

# Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments

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**Abstract** World phosphorus (P) resources are limited and may be exhausted within 70–175 years. Therefore recycling of P from waste materials by chemical or thermal processes is important. This study evaluated the effectiveness of recycled P products from sewage sludge and animal wastes as P fertilizer. Four products were obtained from chemical processes, three magnesium-ammonium-phosphates (MAP) of different sewage treatment plants and a Ca phosphate precipitated from wastewater (Ca-P) and four from thermal processes, an alkali sinter phosphate (Sinter-P), a heavy metal depleted sewage sludge ash (SI-ash), a cupola furnace slag made from sewage sludge (Cupola slag) and a meat-and-bone meal ash (MB meal ash). The effectiveness of these products as P fertilizers compared with triple superphosphate (TSP) and phosphate rock (PR) was determined in a 2-year pot experiment with maize (*Zea mays* L., cv. Atletico) in two soils with contrasting pH (pH(CaCl<sub>2</sub>) 4.7 and 6.6). The parameters used to evaluate the effectiveness were P

uptake, P concentration in soil solution ( $C_{Li}$ ) and isotopically exchangeable P (IEP). MAP products were as effective as TSP in both soils, while Ca-P was only effective in the acid soil. Sinter-P was as effective as TSP in the acid soil, while Cupola slag was in the neutral soil. The products SI-ash and MB meal ash were of low effectiveness and were comparable to PR. The effect of the fertilizers on IEP, but not on  $C_{Li}$ , described their effectiveness. Recycled P products obtained by chemical processes, especially MAP, could be directly applied as P fertilizers, while products such as SI-ash and MB meal ash are potential raw materials for P fertilizer production.

**Keywords** Phosphorus recycled products · P fertilizer efficiency · Isotopically exchangeable P · P in soil solution · Struvite · Ash · Slag · Soil reaction

## Abbreviations

P-0	Unfertilized
TSP-60	Triple superphosphate (60 mg P kg <sup>-1</sup> )
TSP-200	Triple superphosphate (200 mg P kg <sup>-1</sup> )
PR	Phosphate rock
Ca-P	Calcium phosphate
MAP-Sb	Magnesium-ammonium-phosphate (MAP) Seaborne
MAP-Gf	MAP Gifhorn
MAP-St	MAP Stuttgart

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Sinter-P	Sinter phosphate
Sl-ash	Sewage sludge ash
MB meal ash	Meat and bone meal ash

## Introduction

Phosphorus (P) supply is a major constraint on the quantity and quality of food production. However, P resources are limited and according to current calculations, the economically exploitable reserves will be exhausted in 70–100 years (Steen 1998; Cordell et al. 2009) and the reserve base in about 175 years (Smit et al. 2009). Therefore, it is necessary to reduce the dependence on industrial fertilizers by recovering and reusing P from the food production and consumption chain (Cordell et al. 2009). This recovery can be achieved by recycling P from human excreta and animal wastes. However, the direct application of wastewaters or sewage sludge on agricultural land involves several problems. Among these are the high levels of heavy metals they may contain and hazardous organic compounds of anthropogenic origin such as antibiotics, hormones and other pharmaceuticals and human pathogens (Balmer 2004; Dentel 2004; Adam et al. 2009a).

In order 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 wastewater, sewage sludge and animal wastes (SCOPE 2003). In Germany, several processes have been tested to recover P from sewage sludge. Among the more important processes are the precipitation of P as magnesium-ammonium-phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP or struvite) (Günther et al. 2008; Phan et al. 2009) and calcium-phosphate (Ca-P) (Ehbrecht et al. 2009). Furthermore, P recovery can be achieved by thermo-chemical processes, such as incineration, sintering or smelting sewage sludge or animal wastes (Adam et al. 2009b; Scheidig et al. 2009). Recycled P products obtained by chemical and thermo-chemical processes vary in their P content and water solubility and thus the amount of plant-available P differs between recycled P products.

Magnesium-ammonium-phosphate products can contain up to 12.65% P in pure compound, while

MAPs from P recycling contain from 6 to 12% P (Johnston and Richards 2003; Kern et al. 2008; Weidelener 2010). However, the mineral composition and solubility of MAP depend on different factors. Depending on the raw material, MAP may contain heavy metals such as Pb, Cd, Cr, Cu, Ni and Zn, although at concentrations below the maximum specified in European Union directives (Phan et al. 2009). Weidelener (2010) found that MAP products obtained in a laboratory-scale process contained on average 0.7% Al, 0.3% Ca and 0.2% Fe. The process of P recovery as MAP can vary in the way heavy metals are removed and the chemicals used to achieve the optimum pH for precipitation, obtaining phosphate salts of Ca and Fe as impurities (Phan et al. 2009). The solubility of pure MAP is considered to be low,  $0.23 \text{ g L}^{-1}$ , compared with about  $18 \text{ g L}^{-1}$  for  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Weast 1970). In spite of this low solubility several studies have found that struvite from sewage sludge is as effective as water-soluble P fertilizers in alkaline, neutral and slightly acid soils (Johnston and Richards 2003; Plaza et al. 2007; Massey et al. 2009). This shows that in spite of the low solubility of MAP, the soil provides conditions that favour its solubilization.

