesados (SI-ash) y un fosfato alcalino sinterizado de restos de carne y hueso animal (Sinter-P). Los productos reciclados fueron comparados con SFT y RF. El experimento de campo se realizó en dos suelos franco limoso y en un suelo arcillo limoso, todos con un contenido bajo de P (alrededor de 20 mg P kg<sup>-1</sup> de suelo). La fertilización fue realizada en una sola dosis para una rotación de tres años, con una dosis sub-óptima de 60 kg P ha<sup>-1</sup> para todos los tratamientos, más una dosis alta con SFT (100 kg ha<sup>-1</sup>) y un testigo sin fertilizar. Los fertilizantes reciclados no aumentaron el CAL-P ni la concentración de P en la solución del suelo. La absorción de fósforo por los cultivos, así como el rendimiento no fueron afectados por la fertilización con P y sólo un suelo en el primer año, mostró un efecto significativo en la absorción de P con el producto MAP-Sb. Por lo tanto, no fue posible confirmar nuestra hipótesis. Sin embargo, los productos reciclados de P provenientes de procesos químicos fueron en tendencia, más eficientes que los productos térmicos.

El experimento en macetas se realizó con dos suelos provenientes del experimento de campo y con un suelo arenoso de bajo pH, el cual no se encuentra bajo cultivo. El

experimento se estableció por dos años y los suelos fueron plantados con maíz. En este estudio, 8 productos fueron evaluados, cuatro obtenidos por procesos químicos (3 MAP de diferentes plantas de tratamiento de aguas residuales y un fosfato de calcio precipitado [Ca-P]) y cuatro productos provenientes de tratamientos térmicos (cenizas de lodo sanitario con baja concentración de metales pesados [SI-ash], un fosfato alcalino sinterizado de carne y hueso animal [Sinter-P], una escoria de lodos sanitarios [Cupola slag] y un producto de la mono incineración de restos de carne y hueso animal [MB meal ash]). Los productos fueron comparados con SFT y RF. Los fertilizantes fueron aplicados en dosis de 60 mg P kg<sup>-1</sup> suelo. Los parámetros evaluados fueron la absorción de P (PU), producción de materia seca (MS), la concentración de P en la solución del suelo y el CAL-P. Los productos MAP fueron tan efectivos como el SFT en aumentar la absorción de P y la producción de MS de las plantas de maíz. El Ca-P sólo fue efectivo en el suelo de bajo pH, siendo similar a la RF. Los productos obtenidos por procesos térmicos fueron de menor eficiencia, siendo similares a la RF, aunque los productos Sinter-P y Cupola slag fueron tan efectivos como SFT, el primero en el suelo de bajo pH (pH 4,4) y el segundo en un suelo de pH neutro (pH 6,8).

Mediante fraccionamiento químico del P del suelo y del P isotópicamente intercambiable (IEP), se evaluó el destino del P aplicado. Además, estos análisis tuvieron como objetivo identificar desde que fracción de P del suelo absorbieron P las plantas.

Paralelamente a las macetas plantadas, otras fueron mantenidas húmedas sin plantar durante dos años, las cuales fueron usadas para evaluar el destino del P aplicado como fertilizante. Para este estudio, solo los suelos Düshorn (pH 4,4) y Gieboldehausen (pH 6,8) fueron usados. Para evaluar las diferentes fracciones de P del suelo se usó un procedimiento de fraccionamiento secuencial. Los extractantes y el orden utilizado fueron los siguientes: resinas de intercambio aniónico (Resina-P<sub>i</sub>), NaHCO<sub>3</sub> 0,5 M, NaOH 1 M, HCl 1 M, HCl concentrado y H<sub>2</sub>SO<sub>4</sub> concentrado con H<sub>2</sub>O<sub>2</sub> (P residual). El P extractado con la solución del suelo, P extractado con NaHCO<sub>3</sub> y NaOH es P asociado a hidróxidos de Al y Fe, P extractado con HCl 1M y HCl concentrado es P inorgánico ligado a Ca y el P residual representa el P ocluido.

Los resultados indicaron que el P de los productos MAP fue extraído principalmente por las resinas de intercambio aniónico, NaHCO<sub>3</sub> y NaOH en ambos suelos y fue similar a SFT. El P

del Ca-P se encontró principalmente en Resina-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub> y NaOH-P<sub>i</sub> en el suelo ácido. Sin embargo, en el suelo neutro, el P del Ca-P fue encontrado con NaOH y con HCl 1M, indicando que es similar a la RF.

Los productos provenientes de procesos térmicos pueden ser separados en dos grupos de acuerdo al procedimiento de extracción secuencial. El P de los productos de Sinter-P y de Cupola slag en el suelo ácido fue extraído principalmente con resina de intercambio aniónico, NaHCO<sub>3</sub> y NaOH, sin embargo, la cantidad de P extraído con resina fue inferior al del P del SFT. Los productos SI-ash y MB meal ash se situaron en un segundo grupo, siendo similares a RF. El P de estos productos fue extraído principalmente con HCl 1M, aunque en el suelo neutro se encontró P extractable con NaHCO<sub>3</sub>.

Para estudiar desde que fracciones absorben P las plantas de maíz, se procedió a la extracción secuencial de P en el suelo proveniente de las macetas con plantas. En el suelo ácido las plantas absorbieron P de las fracciones más disponibles (Resina-P<sub>i</sub> y NaHCO<sub>3</sub>-P<sub>i</sub>). Por otra parte, en el suelo neutro, la plantas de maíz absorbieron P desde Resina-P<sub>i</sub>, NaHCO<sub>3</sub>-P<sub>i</sub>, así como de NaOH-P<sub>i</sub> y de HCl 1M-P<sub>i</sub>.

El P isotópicamente intercambiable (IEP) fue evaluado en los suelos fertilizados con los productos reciclados y con los fertilizantes SFT y RF. Se observó que los productos MAP aumentaron el IEP en una cantidad similar al SFT en ambos suelos. El Ca-P fue más eficiente en el suelo ácido, mostrando un IEP similar al obtenido con los productos de MAP y RF. El producto térmico Sinter-P mostró un IEP comparable a SFT en el suelo ácido y el producto Cupola slag fue similar a SFT en ambos suelos. Los otros productos térmicos, SI-ash y MB meal ash no incrementaron el IEP en ninguno de los dos suelos.

En conclusión, los productos fosforados provenientes del reciclaje de P, MAP, fueron igualmente eficientes como el SFT en incrementar el P disponible para las plantas. El Ca-P sólo fue eficaz en condiciones de acidez (pH 4,4). El producto fosforado obtenido por proceso térmico, Sinter-P fue más eficaz en el suelo ácido que en condiciones neutras. El producto Cupola slag fue tan eficiente como SFT en condiciones neutras (pH 6,8). Los productos térmicos SI-ash y MB meal ash no fueron efectivos y son comparables a la RF en ambas condiciones de pH del suelo.

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#### **Contributions to Conferences**

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