

## Article

# Phosphorus Availability from German Sewage Sludge Ashes to Plants Cultivated in Soilless Growing Media of Contrasting pH

Daniel Hauck <sup>1,2,\*</sup>, Dieter Lohr <sup>1</sup>, Elke Meinken <sup>1</sup> and Urs Schmidhalter <sup>2</sup> 

<sup>1</sup> Institute of Horticulture, Weihenstephan-Triesdorf University of Applied Sciences, Am Staudengarten 14, 85354 Freising, Germany

<sup>2</sup> Chair of Plant Nutrition, Technical University Munich, Emil-Ramann-Straße 2, 85354 Freising, Germany

\* Correspondence: daniel.hauck@tum.de

**Abstract:** Sewage sludge ash (SSA) as a secondary phosphorus (P) source may help to conserve global rock phosphate deposits if used in the base fertilization of soilless growing media. Plant availability of SSA-P was studied in a pot experiment with marigolds in a peat-based growing medium of contrasting pH (4.5, 6.0). Six SSAs were included in the study and compared to water-soluble monocalcium phosphate (MCP) and rock phosphate (RockP). In addition to the efficacy of SSA-P, calcium chloride + diethylenetriaminepentaacetate (CAT) and calcium-acetate-lactate (CAL), as commonly used extractants in Germany to analyze plant-available P in growing media, were tested in terms of their ability to predict plant P uptake. No SSA reached the relative P use efficiency (rPUE) observed for MCP. However, at a growing medium pH of 4.5, the average rPUE for SSA was 70% of the MCP rPUE. Compared to RockP, at a growing medium pH of 6.0, SSAs resulted in an rPUE of nearly the same low level. In contrast, at pH 4.5, the rPUE from SSAs was mostly lower than that from RockP, and there were differences in rPUE among SSA origins. Therefore, in addition to a variation in particle size distribution, there might be differences in the P-bearing phase. Sewage sludge ashes represent a promising substitute for primary P sources only in crops requiring a low pH in the growing medium. The extractants CAT and CAL, on their own or in combination, did not reflect plant P uptake from SSA. To improve the prediction of plant-available SSA-P, solvent modifications or additional extractants might be promising and should be subjected to further research.

**Keywords:** fertilization; horticulture; phosphorus recycling; monoincineration ash; pH effect; secondary P source; plant production



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## 1. Introduction

Phosphorus (P) fertilizers are crucial for ensuring crop production [1]. However, rock phosphate (RockP) deposits primarily used for fertilizer production will be depleted within the next centuries [2,3]. Closing the P cycle in agriculture is necessary to secure sustainable use of the limited resource RockP [4–7]. In this light, P recovered from secondary sources may help close the cycle. A high potential for P recovery is found in sewage sludge ash (SSA) [8,9], which occurs in large quantities. In Germany, approximately 1.8 million tons of dry sewage sludge (SS) arise annually [10]. Nearly 70% of this sludge is incinerated with increasing occurrence [10] due to stricter regulations for the application of SS [11]. When used as fertilizer, SSA has fewer harmful environmental effects (no organic pollutants and pathogens, less volatile heavy metals) than SS [8]. In addition, the availability of SSA-P must also be considered in crop production.

In monoincinerated SSAs, the relevant P compounds driving plant P availability are different forms of iron and aluminum phosphates (FeP, AlP) as well as calcium phosphates (CaP) of higher crystallinity [12]. In soil-based crop production, Ca-associated P forms (e.g., whitlockite and hydroxylapatite) have been reported to be more available to plants than AlP and FeP (e.g., variscite and vivianite). This was especially found in

acidic soils [13,14]. In SSAs, the proportion of these P forms varies among ashes [15]. This variability is due to the chemical composition of the initial sewage sludge [16] driven by the P elimination strategy of the wastewater treatment plant (P elimination with or without Al/Fe flocculants) [17] and seasonal variations in the treated wastewater [18]. Kratz et al. [15] summarized the plant availability of SSA-P from low to medium, reporting equivalents from 0 to 52% of fully plant-available P forms (e.g., monocalcium phosphate).