The P content of products precipitated as Ca-P from wastewater varies from 12% (Ehbrecht et al. 2009) to 20% (Hui-Zhen et al. 2009). The solubility of this Ca-P can be assumed to be higher than that of well crystallized Ca-P. Only a few experiments with recovered Ca-P products have been conducted to evaluate their effectiveness as P fertilizer (Johnston and Richards 2003; Römer 2006; Bauer et al. 2007). Bauer et al. (2007) found that P recovered as Ca-P from pig slurry was more available when the granule size of the product was below 1 mm, but it was not as effective as TSP, despite the acid reaction of the soil used in the experiment.

As regards P products recovered by thermo-chemical processes, sewage sludge and animal wastes can be treated in rotary furnaces to obtain ash that contains P. However, simple incineration does not remove the heavy metals from the raw material. This can be achieved by the addition of a chlorine donor, as described by Adam et al. (2009b), or by means of a smelting process (Scheidig et al. 2009). The P content of these products varies from 2 to 9% P (Jakobsen and Willett 1986; Zhang et al. 2002; Adam et al. 2009b). Besides heavy metals, sewage sludge products may

contain significant amounts of Al and Fe (Zhang et al. 2002).

Since plants absorb P from the soil solution, to become effective a P fertilizer must dissolve in soil water. Once the P dissolves in the soil solution it may subsequently be adsorbed to the soil particles or precipitate, but both forms stay in equilibrium with the soil solution and remain available to the plant. The amount of a fertilizer that dissolves and reacts with the soil can be estimated using some form of extractant, but more specifically by measuring the increase in isotopically exchangeable P (IEP). Comparing the increase with that obtained with TSP, which is about 100% soluble, gives an estimate of the proportion of the test fertilizer that dissolves in the soil water.

The aim of the experiments reported in this paper was to compare the effectiveness of recycled P products, triple superphosphate (TSP) and phosphate rock (PR) in increasing P uptake by maize under acid and neutral soil conditions. The effectiveness was related to the chemical composition of the P products and their ability to increase the P concentration in soil solution and IEP. In addition, the effect of soil

properties on dissolution of P from the P products was studied.

## Materials and methods

### Recycled P fertilizers

Eight different materials were tested with regard to their effectiveness as P fertilizers for P uptake of maize (*Zea mays* L., cv. Atletico) in a pot experiment on two different soils over 2 years. The materials used were: three magnesium-ammonium-phosphates (MAP) from different sewage treatment plants (MAP-Sb, MAP-Gf and MAP-St), a precipitated calcium phosphate from municipal wastewater (Ca-P), an alkali sinter phosphate made from meat-and-bone meal (Sinter-P), a cupola furnace slag (Cupola slag) made from sewage sludge, a heavy metal depleted sewage sludge ash (Sl-ash) and a meat-and-bone meal ash (MB meal ash) (Table 1). In addition, two commercial fertilizers with different P availability, triple superphosphate (TSP) and phosphate rock (PR), were used as reference P fertilizers. All products were finely ground to pass a

**Table 1** Description of the recycled P products obtained from different waste materials tested in the experiment

Material	Description
<i>Obtained by chemical processes</i>	
Ca-P	Phosphorus precipitated as calcium phosphate (Ca-P) by crystallization of P from wastewater with tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ), a calcium silicate hydrate (CSH) mineral (Ehbrecht et al. 2009; Petzet and Cornel 2009).
MAPs	Phosphorus from sewage sludge precipitated by different procedures as magnesium-ammonium-phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), also called struvite.
MAP-Sb	Provided by the Seaborne wastewater treatment plant at Owschlag, Schleswig–Holstein, Germany (Seaborne-EPM-AG 2010).
MAP-Gf	Provided by the Gifhorn wastewater treatment plant (Günther et al. 2008).
MAP-St	Provided by the Department of Wastewater Management (Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft), Stuttgart University (Weidener 2010).
<i>Obtained by thermal processes</i>	
Sinter-P	Phosphorus recovery by calcination of a mixture of meat-and-bone meal, sodium carbonate and silica in a rotary furnace at over 1,000°C. Sinter-P might be comparable to the alkali sinter phosphate (Rhenania phosphate) fertilizer formerly used in Germany (VTS 2010).
Cupola slag	Phosphorus recovery from sewage sludge and filter dust by smelting with the addition of limestone or dolomite. The energy for the smelting process is given by metallurgical coke. Cupola slag might be comparable to the Thomas phosphate fertilizer (Scheidig et al. 2009).
Sl-ash	Phosphorus recovery from sewage sludge by mono-incineration. The P material obtained contains P mainly as $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}_{1-x}(\text{OH})_x$ (Adam et al. 2009b).
MB meal ash	Phosphorus recovered by mono-incineration of meat-and-bone meal in a rotary furnace at 1,000°C (VTS 2010).

