

## RESEARCH PAPER

# Increased phosphorus availability from sewage sludge ashes to maize in a crop rotation with clover

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**Abstract**

A recycling of Phosphorus (P) from the human food chain is mandatory to secure the future P supply for food production. However, many available recycled P fertilizers from sewage sludge do not have an adequate P bioavailability and, thus, are not suitable for their application in soils with pH >5.5–6.0, unless being combined with efficient mobilization measures. The aim of the study was to test the P mobilization ability of red clover (*Trifolium pratense* L.) from two thermally recycled P fertilizers for a subsequently grown maize. Two sewage sludge ashes (SSA) were investigated in a pot experiment at soil pH 7.5 with red clover differing in its nitrogen (N) supply (added N fertilizer or biological N<sub>2</sub> fixation (BNF)), followed by maize (*Zea mays* L.). Shoot dry matter of maize was almost doubled when N supply of previous grown clover was covered by BNF, instead of receiving added N fertilizer. Similarly, shoot P removal of maize following clover with BNF was significantly increased. It is suggested that the P mobilization is related to the BNF, and a proton release of N<sub>2</sub> fixing clover roots led to the measured decrease in soil pH and thereby increased P availability of the tested fertilizers.

**KEYWORDS**

organic farming, phosphorus mobilization, pot experiment, red clover, sewage sludge ash

## 1 | INTRODUCTION

Phosphorus (P) is an essential component of all living organisms. Thus, a sufficient P supply for plants is a key factor in agricultural production. Phosphorus fertilizer production is based on mined phosphate rock (PR). Approximately 80% of P from mined PR is used for fertilizer production (Scholz et al., 2014). Future availability of the world's main source of phosphorus is uncertain (Cordell, 2010). New technologies have been developed to recycle P from urban areas back to agriculture. An overview of different P recovery technologies from municipal wastewater has been published by Egle et al. (2015). Recycled P fertilizers from urban wastewater show huge

differences in P bioavailability, depending on their production process and soil pH (Cabeza et al., 2011; Möller et al., 2018; Wollmann et al., 2018). Struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6 H<sub>2</sub>O) has been shown to be an effective P fertilizer when applied to a wide range of soil pH while the efficacy of untreated sewage sludge ashes (SSA) strongly depends on the soil pH (Möller et al., 2018; Nanzer et al., 2014).

There are different approaches to increase P bioavailability of fertilizers, such as a soil or seed inoculation with bioeffectors (e.g. bacteria, fungi, algae extracts) to increase mineralization and solubilization of orthophosphates (Meyer et al., 2017; Wollmann et al., 2018), or the use of P-efficient crops within the crop rotation (Richardson et al., 2009). It has been suggested that legumes are able to take up

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P from sparingly soluble soil P fractions (Hassan et al., 2012) and increase internal P cycling (Horst et al., 2001). In soils with pH >7.0, P availability might be enhanced through a rhizosphere acidification, resulting from a proton release during biological N<sub>2</sub> fixation (BNF) of legumes (Hauter & Steffens, 1985; Hinsinger et al., 2003) and the uptake of cations from soil solution. Several studies have shown an increased P availability of PR when applied to leguminous crops. Hauter and Steffens (1985) reported an increased P removal of red clover with BNF, compared to clover with added N fertilization in shoots (+2.08%) and roots (+14.2%) in combination with PR fertilization. Vanlauwe et al. (2000) reported a higher maize P removal from PR in a crop rotation with different bean species (*Mucuna pruriens* L. and *Lablab purpureus* L.) compared to a maize monoculture.

The aim of this study was, to evaluate the fertilizer efficiency of mineral P fertilizers recycled from sewage sludge in combination with biological P mobilization. The objective was, to investigate the P mobilization potential of red clover for such recycled P fertilizers within a crop rotation with maize. Two sewage sludge ashes (Mg-SSA and Na-SSA) and PR (Naturphosphat P26, Timac AGRO, Austria) were tested for their P availability on maize with previous cultivation of red clover. We hypothesized that (1) if red clover covers its N supply by biological N<sub>2</sub> fixation (BNF), it is able to mobilize soil P and P from PR and SSA, because the soil acidification by clover roots under BNF leads to a dissolution of sparingly soluble P compounds, and (2) If maize is grown after clover with BNF, P availability of PR and SSA to maize can be enhanced, because the P mobilization by clover can be measured also in the subsequent crop.