Besides soil-based production, relevant cropping systems use soilless growing media. In 2021, approximately 12 million cubic meters of growing media were produced in Germany [19], consisting primarily of peat and organic and mineral peat substitutes (e.g., wood fiber, green compost and clay). Base growing media fertilization utilizing SSA-P could help to conserve finite RockP reserves. However, the results concerning the efficacy of SSA-P derived from soil-based production might not be transferable to soilless cultivation, as P dynamics, mainly driven by P buffering capacity, differ between mineral soils and growing media. As the primary growing medium constituent, peat has a negligible ability to buffer P [20]. As such, the resulting higher P mobility in growing media enables roots to expand their depletion zone by approximately ten times compared to mineral soil [20]. Consequently, roots' enhanced and overlapping depletion zones promote higher spatial P accessibility in soilless cultivation. In addition, peat's low P buffering capacity also means that the chemical availability of P entirely depends on the equilibrium position between dissolved and solid P. The pH in the growing medium, among other things influenced by the cultivated crop [21], contributes to the equilibrium position depending on present P compounds. The plant availability of Ca-associated P decreases with increasing pH, whereas the reverse is true for Fe- and Al-associated P.

To the best of the authors' knowledge, the suitability of P recovered from wastewater for crop production in growing media has been investigated in only a few studies [22,23], and none of them compared different SSAs. Therefore, this was investigated in the present research work. In addition to the lack of knowledge about the efficacy of SSA-P in growing media-based crop production, the feasibility of commonly used methods of growing media analyses predicting plant available P remains unknown. To assess plant-available P in growing media, extraction-based methods established in Germany use calcium chloride + diethylenetriaminepentaacetate (CAT) and calcium-acetate-lactate (CAL) as solvents. According to Alt et al. [24], readily soluble P is well indicated by the CAT method, whereas less soluble but plant-available P reserves, such as iron and aluminum phosphates, are underestimated [25]. In contrast, CAL frequently overestimates plant P availability, especially when sparingly soluble CaP is applied or growing media are rich in clay and high in pH, respectively [24,26]. To overcome these solvent-specific limitations in over- and underestimating P pools, Hauck et al. [23] developed a new approach combining CAT- and CAL-extractable P by using secondary P sources. However, the developed model is valid for a growing medium pH of 6.0 commonly used in soilless production. Thus, it remains questionable whether this new approach is suitable to characterize the plant availability of SSA-P irrespective of the growing medium pH.

To address the identified knowledge gaps regarding plant availability of SSA-P in soilless plant production and its predictability, a pot trial was conducted using marigold (*Tagetes patula* × *erecta*) as a P-sensitive model plant. Different SSAs were tested in a peat-based growing medium under contrasting pH values (4.5 and 6.0), and their P efficacy was compared to water-soluble monocalcium phosphate (MCP) and RockP as controls. The prediction model, according to Hauck et al. [23], was used to assess P availability. We hypothesized that (1) the plant availability of SSA-P cannot compete with that of water-soluble P, (2) one single solvent is not suitable for assessing the plant availability of SSA-P through growing media analyses, and (3) the combined approach by Hauck et al. [23] improves the prediction of plant P availability, irrespective of the growing medium pH.

## 2. Materials and Methods

### 2.1. SSAs and Control Fertilizers

Six SSAs obtained from German mono-incineration plants (one batch each from three origins and three batches from one origin) were tested as P fertilizers in this study (Table 1). To characterize the SSAs, the particle size distribution was measured in triplicate using an SDC–Microtrac S3500 laser diffraction system (Microtrac, Montgomery Ville, PA, USA) (Table 2). In addition, after acid digestion in aqua regia [27], the total content of P and heavy metals of the SSAs was measured in duplicate with ICP-OES (iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany) using the following wavelengths (in nm): P 213.6, As 189.0, Cd 228.8, Tl 190.8, Hg 184.9, Ni 231.6, Pb 220.3.