The materials were preliminary products obtained during the development of the processes

500 µm mesh before being applied as fertilizers. Some properties of the fertilizers are listed in Table 2. Total P was determined colorimetrically following digestion with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (Ostmann 1995). The concentrations of other main elements was determined on fused lithium tetraborate glass discs by X-ray fluorescence (XRF) with a Philips PW 1460 automated sequential spectrometer (Hartmann 1994). Element concentrations are expressed as percentage by weight of the air-dried material.

### Description of the experiment

The pot experiment was performed with 5.5 kg soil in 6-L pots with maize plants over 2 years. The soils used were a loamy soil with pH(CaCl<sub>2</sub>) 6.6 and a sandy soil with pH(CaCl<sub>2</sub>) 4.7, the latter taken from a long-term fallow site. Details of the soils are shown in Table 3. Phosphate was applied only in the first year, at a suboptimal rate of 60 mg P kg<sup>-1</sup> soil for each P compound, plus unfertilized and highly fertilized (200 mg P kg<sup>-1</sup>, TSP-200) controls. Furthermore, in the first year, the pots were fertilized

with (per pot) 1 g K as K<sub>2</sub>SO<sub>4</sub>, 0.2 g Mg as MgSO<sub>4</sub> 7H<sub>2</sub>O, and 0.5 g N as NH<sub>4</sub>NO<sub>3</sub>. Two further applications of 0.3 g N per pot, as Ca(NO<sub>3</sub>)<sub>2</sub>, were made. After fertilization, the soil was mixed, watered and incubated for 3 weeks. Thereafter maize was sown (4 plants per pot, reduced to 2 plants per pot after 1 month). Each pot was irrigated daily with demineralized water during the experiment to maintain a water content of 75% water-holding capacity, with any leached water being returned to the pots. Each treatment comprised 4 replicates. In addition, one pot in each treatment was kept without plants but watered regularly for the whole experimental period to maintain the same soil moisture content as in the pots with plants.

### Soil and plant material sampling

Before starting with the experiment, the soils were analyzed for pH, organic matter and texture (Table 3). The soil samples from the experiment were collected after three weeks of incubation with the different P products for the determination of P in

**Table 2** Phosphorus concentration, P solubility and element composition in the fertilizers and recycled P products

Material	Total P (%)	Proportion of total P soluble in		P solubility (µmol L <sup>-1</sup> ) <sup>§</sup>	Ca (%)	Mg (%)	Al (%)	Fe (%)	Si (%)
		Water (%) <sup>*</sup>	2% citric acid (%) <sup>†</sup>						
Reference fertilizers									
Triple superphosphate (TSP)	20.1	90	–	115,849	17.2	0.1	0.3	0.1	0.0
Phosphate rock (PR)	11.8	<0.01	17.0	6	33.0	0.5	0.3	0.2	3.6
Obtained by chemical processes									
Ca-P	11.1	4.1	48.6	2,901	20.1	0.3	0.2	0.2	14.0
MAP-Sb	11.0	1.1	51.0	761	1.6	8.6	0.8	0.4	0.0
MAP-Gf	9.6	0.8	47.0	508	8.6	5.5	0.3	5.5	0.8
MAP-St	11.8	1.9	43.6	1,427	0.5	8.3	0.4	1.0	0.0
Obtained by thermal processes									
Sinter-P	11.3	0.3	34.5	201	22.8	0.8	3.0	1.9	7.8
Cupola slag	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sl-ash	7.8	6.4	31.4	3,210	14.9	1.1	3.3	8.8	10.5
MB meal ash	16.4	0.1	23.8	53	32.1	0.7	0.9	0.8	0.0

*n.d.* not determined

<sup>\*</sup> 5 g material extracted with 250 mL water

<sup>†</sup> 2.5 g material extracted with 250 mL 2% citric acid

<sup>§</sup> With the exception of TSP, P solubility is the P concentration in water in equilibrium with the solid fertilizer as determined in the water solubility procedure (<sup>\*</sup>)

**Table 3** Characteristics of the two soils used in the pot experiment

Soil	Clay (%)	Silt (%)	Sand (%)	Organic matter (%)	pH in CaCl <sub>2</sub> (1:2.5)	Available P CAL <sup>(*)</sup> extractable P (mg kg <sup>-1</sup> )
Acid sandy	2.1	5.3	92.6	5.3	4.7	24.2
Neutral loamy	25.0	65.5	9.5	2.8	6.6	21.0

(\*) Calcium-acetate-lactate extractable P

soil solution in the moist soil and after 2 years for the measurement of IEP. The samples for IEP determination were air-dried and sieved to 2 mm. The maize plants were harvested at beginning of flowering, at day 80 and 70 day after sowing for the first and second year, respectively. At harvest, above-ground biomass and P concentration were determined.