## 2 | MATERIALS AND METHODS

### 2.1 | Recycled P fertilizers and substrate used in the pot experiment

Two thermally recycled P fertilizers from sewage sludge and PR were used as fertilizers in the experiment. The Mg-containing SSA (Mg-SSA) was produced at 950 °C based on the ASH DEC<sup>®</sup> process (Outotec), showing a low plant P availability (Cabeza et al., 2011; Wollmann et al., 2018). The dominant P-bearing phase in Mg-SSA are Ca- and Mg- phosphates, including chlorapatite, stanfieldite and farringtonite (Adam et al., 2009). Na-SSA was produced by calcination of sewage sludge ash with sodium under reducing conditions in a modified ASH DEC<sup>®</sup> process. P-bearing minerals (mainly CaNaPO<sub>4</sub>) in Na-SSA have a higher reactivity than untreated ashes (Herzel et al., 2016), resulting in a high P bioavailability (Möller et al., 2018). Despite its chemical analogy to Rhenania-P after calcination of the SSA, the fertilizer is called 'Na-SSA', following

the term that is used for this fertilizer in recent literature ('Na-SSA' (Wollmann & Möller, 2018); 'SSA-Na', (Vogel et al., 2018)). Further information on specific production conditions of the ashes has been published by Wollmann et al. (2018) and Wollmann and Möller (2018). The total P concentration (mg P g<sup>-1</sup> DM) of ashes was 76.3 (Na-SSA) and 57.2 (Mg-SSA).

The used substrate was a 1:1 mixture (on DM weight basis) of a silty sandy loam soil, based on a long-term unfertilized grassland (0–30 cm depth), and silica sand. Soil chemical and physical properties included: pH: 7.5 (CaCl<sub>2</sub>; VDLUFA, 1991), total P: 554 mg P kg<sup>-1</sup> DM, bioavailable P<sub>CAL</sub> (calcium-acetate-lactate extractable P (Schüller, 1969)): 22.0 mg P kg<sup>-1</sup> DM, total N: 1750 mg kg<sup>-1</sup> DM, mineral N: 33.6 mg kg<sup>-1</sup> DM, carbonates: 47 mg g<sup>-1</sup> DM, organic carbon: 18 mg g<sup>-1</sup> DM, clay: 192 mg g<sup>-1</sup> DM, silt: 488 mg g<sup>-1</sup> DM, sand: 320 mg g<sup>-1</sup> DM.

### 2.2 | Experimental setup

A greenhouse pot experiment was conducted in 1.8 L pots to test the P mobilization potential of red clover for subsequently grown maize. Pot substrate and fertilizers were mixed in April 2015, according to a target of 30.4 mg fertilizer P pot<sup>-1</sup> or 32 mg fertilizer P kg<sup>-1</sup> soil, corresponding to 41.6 kg P ha<sup>-1</sup> (per 10 cm at a bulk density of 1.3 g cm<sup>-3</sup> (Müller & Zhang, 2019)). Eight replicates of each P fertilizer treatment were prepared. Per pot, five plants of red clover (cv. Astur, Delley AG, Switzerland) were sown. Per kg soil DM, 100 mg K (K<sub>2</sub>SO<sub>4</sub>) and 100 mg Mg (MgSO<sub>4</sub>) were applied. Magnesium amounts contained in Mg-SSA (54.3 mg Mg g<sup>-1</sup>) were compensated for in the Mg fertilization. An initial N fertilization (35 mg N kg<sup>-1</sup> soil DM as Ca(NO<sub>3</sub>)<sub>2</sub>) was applied to all pots, in order to promote early growth. Aboveground biomass of clover was harvested three times at flowering; nine, 14 and 21 weeks after sowing, respectively. After first and second harvest of clover, 4 replicates of each P fertilizer treatment received additional N fertilization (Ca(NO<sub>3</sub>)<sub>2</sub>), to prevent BNF. Fertilization rates of N were varied according to the calculated N removal with the aboveground biomass. The N removal with aboveground biomass of clover was assumed to be 40 mg N g<sup>-1</sup> DM (Jungk, 1977) and ranged between 184–284 mg N pot<sup>-1</sup> (first harvest), and 152–192 mg N pot<sup>-1</sup> (second harvest). The N supply of the remaining 4 replicates with clover cultivation was covered by BNF. According to good practice in previous experiments, all pots were kept at 50% water holding capacity using deionized water.