**Table 1.** Overview of the tested sewage sludge ashes.

SSA	Incineration Facility	Information about the Wastewater Treatment Plant *		P Removal
		Origin of Sewage Sludge	Type of Wastewater	
Trollins (batches 1–3)	Steinhaeule by Neu-Ulm city	Wastewater association Klaerwerk Steinhaeule	Municipal, few industrial	Al + Fe salts
Ostrau	Emter GmbH by Altenstadt city	Various bavarian wastewater treatment plants	Municipal	No data available
Luenen	Innovatherm GmbH by Luenen city	Wastewater associations, industrial companies (pharmaceutical, chemical, metal processing)	Municipal, industrial	No data available
Grosslappen	Gut Grosslappen by Munich city	Wastewater treatment plant Gut Grosslappen	Municipal, few industrial	Biological + Al salts

\* Source: personal communication.

**Table 2.** Particle size distribution of the SSAs expressed as a percentage of the total number of particles. The total content of P is indicated in g (kg dry matter (DM))<sup>−1</sup> and heavy metals in mg (kg DM)<sup>−1</sup> of the SSAs.

SSA	<160 μm	160–630 μm	>630 μm	P <sub>total</sub> g (kg DM) <sup>−1</sup>	As	Cd	Tl	Hg	Ni	Pb
	% of Total Particles									
Trollins1	64	36	0	67.0	14.6	1.3	<0.5 *	<0.5 *	56.1	64.2
Trollins2	51	49	0	58.5	13.8	10.5	<0.5 *	<0.5 *	49.3	65.6
Trollins3	55	45	0	59.9	13.7	11.3	<0.5 *	<0.5 *	53.3	64.9
Ostrau	34	39	27	88.6	8.0	17.4	<0.5 *	<0.5 *	39.5	45.3
Luenen	69	31	0	22.4	17.2	20.7	<0.5 *	<0.5 *	285.3 †	222.1 †
Grosslappen	65	35	0	96.4	16.6	10.4	<0.5 *	<0.5 *	39.0	103.0

\* Values smaller than the declaration threshold according to the German fertilizer ordinance (2012, last amended 2019). † Values above the limit according to the German fertilizer ordinance (2012, last amended 2019).

As control fertilizers, water-soluble MCP (Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O, analytical grade, Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany) and finely ground RockP (Hyperphos, producer unknown) were used.

### 2.2. Growing Medium

White peat (Pater Erden GmbH, Sinnatal-Altengronau, Germany) (Table 3) was used as the growing medium. A P-free multi-nutrient fertilizer (19-0-15) with trace elements (custom blend, Planta Düngemittel GmbH, Regenstau, Germany) was dissolved for base fertilization in deionized water and evenly mixed into the peat at a level of 200 mg N L<sup>−1</sup>. After base fertilization, the peat was split into two equal parts and limed to pH 4.5 (typical for acidophilic plants, such as Azalea) and 6.0 (typical for most ornamental plants) using Otterbein Naturkalk (85% CaCO<sub>3</sub>, Zement- und Kalkwerke Otterbein GmbH und Co.

KG, Großenlueder-Mues, Germany). Subsequently, SSAs and control fertilizers were homogeneously mixed into individual growing medium portions at 70 mg aqua regia extractable P L<sup>-1</sup> (equivalent to 25 mg P pot<sup>-1</sup>). SSAs and RockP were applied in solid form, whereas fully water-soluble MCP was provided as a solution. To ensure equal amounts of P per pot, the growing medium was added to the pots by weight immediately before transplanting the precultivated marigold seedlings.

**Table 3.** Characterization of white peat. The degree of degradation according to the von Post scale and the particle size in millimeters taken from the manufacturer’s declaration. The pH is indicated in CaCl<sub>2</sub> [28]; water-soluble salts are expressed in grams of KCl per liter [29], and CAT-soluble N, P and K are expressed in milligrams per liter [30].

	Degree of Degradation *	Particle Sizemm	pH (CaCl <sub>2</sub> )	Salts (H <sub>2</sub> O)g KCl L <sup>-1</sup>	N (CAT)	P (CAT) mg L <sup>-1</sup>	K (CAT)
White peat	H3–H5	<8	3.1	0.10	17	0	8

\* From H1 (non-decomposed bog plants) to H10 (fully decomposed bog plants).