#### Analytical procedure

##### Soil

Before the start of the experiment, subsamples of soil were collected to measure organic matter (OM), soil pH and soil texture. OM was analyzed with the Walkley and Black oxidation procedure (Nelson and Sommers 1982). Soil pH was measured in 0.01 M CaCl<sub>2</sub> (1:2.5), and texture by means of the hydrometer method (Day 1965). Soil solution was obtained by a modified displacement procedure according to Adams (1974). For this, about 300 g moist soil from the pots were placed directly into 30-cm high cylinders with a hole at the bottom. The soil column was covered by a 2 cm layer of sand, and water was added at the top drop-wise at about 5–10 mL per hour. The first 20 mL of solution coming out at the bottom after several hours was the pure displaced soil solution, as checked using a non-adsorbed reagent (KSCN) added to the water. The P concentration in the soil solution was measured colorimetrically by the method of Murphy and Riley (1962).

The IEP content was determined at the end of the second year of the experiment in the pots without plants with similar moisture content to the planted pots. For this, 2 g air-dried soil sieved to 500 μm were weighed into 50 mL plastic tubes. Then, 8 mL distilled water and 7 mL of carrier-free solution of H<sub>3</sub><sup>33</sup>PO<sub>4</sub> with a radioactivity of about 0.04–0.06 MBq were added. The samples were shaken for 5 day and then centrifuged at 4,000 rpm. The ratio of <sup>33</sup>P to <sup>31</sup>P

in the supernatant solution had to be determined, but the <sup>31</sup>P concentration is often very low and its determination would be very inaccurate. Therefore, the solution was concentrated by a factor of about five using an anion exchange resin. Ten mL aliquots of supernatant were placed in 13 mL tubes with an anion exchange resin strip (9 × 15.5 mm, anion resin PC Acid 35, PCA Company, Germany) and shaken for 24 h. The resin strips were then carefully placed in 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 according to Murphy and Riley (1962). The radioactivity of P in the HCl extract was measured with a liquid scintillation analyzer (Perkin Elmer TRICARB 2800 TR). IEP was calculated based on the theoretical relationship:

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

where IEP is the isotopically exchangeable P in mg kg<sup>-1</sup> soil,  $C_L/r_t$  is the ratio of P concentration in solution ( $C_L$ , mg L<sup>-1</sup>) to 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 behaviour and that the same relationship between <sup>31</sup>P and <sup>33</sup>P is maintained in anion exchange resin strips as is present in the supernatant solution.

##### Plant material

Plants were dried to constant weight at 65°C 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 in the digest was measured colorimetrically by the molybdenum-vanadate method (Scheffer and Pajenkamp 1952). Total P uptake (PU) was calculated from shoot dry matter and shoot P concentration.

### Relative fertilizer efficiency

The relative fertilizer efficiency (RFE) for the 2-year experiment was taken as a parameter to rank the P sources with respect to TSP. The RFE compares the increase in PU due to a specific fertilizer to the increase in PU due to the standard water-soluble P fertilizer TSP:

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

where  $\text{PU}_{\text{treatment}}$  is the PU obtained by a specific P fertilizer,  $\text{PU}_{\text{control}}$  is that of the unfertilized control and  $\text{PU}_{\text{TSP}}$  that obtained from triple superphosphate.

### Data analysis and experimental design

Statistical analysis was performed using Statistica 9.0 (StatSoft, Inc. Tulsa, USA). The experiment was arranged in a completely randomized design, with 11 treatments and four replicates. The fertilizers were considered main factors according to one-way ANOVA (Quinn and Keough 2002). The ANOVA test was followed by a Tukey test at the 0.05 level of significance to compare means of treatments. Simple linear regression was used to analyze the relationship between PU and IEP or  $C_{\text{Li}}$ .

## Results and discussion

In the pot experiments the different fertilizers were studied as sources of P for plant growth. Shoot yield and P uptake (PU) were measured and since these were closely related, either one reflects the effectiveness of a product as a P fertilizer. We used PU, which is expressed per kg soil, as it also allowed us to make quantitative comparisons with soil data, mainly IEP, which is also expressed per kg soil.

### Phosphorus in soil solution and isotopically exchangeable P

The P concentration in the soil solution ( $C_{\text{Li}}$ ) was affected differently depending on the fertilizer (Table 4). Half the 10 fertilizers tested increased  $C_{\text{Li}}$  significantly. In both soils TSP increased  $C_{\text{Li}}$  the most and PR had no effect, while Ca-P increased  $C_{\text{Li}}$  in the acid soil but failed to do so in the neutral soil.

**Table 4** Phosphorus concentration in soil solution three weeks after application of 60 mg P kg<sup>-1</sup> soil in the form of triple superphosphate (TSP), phosphate rock (PR) or recycled P products to two soils

P source	P in soil solution	
	Acid sandy soil (μmol L <sup>-1</sup> )	Neutral loamy soil (μmol L <sup>-1</sup> )
Controls		
P-0	2.1ab	0.6a
TSP	7.2f	14.8d
PR	2.0ab	0.7a
Products obtained by chemical processes		
Ca-P	4.6de	1.5ab
MAP-Sb	6.0ef	9.0b
MAP-Gf	3.7bcd	4.0c
MAP-St	6.6f	8.9c
Products obtained by thermal processes		
Sinter-P	3.9cd	2.3ab
Cupola slag	1.7a	4.2b
Sl-ash	2.2ab	1.7ab
MB meal ash	2.4abc	1.8ab

Different letters denote significant differences between treatments (Tukey,  $P < 0.05$ )

MAP-Gf was the reverse, increasing  $C_{\text{Li}}$  in the neutral soil but not the acid soil. The other two MAPs increased  $C_{\text{Li}}$  in both soils similarly to TSP. Of the thermal products,  $C_{\text{Li}}$  was only increased by Sinter-P in the acid soil and by Cupola slag in the neutral soil. The ashes, Sl-ash and MB meal ash, were ineffective in increasing  $C_{\text{Li}}$ .