Biomass DM of clover was determined by weighing after it had been dried at 60 °C until constant weight. After third harvest date of clover, pot soil of each pot was wrapped and mixed thoroughly. When dissected, clover root nodules

showing a reddish inside coloration indicated a functioning BNF (Virtanen et al., 1947). Bulk soil and rhizosphere soil was collected separately for pH measurement. Rhizosphere soil was obtained by gently wiping of soil adhering to clover roots after shaking off looser particles, as described by Mat Hassan et al., 2013. Despite careful handling, we cannot completely exclude the possibility of soil sample contamination with fragments of roots and root hair. Soil was returned to pots with clover roots remaining inside. Then, one maize plant (cv. Colisee, KWS Saat SE, Germany) was sown in each pot. During maize cultivation, soil was fertilized with ( $\text{kg}^{-1}$  soil DM) 230 mg N ( $\text{Ca}(\text{NO}_3)_2$ ), 50 mg Mg ( $\text{MgSO}_4$ ) and 235 mg K ( $\text{K}_2\text{SO}_4$ ). Maize was cultivated for 12 weeks (Oct - Dec 2015). During maize cultivation, additional light was used in the greenhouse for  $10 \text{ h d}^{-1}$  with an average light intensity of  $430 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , measured at the height of maize shoot tips. Plants were harvested at flowering stage. Aboveground plant biomass was dried at  $60^\circ\text{C}$  until constant weight and DM content was then determined by weighing.

## 2.3 | Laboratory analysis and calculations

### 2.3.1 | Phosphorus concentration in plant tissue

Dried aboveground plant material of clover and maize was ground using a laboratory disk mill (TS 250, Siebtechnik GmbH, Mülheim an der Ruhr, Germany) and 0.5 g of plant material was extracted in concentrated nitric acid ( $\text{HNO}_3$ ) using the chemical digestion method according to Verband Deutscher landwirtschaftlicher Untersuchungs- und Forschungsanstalten (Kerschberger et al. 2007; VDLUFA, 2011). The P concentration in the extract was measured colorimetrically (Gericke & Kurmies, 1952). Phosphorus removal was calculated from shoot DM and P concentration.

### 2.3.2 | Soil pH

Soil pH of bulk soil and rhizosphere soil after clover cultivation was measured in a 1:2.5 mixture with  $\text{CaCl}_2$  using a digital pH-meter (Metrohm E 532, Herisau, Switzerland).

### 2.3.3 | Calculation of P mobilized by clover with BNF

The amount of additional fertilizer P removal of clover with BNF was calculated as the difference between shoot P removal of BNF clover and clover with added N fertilizer.

The amount of additional fertilizer P removal of maize following clover with BNF, compared to maize following clover with added N fertilizer (% of applied P), was calculated according to the following formula:

$$\text{Additional fertilizer Removal} = \frac{(\text{Removal}_{\text{BNF}} - \text{Removal}_{\text{added N}})}{30.4} * 100$$

where: 'P removal' refers to the shoot P content of maize following clover with different N supply (BNF = biological  $\text{N}_2$  fixation of clover; added N = added N fertilizer 3to clover), in relation to the amount of applied fertilizer P per pot ( $30,4 \text{ mg P pot}^{-1}$ ).

## 2.4 | Data analysis

The experiment was arranged in a completely randomized design including 10 treatments with four replicates, respectively. Two-way ANOVA was performed to study the effect of different P fertilization and N supply of clover, and their interaction on DM, P concentration and P removal with clover and maize biomass, and pH of soil solution (SigmaPlot 11.0). After finding significant differences, all pairwise multiple comparison of the means was conducted (Tukey test, level of significance: 0.05). One-way ANOVA was performed to study the additional fertilizer P removal of clover and maize after clover cultivation with BNF.