### 2.3. Cultivation Management and Experimental Design

*Tagetes patula* × *erecta* ‘Zenith Red F1’ (Floranova Ltd., Foxley, UK) was used as a P-sensitive model plant. Seeds were sown in weakly fertilized peat (70 mg N, 40 mg P and 75 mg K L<sup>-1</sup>) limed to pH 5.5. After pre-cultivation for 10 days, seedlings were pricked individually into plastic pots (diameter 10 cm, volume 400 mL; Teku, Pöppelmann Kunststoff-Technik GmbH & Co. KG, Lohne, Germany). For each treatment, the number of planted pots was 48. They were split into four repeats and arranged in a randomized block design in the greenhouse. The greenhouse’s climate control system was adjusted to 22/20 °C (day/night) for heating and 25 °C for ventilation. Plants were fertilized weekly according to the nutrient demand determined in previous trials (data not shown). For this fertilization, the P-free fertilizer used for base fertilization was dissolved in deionized water and applied in doses of 20 mg N per plant (once in week 2, twice in week 3 and three times in week 4). Between the fertilization events, irrigation was performed from above with deionized water to maintain adequate moisture in the growing medium according to good horticultural practice. To prevent nutrient leaching, the pots were placed into saucers and flushed twice with deionized water during cultivation. Leachates and rinse water were poured back into the pots. Due to infestations of thrips and leaf miners, the plant protection agent Conserve (Corteva Agriscience Germany GmbH, Munich, Germany) was used three times at a concentration of 0.075%. After four weeks of cultivation, 90% of the plants reached flowering (marketable stage) and were harvested.

### 2.4. Data Collection

For data collection at harvest time, pots of each treatment were pooled per replicate. First, the fresh weight of the shoots was determined. Then, the plant material was dried in a forced-air oven at 70 °C, and the dry weight was recorded after reaching weight constancy. For analyses of P content, the plant material was ground to a particle size <0.5 mm using a centrifugal mill (ZM1, Retsch, Haan, Germany) and digested in a mixture of HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> under pressure in a microwave oven (Multiwave ECO, Anton Paar, Graz, Austria) according to Miller [31]. Subsequently, P analyses were performed using ICP-OES (iCap 6000 DV, Thermo Fisher Scientific, Dreieich, Germany). The P uptake of plants was calculated by multiplying the P content by the dry weight, and the relative phosphorus use efficiency (rPUE) was expressed as the percentage of applied P.

In addition to the plant analyses, the amounts of CAL-soluble phosphate (P<sub>CAL</sub>) and CAT-soluble phosphate (P<sub>CAT</sub>) in the growing medium were analyzed at the start of the trial and at harvest time. For P<sub>CAL</sub>, the extraction ratio was 1 + 20 (M + V) and the extraction time 90 min [32]. For P<sub>CAT</sub>, the extraction ratio was 1 + 8 (M + V), and the extraction

time 60 min [30]. After filtration, the P concentration in the filtrates were determined analogously to the plant analysis by ICP-OES.

For quality assurance of analytical data, sample duplicates were performed and reference materials were used. In cases of unexplainable differences between sample duplicates, the analyses were repeated. The use of analytical instruments was according to the manufacturers' user manual.

### 2.5. Statistical Analysis

Minitab V18 (Minitab Inc., State College, PA, USA) was used for the statistical analysis, and MS Excel 2016 (Microsoft Corporation, Redmond, WA, USA) was used for data visualization. For plant fresh weight as well as P content and P uptake of the plants, at first, a two-way ANOVA using the GLM function was performed. Due to the interaction between the factors SSA and pH, SSAs were compared to the controls MCP and RockP separately for each pH using Dunnett tests ( $p < 0.05$ ). After removing the control treatments, the effects of SSA type and growing medium pH on rPUE were tested similarly using Tukey tests ( $p < 0.05$  and  $p < 0.001$ ). The P uptake in relation to the extractable P amount in the growing medium at the trial start ( $P_{CAT}$ ,  $P_{CAL}$ , respectively) was visualized in a scatter plot. The same was done for the plant-available P estimated by the prediction model of Hauck et al. [23]. A correlation coefficient was not calculated due to pH-specific clusters, leading to spurious correlations and thus misinterpretations [33].