The IEP value can help assess the proportion of a P fertilizer that dissolves in soil water. As a P fertilizer dissolves in the soil solution the P becomes adsorbed to soil particle surfaces or precipitates as a salt, but mostly remains in equilibrium with the soil solution. This was easily seen for TSP in this study. The 60 mg P kg<sup>-1</sup> soil added increased IEP (Fig. 1, right) by 53 mg kg<sup>-1</sup> in the acid soil and 42 mg kg<sup>-1</sup> in the neutral soil, i.e. 88 and 70% of the TSP remained in equilibrium with the soil solution even 2 years after its application. The fraction that was not accessible to isotopic exchange probably underwent some slow long-term reactions which did not equilibrate with the soil solution within the five days of equilibration in IEP determination (Barrow and Shaw 1975). Alternatively, it may have precipitated as Ca phosphates or Fe/Al phosphates, which are not accessible to



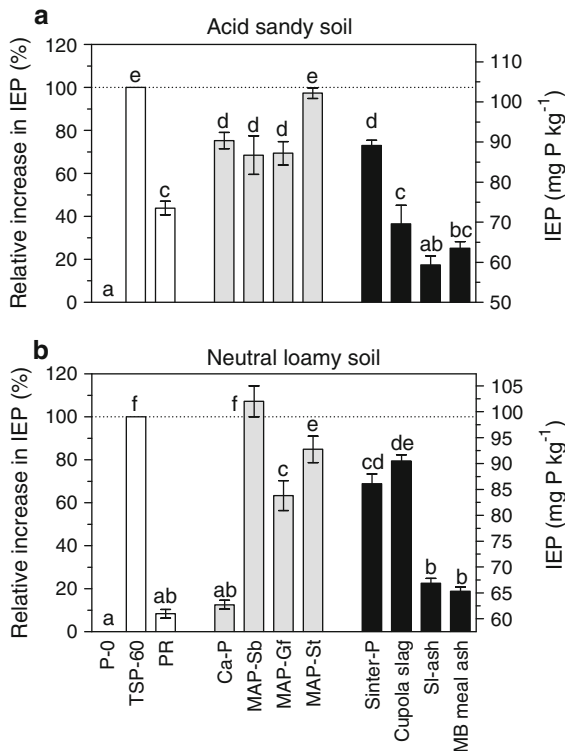
isotopic exchange (Machold 1962, 1963). Such slow long-term reactions and/or P precipitation were apparently more pronounced in the neutral soil than in the acid soil.

In order to assess how much of the other fertilizers dissolved in the soil solution, the increase in IEP caused by each was expressed as a proportion of the increase in IEP caused by the water-soluble TSP (Fig. 1, left). Using this parameter indicated that 44% of PR and 76% of Ca-P dissolved in the acid soil (Fig. 1a), while in the neutral soil (Fig. 1b) the dissolution of these fertilizers was not significant. The higher dissolution of Ca-containing P fertilizers in acid soils can be attributed to the higher  $H^+$  concentration (Kirk and Nye 1986; Alloush 2003). The MAPs dissolved similarly in both the acid and neutral soils, by 65–100%, and were therefore similar

to TSP. The high dissolution of the MAPs in the soil solution, in contrast to the small proportion of 1–2% that dissolved in water (Table 1), may be explained by the low P concentration in the soil solution of 4–9  $\mu\text{mol L}^{-1}$  (Table 4), which is much lower than the solubility of the MAPs, 508–1,427  $\mu\text{mol L}^{-1}$ .

Depending on the process used to obtain the thermal products, their effectiveness in increasing IEP was very different. Sinter-P increased IEP effectively in the acid soil and the neutral soil and was thereby comparable to the MAPs and almost to TSP. In contrast, the effect of Cupola slag on IEP depended on soil pH, as it increased IEP strongly in the neutral soil but much less in the acid soil. The ashes (SI-ash and MB meal ash) had only a small and sometimes non-significant effect on IEP, indicating that there was almost no dissolution of their P compounds.