## 3 | RESULTS

### 3.1 | Biomass production of clover and maize

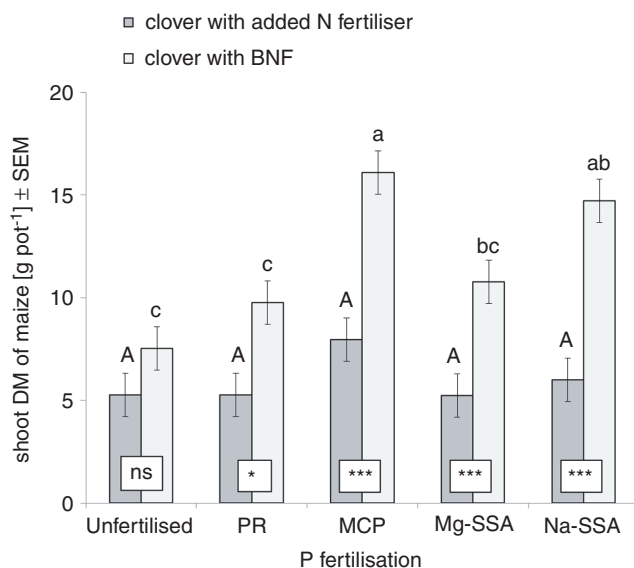
Both the fertilization with different P fertilizers and the N supply of clover significantly influenced shoot DM of clover and maize plants (Table 1, Figure 1). Fertilization with Na-SSA resulted in high shoot DM of clover, at the same level as MCP fertilization. When fertilized with Mg-SSA, DM of clover did not differ from the unfertilized control. Shoot DM of clover was significantly decreased without added N fertilizer (Table 1). Concerning DM of maize plants, there were significant interactions between both factors: different P fertilizers and the N supply of clover. Apart from the unfertilized control, maize biomass was significantly increased in all treatments, when grown after clover with BNF (Figure 1). Differences in DM among the P fertilizer treatments were not significant when grown after clover with added N fertilizer. When grown after clover with BNF, shoot DM of maize was highest in the treatments Na-SSA and MCP, whereas Mg-SSA did not differ from PR and the unfertilized control (Figure 1).

**TABLE 1** Mean shoot DM ( $\text{g pot}^{-1}$ ), P concentration and P removal  $\pm$  SEM of clover and maize plants grown in the pot experiment in dependency of fertilization with different P fertilizers (SSA = sewage sludge ash, treated with Mg or Na, MCP = monocalcium phosphate) and different pre-crop treatment

	Mean shoot DM ( $\text{g pot}^{-1}$ )	Mean shoot P concentration ( $\text{mg P g DM}^{-1}$ )		Mean shoot P removal ( $\text{mg P pot}^{-1}$ )		
	Clover	Clover	Maize	Clover	Maize	
<b>P fertilizer</b>						
Unfertilized	10.6 b	1.73	ns	0.69 ab	17.4 b	4.37 b
Phosphate Rock	10.3 b	1.83		0.73 ab	17.7 b	5.17 b
MCP	13.9 a	1.98		0.65 b	26.0 a	7.29 a
Mg-SSA	11.4 ab	1.79		0.64 b	18.8 b	4.71 b
Na-SSA	13.9 a	1.87		0.79 a	23.4 a	7.08 a
SEM	0.78	0.07		0.03	0.86	0.39
<b>Pre-crop treatment</b>						
Clover with added N fertilizer	12.9 A	1.70 B		0.81 A	20.8	ns
Clover with BNF	11.2 B	1.98 A		0.59 B	20.4	6.72 A
SEM	0.49	0.04		0.02	0.55	0.25

Note: BNF, biological  $\text{N}_2$  fixation; SEM, pooled standard error of the mean.

Lower case letters indicate differences between P fertilization, capital letters indicate differences between pre-crop treatment, ns = not significant (Tukey,  $p \leq 5\%$ ).