At this point it may be interesting to consider the interrelationships between the solubility of the fertilizers in water (Table 2) and their effect on P in soil solution (Table 4) and on IEP (Fig. 1). The P concentration in water (Table 2) was always higher, even for PR, than the P concentration in the soil solution,  $C_{Li}$ , after the fertilizers were added to the soil. If the whole fertilizer had the same solubility as measured in water, e.g. 6  $\mu\text{mol L}^{-1}$  for PR or 3,210  $\mu\text{mol L}^{-1}$  for SI-ash, then the fertilizer should have dissolved completely because its solubility is above  $C_{Li}$ . However, this was not the case, as the increase in IEP due to most fertilizers was less than that of the water-soluble TSP. SI-ash, which had very high solubility in water, still only dissolved to about 20% in the soil solution (Fig. 1). This indicates that all these fertilizers are not pure products but a mixture of some compounds of higher solubility, as indicated when dissolved in water, and a large proportion of compounds with low solubility of below a few  $\mu\text{mol L}^{-1}$ , as indicated in soil solution. Even the MAPs from P recycling were not pure products, as 30–40% did not dissolve in the soil solution (Fig. 1). This shows that the solubility of a P fertilizer in water is not a good parameter to characterize its effectiveness as a P source for plants, as also discussed later. Furthermore, the proportion of P that dissolved in 2% citric acid (Table 2) did not reflect the proportion that would dissolve in the soil solution as shown by the increase in IEP (Fig. 1).



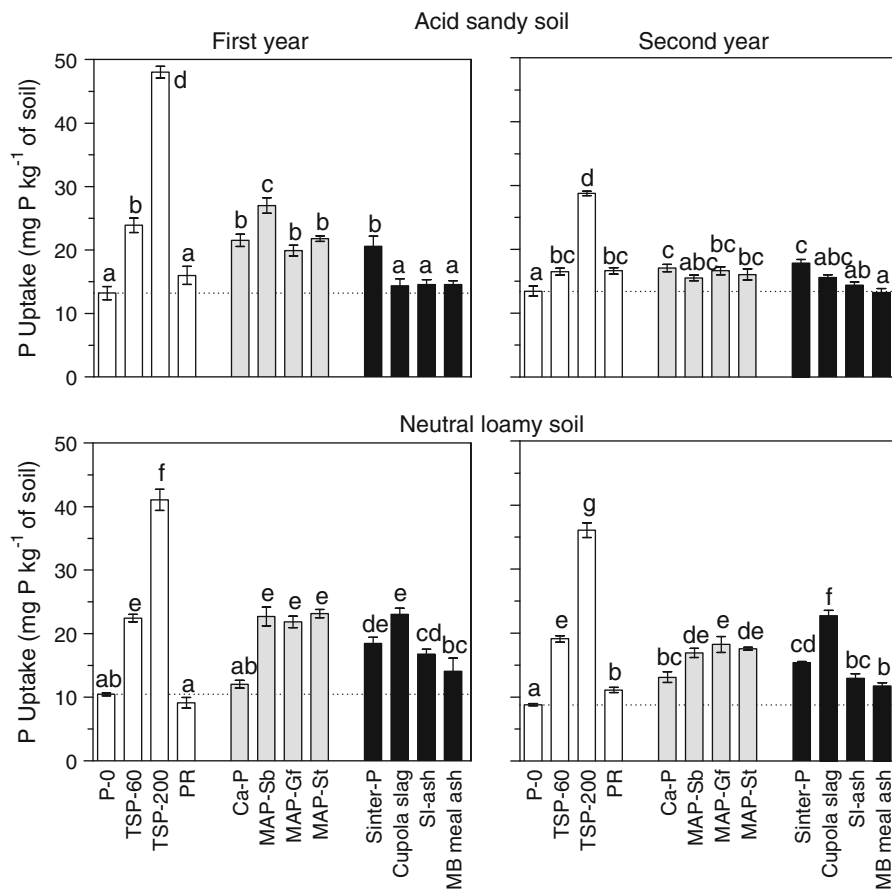
**Fig. 1** Absolute and relative increase in isotopically exchangeable P (IEP) in unplanted soils 2 years after fertilization. To calculate the relative increase in IEP, the increase of IEP from TSP was set to 100%. Data are means of 3 replicates and error bars represent the standard error of the means. Different letters denote significant differences between treatments (Tukey,  $P < 0.05$ )

## Phosphorus uptake and relative fertilizer efficiency

In both soils tested here, P uptake (PU) by maize plants increased significantly due to a P application of  $60 \text{ mg kg}^{-1}$  soil as TSP (Fig. 2). This rate was still on the ascending part of the response curve, since P uptake increased further with a P application rate of  $200 \text{ mg kg}^{-1}$ . This condition of being on the ascending part of the response curve is required for a valid comparison of different fertilizers (Barrow 1985).

In the first year, PU on both soils was twice as large for TSP-60 as for the unfertilized control (P-0). In the second year, PU in the P-0 treatment was similar to that in the first year, while the response to TSP-60 decreased strongly in the acid soil but

remained similar in the neutral soil. The decreased response in the acid soil was not because of depletion of added P, since only about 20% of the P applied had been removed in the first year and since most of the P applied remained isotopically exchangeable even after the second year (see Fig. 1a). A possible reason could have been some growth limitation that restricted P use from the fertilizers in the second year. In the neutral soil, this limitation was much less pronounced, as the increased PU from TSP-60 was similar in both years. In both soils PR caused no significant increase in PU in the first year, but a small but significant increase in the second year. Ca-P increased PU more than PR in the acid soil, where it had a similar effect to the MAPs. In the neutral soil it increased PU only in the second year, but its effect



**Fig. 2** Phosphorus uptake by maize, expressed per kg soil, grown for 2 years on an acid sandy soil and a neutral loamy soil fertilized with different reference and recycled P fertilizers. Treatments were applied in a dose of  $60 \text{ mg P kg}^{-1}$  soil,

except TSP-200 ( $200 \text{ mg P kg}^{-1}$  soil). Data are means of 4 replicates and error bars represent the standard error of the means. Different letters denote significant differences between treatments (Tukey,  $P < 0.05$ )



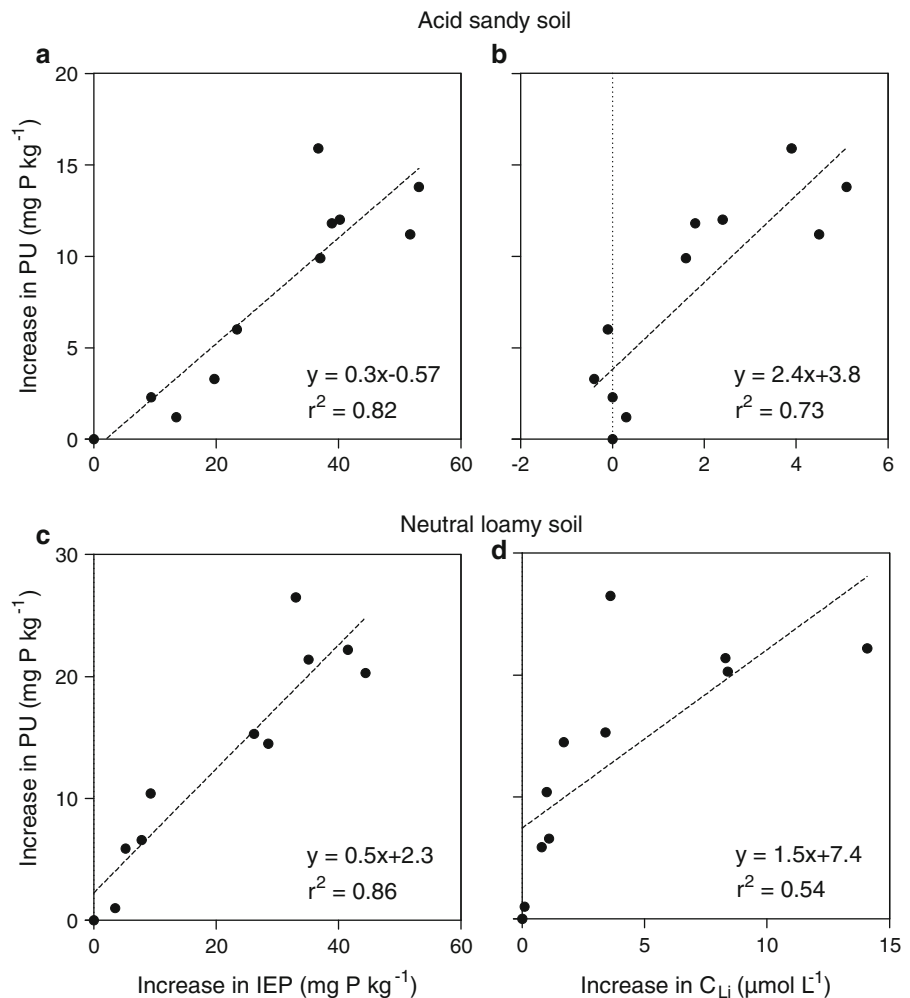
was much lower than that of the MAPs. The MAPs increased PU similarly to TSP, with the increase again being much smaller in the second year than in the first year in the acid soil, while in the neutral soil it was almost equal in both years.

Of the thermal products, in the acid soil only Sinter-P increased PU significantly and was comparable to TSP. Sinter-P was also effective in the neutral soil, as were all other thermal products tested. The most effective was Cupola slag, which in the second year was even more effective than TSP, presumably due to slow reaction of the product with the soil. This kind of long-term reaction is not a new finding for thermally treated P products. Bolland and Bowden (1982) found that PRs calcined either at 500 or 900°C increased their plant-available P over time

in a field experiment. The increase in PU caused by the ashes in the present study, even though statistically significant, was small in absolute terms.