**FIGURE 1** Shoot DM ( $\text{g pot}^{-1}$ ) of maize grown in the pot experiment after clover with different pre-crop treatments (BNF = biological  $\text{N}_2$  fixation) and fertilized with different recycled P fertilizers and control fertilizers (PR = Phosphate Rock, MCP = monocalcium phosphate, SSA = sewage sludge ash, treated with Mg or Na). Data are means of four replicates and error bars represent standard error of the mean. Different letters indicate significant differences between P fertilizer treatments when grown after clover with added N fertilizer (upper case letters) or after clover with biological  $\text{N}_2$  fixation (lower case letters) (Tukey,  $p \leq 5\%$ ). Asterisks indicate significant differences within the same P fertilizer treatment as \*\*\* (significant at  $p \leq 0.001$ ), \* (significant at  $p = 0.005$ ) and ns (not significant)

### 3.2 | Shoot P removal and P concentration of clover

Shoot P concentration of clover biomass was not influenced by P fertilization, but by N supply. BNF significantly increased shoot P concentration compared to clover with added N fertilizer (Table 1). Shoot P removal of clover was influenced by different P fertilization, but not by the N supply (Table 1). The total P removals of all three clover harvests ranged between  $17.4 \text{ mg pot}^{-1}$  (Unfertilized) and  $26.0 \text{ mg pot}^{-1}$  (MCP). The statistically higher P removals in the Na-SSA and the MCP treatments corresponded to 19.7% and 28.3% of total applied fertilizer P, respectively. Different N supply paths did not affect shoot P removal of clover.

### 3.3 | Shoot P removal and P concentration of maize

When clover was cultivated previously, significantly higher shoot P removal of maize was achieved when N supply of clover was covered by BNF (overall mean:  $6.72 \text{ mg P pot}^{-1}$ ) instead of added N fertilizer (overall mean:  $4.73 \text{ mg P pot}^{-1}$ ) (Table 1). The highest overall mean P removals were found with the fertilizer treatments MCP ( $7.29 \text{ mg pot}^{-1}$ ) and Na-SSA ( $7.08 \text{ mg pot}^{-1}$ ), while the mean removals of the treatments PR and Mg-SSA did not differ from the unfertilized control (Table 1).

With added N fertilizer to clover, no P fertilizer effects in the subsequent maize crop were measured for

the treatments PR and Mg-SSA, compared to the unfertilized control, and only a slight increase in P removal in the treatments MCP (7.27% of applied P) and Na-SSA (5.72% of applied P) were measured. Shoot P removal of maize was significantly higher when grown after clover with BNF (6.72 mg P pot<sup>-1</sup>) compared to clover with added N fertilizer (4.73 mg P pot<sup>-1</sup>). The additional fertilizer P removal of maize following clover with BNF, compared to clover with added N fertilizer, ranged between (mg P pot<sup>-1</sup>) 1.69 (Mg-SSA) and 3.54 (Na-SSA) (Table 2), corresponding to 5.57% and 11.6% of applied P, respectively.

### 3.4 | pH value of bulk soil and rhizosphere soil

Soil pH of bulk soil and rhizosphere soil after clover cultivation was significantly influenced by the different N supply during clover cultivation, independently from the P fertilization (Table 3). On average, pH decreased from 7.47 (added N fertilizer) to 7.34 (BNF) in bulk soil, and from 7.37 (added N fertilizer) to 7.19 (BNF) in rhizosphere soil.

## 4 | DISCUSSION

### 4.1 | Phosphorus mobilization by red clover grown with BNF

The results indicate that the growth of clover and maize was limited by the plant P availability in soil (Table 1, Figure 1). Furthermore, although the P removals by clover accounted for at maximum 28.3% (MCP) of applied fertilizer P, growth of subsequent maize was strongly limited by the P availability in all treatments. This indicates that soil and fertilizer P were not able to compensate for the P removals from clover. Despite the extremely low P level of some 0.06% P in maize

plants, no optical signs of P deficiency, such as anthocyanin colouring of biomass, was visible.

The hypothesized P mobilization potential of red clover with BNF to enhance removals of soil and fertilizer P (hypothesis 1) has to be rejected for clover plants itself, because clover grown with BNF was not able to increase its own shoot P removal compared to clover supplied with added N fertilizer (Table 1). Also, in the unfertilized control, clover with BNF was not able to enhance its own P supply (data are not shown) as well as the P supply of a following maize (Figure 1), indicating that there was no mobilization of soil P through clover cultivation with BNF.

However, hypothesis 2, assuming that a clover growth with BNF is able to enhance the crop growth of a subsequently grown maize, could be confirmed for all treatments receiving P fertilizer (Figure 1).

The decreased soil pH after clover cultivation with BNF (Table 3) support the hypothesis that a proton release from roots of clover with BNF led to a dissolution of sparingly soluble P, like calcium-phosphates (Gerke et al., 2000; Hauter & Steffens, 1985). Changes in soil pH have influenced the plant P availability to the subsequent maize. Other possible mechanisms that might have contributed to the P mobilization by clover, yet were not investigated in the experiment, include a growth promotion of plant growth promoting rhizobacteria (Horst et al., 2001; Pypers et al., 2007) and a mobilization of adsorbed P (from soil or fertilizers) by the excretion of citrate from red clover roots (Gerke et al., 2000).

### 4.2 | Phosphorus mobilization by clover with BNF for subsequent maize

The higher additional P removal of maize in all treatments with added P fertilizer (Table 2) shows that clover grown with BNF was able to enhance the availability of the applied fertilizer P to the subsequent crop, even for the non-reactive P fertilizer Mg-SSA.

	Additional P removal of clover with BNF ± SEM		Additional P removal of maize ± SEM	
	(mg P pot <sup>-1</sup> )	ns	(mg P pot <sup>-1</sup> )	(% of applied P)
Unfertilized	-0.47 ± 2.08	ns	0.90 ± 0.76	ns
Phosphate Rock	-0.39 ± 1.66		2.16 ± 0.82	7.09 ± 2.70
MCP	-3.22 ± 2.02		2.33 ± 0.53	7.65 ± 1.75
Mg-SSA	0.20 ± 1.38		1.69 ± 0.33	5.57 ± 1.09
Na-SSA	-3.35 ± 2.60		3.54 ± 1.09	11.6 ± 3.59
Mean	-1.45 ± 1.93		2.12 ± 0.36	7.99 ± 1.25

TABLE 2 Mean additional P removal ± SEM of clover and maize after clover cultivation with biological N<sub>2</sub> fixation (BNF) compared to clover with added N fertilizer, and fertilization with different P fertilizers

Note: (SSA = sewage sludge ash, treated with Mg or Na, MCP = monocalcium phosphate) and control fertilizers. ns = not significant, SEM = standard error of the mean (ANOVA,  $p \leq 5\%$ ).

**TABLE 3** pH (CaCl<sub>2</sub>) of soil solution measured after clover cultivation in bulk soil and rhizosphere soil, in dependency of different N supply of clover (BNF = biological N<sub>2</sub> fixation) and fertilization with different P fertilizers

N supply of clover (N)	P fertilizer (P)	pH	
		Bulk soil	Rhizosphere soil
Added N fertilizer	Unfertilized	7.5	7.4
	Phosphate Rock	7.5	7.4
	MCP	7.5	a 7.4
	Mg-SSA	7.5	7.4
	Na-SSA	7.5	7.4
	Mean	7.5	7.4
BNF	Unfertilized	7.4	7.2
	Phosphate Rock	7.4	7.3
	MCP	7.3	b 7.2
	Mg-SSA	7.3	7.2
	Na-SSA	7.4	7.2
	Mean	7.4	7.2
Source of variation (ANOVA)			
P		0.106 <sup>ns</sup>	0.478 <sup>ns</sup>
N		<0.001 <sup>***</sup>	<0.001 <sup>***</sup>
P × N		0.235 <sup>ns</sup>	0.134 <sup>ns</sup>

Note: (SSA = sewage sludge ash, treated with Mg or Na, MCP = monocalcium phosphate) and their interaction. Different letters indicate differences between different N supply of clover. *F*-values of two-way ANOVA indicate source of variation as \*\*\* (significant at  $p \leq 0.001$ ) and ns = not significant.

The results illustrate, that the P fertilizer effects of PR and Mg-SSA were stronger to the following maize (accounting for 7.09% and 5.57% of the applied P fertilizer (Table 2)) than to the clover itself (Table 1, Figure 1), at least considering the plant shoots that were investigated in the experiment. Hauter and Steffens (1985) reported a strongly increased DM, density and surface of red clover roots when grown under BNF, compared to clover with added N fertilizer, while aboveground biomass was the same in both treatments. Thus, an increased exploitation of soil volume through an increased root biomass of clover with BNF might have contributed to a better utilization of available P in soil solution. This assumption is supported by findings of Gerke et al. (2000), who reported an increased P removal within dense root systems, because mobilized P, which is transported away from a single root can be absorbed by neighbouring roots in the close proximity.