The fertilizers tested affected the P availability in soil by affecting the quantity factor, i.e. the IEP, as well as the intensity factor, i.e. the concentration of P in soil solution ( $C_{Li}$ ). To test which of these two factors had the greatest effect on PU, the increase in PU was plotted against the increase in IEP and that in  $C_{Li}$  (Fig. 3). As Fig. 3a and c show, in both soils the increase in PU was clearly linearly related to the increase in IEP, with an intercept close to the origin and a high  $r^2$  of above 0.8. In contrast, the increase in PU was not linearly related to the increase in  $C_{Li}$ , as shown by the lack of fit of the regression line (Fig. 3b, d). These results indicate that in this

**Fig. 3** Increase with respect to unfertilized soil in phosphorus uptake (PU) due to different P fertilizers, related to the increase in isotopically exchangeable P (a, c) and the increase in P in soil solution,  $C_{Li}$  (b, d) caused by addition of the same reference and recycled P fertilizers to an acid sandy soil and a neutral loamy soil



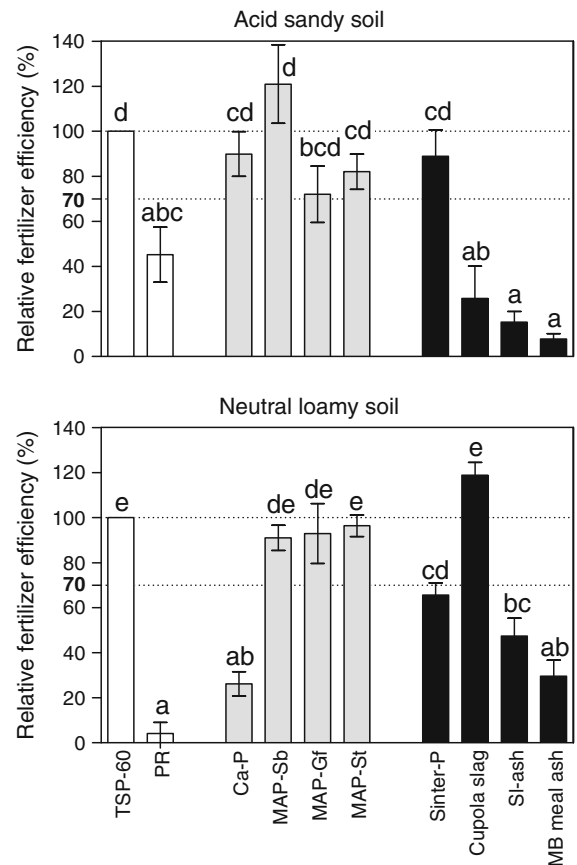
experiment the quantity factor, IEP, was more closely related to P uptake by maize than the intensity factor, P concentration in the soil solution.

Whether the quantity or the intensity determines the uptake of a nutrient from soil depends on whether there is inter-root competition (Claassen and Steingrobe 1999). In the case of strong inter-root competition, as was probably the case in the pot experiment described here, the quantity is decisive, while in the case of no inter-root competition, as may be the case for P under field conditions, the intensity, i.e. P in soil solution, determines how much is taken up by a plant. This underlines the need for further field experiments to test the effectiveness of recycled P fertilizers.

The RFE characterizes the effectiveness of a fertilizer with a single number and facilitates the comparison of different fertilizers. As can be seen from Fig. 4, the MAPs and Sinter-P were equally effective as fertilizers in acid and neutral soil conditions to TSP. In contrast, PR and Ca-P were only effective under acid conditions and Cupola slag only under neutral soil conditions. The ashes were of no or low effectiveness under both acid and neutral soil conditions (Fig. 4). The latter is probably due to the presence in ash of compounds of low solubility, such as chlorapatite and stanfieldite, and Al and Fe (Adam et al. 2009b; Nanzer et al. 2009).

## Conclusions

Phosphorus recycling by means of chemical and thermal processes has a high potential to reduce the dependency of agriculture on P fertilizers derived from phosphate rock. This study showed that MAP products were equally effective to TSP in both acid and neutral soils. Sinter-P was effective in both soils, but more so under acid conditions. On the other hand, Ca-P was only effective in the acid soil. Among the other thermal products, Cupola slag was as effective as TSP in the neutral soil, while SI-ash and MB meal ash were of low effectiveness in both soils. Thus, it is necessary to distinguish between P recovery from waste materials and the effectiveness of the products as P fertilizers and to adjust agronomic management according to the soil and the kind of material used as P fertilizer. Our results indicate that MAP products and to a certain extent Sinter-P could be used over a wide range of soil pH. In contrast, Ca-P would be



**Fig. 4** Relative fertilizer efficiency of PR and recycled P products determined in a 2-year pot experiment on two different soils. The increase in P uptake by maize due to TSP was set to 100%. Data are means of 4 replicates and error bars represent the standard error of the means. Different letters denote significant differences between treatments (Tukey,  $P < 0.05$ )

most useful at low soil pH and Cupola slag at neutral or slightly acid soil pH. Overall, P recovery as ash is of low value for direct use as P fertilizer in agriculture, although ash products could probably be used as raw materials for the fertilizer industry. The effectiveness of recycled P products as P fertilizers was not well indicated by their solubility in water or in citric acid, but it was accurately indicated by their dissolution in soil, i.e. the increase in IEP in soil. Therefore further research is needed to characterize the chemical properties that best describe the behaviour of P fertilizers in soil. This would improve the process of P recovery from waste materials and lead to better agronomic management of recycled products as P fertilizers. For a final

agronomic assessment of recycled P products, long-term field experiments are needed.

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