Mat Hassan et al. (2012) reported a depletion of labile and less labile P pools in the rhizosphere of white lupin. However, this P was apparently not taken up by lupin itself, but instead led to an increased growth and P removal of a following wheat (compared to other legume species). Similarly, huge increases in P removal of maize have been reported when cultivated after velvet bean, compared to a sole maize crop rotation (Pypers et al., 2007). Vanlauwe et al. (2000) reported that the legumes *Mucuna pruriens* L. and *Lablab purpureus* L. may have improved the P

availability from RP in excess of their own need and by this contributed to an improved P nutrition of a following maize.

A mobilization effect of P from clover to the subsequently grown maize can be concluded from significant differences in shoot P removal of maize due to N supply of clover following non-significant differences for the clover biomass itself (Table 1). Therefore, clover grown with BNF were able to mobilize sparingly soluble fertilizer P. It is suggested that the reported proton release through BNF of clover (Hauter & Steffens, 1985; Liu et al., 1989) led to a mobilization of sparingly soluble P from recycled fertilizers. These findings are supported by the decreased soil pH after clover cultivation (Table 3), which was pronounced the most in treatments with BNF. It has been shown that the pH difference is even stronger in close proximity of the root surface (Li et al., 1991; Gahoonia et al. 1992). However, in the present test conditions, the observed decrease of pH in rhizosphere soil compared to the initial soil pH was sufficient to mobilize relevant amounts of P. For future studies, we suggest a performance of thermodynamic calculations, which may help to support the assumption that a decrease in soil pH leads to a dissolution of different Ca phosphates (Song et al., 2002) in the rhizosphere.

Besides the mobilization of sparingly soluble P, it is suggested that a recycling of P from decomposed clover roots in addition contributes to an increased P supply

of maize (Horst et al., 2001; Nuruzzaman et al., 2005). Hauter and Steffens (1985) found a higher biomass, density, length and surface of roots from red clover with BNF, compared to those with added N fertilizer. Thus, an increased amount of recycled P from a higher root biomass in these treatments might have contributed to a better P nutrition of the following maize.

The response to the P mobilization mechanisms by clover with BNF was not as high in the unfertilized treatment. (Figure 1). It is suggested that a lack of (bioavailable) P reduced the N<sub>2</sub> fixation (Hellsten & Huss-Danell, 2000; Morton & Yarger, 1990). However, 7.09% of the applied PR could be mobilized by symbiotically grown clover (Table 2). Overall, the additional P removal of up to 11.6% of applied P (Na-SSA) through clover cultivation with BNF (Table 2) is a promising result, underlining the potential of biological P mobilization. We conclude, that red clover with BNF can contribute to an enhanced P supply of a following maize in the crop rotation, but external P inputs are still necessary during maize cultivation to secure optimum plant growth.

Under field conditions, different external factors influence the P fertilizer efficacy and plant growth. This pot experiment was conducted in a substrate of mixed soil and sand, and cannot unreservedly be transferred to field conditions (Wollmann & Möller, 2018). Therefore, field experiments are needed in legume based crop rotations of organic farming systems, to analyse mobilization and immobilization of P from recycled fertilizers, and validate findings from greenhouse trials.

## 5 | CONCLUSIONS

The effect of red clover on the soil P turnover is dependent on the BNF activity, and the P mobilization potential from PR for subsequently grown crops has been shown to be effective also for P fertilizers recycled from sewage sludge. This effect might be dedicated to a decreased soil pH, induced by the proton release during BNF of clover. We conclude that a marginal decrease of pH is sufficient for the mobilization of significant amounts of fertilizer P, but not soil P. Thus, a P fertilization to red clover contributes to an increased P availability for a following maize in the rotation, but, in low P soils, external P inputs to maize are still necessary to secure optimum plant growth. For a specification of P turnover processes in soil, future pot experiments should include the analysis of P species in the substrate (e.g. Hedley fractionation method) before and after clover and maize cultivation. In soil with pH <5.5 the fertilization with recycled P fertilizers to a clover-maize crop rotation might be sufficient to meet the P demand of brood crops, because other P mobilization mechanisms

take place, such as the solubilization of inorganic P compounds by the excretion of carboxylic acids from clover roots.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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