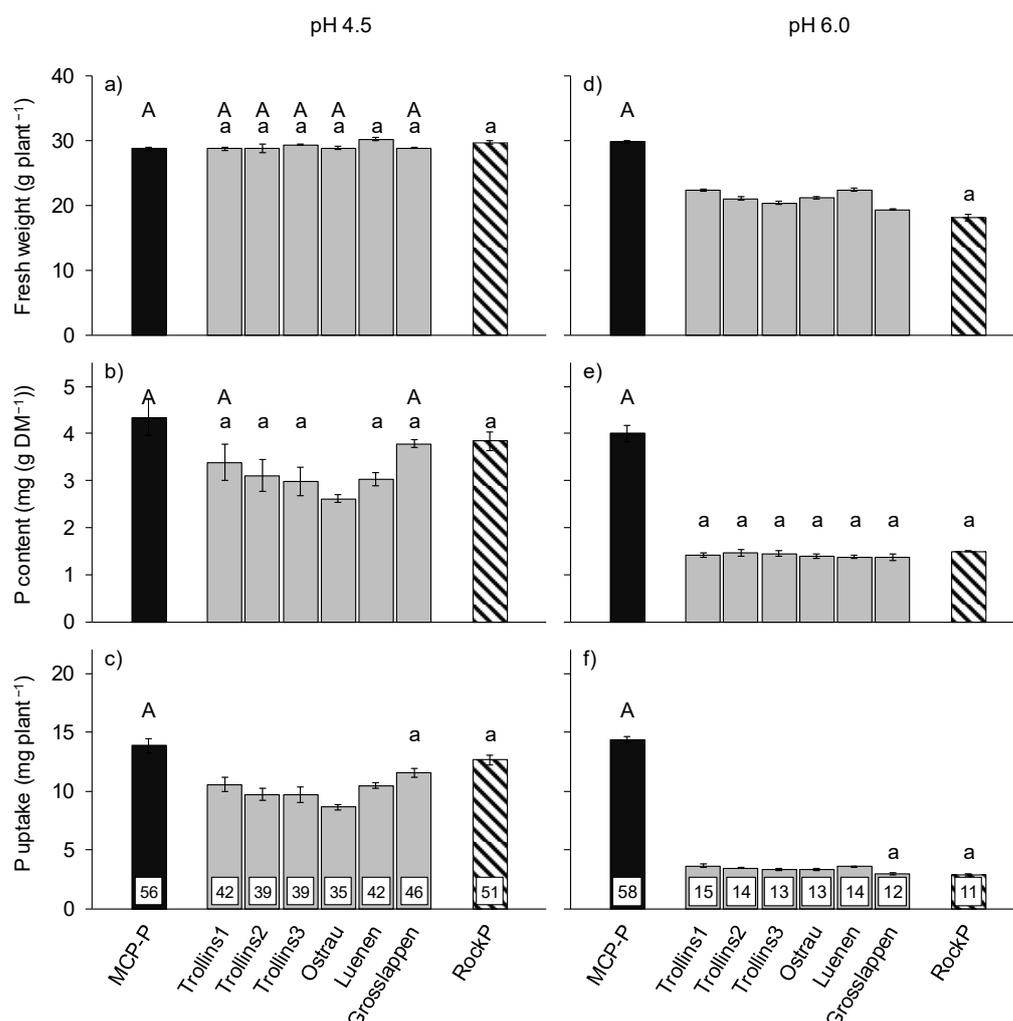
## 3. Results

### 3.1. Efficacy of SSA-P at pH 4.5

At a pH of 4.5 in the growing medium, the fresh weight of plants fertilized with different SSA types ranged from 28.8 to 30.3 g per plant (Figure 1a). No significant differences were found between the SSAs and the RockP control. Only the SSA Luenen led to a slightly higher plant fresh weight than the water-soluble MCP control. Considering the P content of the plants (Figure 1b), several significant differences were observed between the controls and the SSAs. However, in the comparison to RockP ( $3.8 \text{ mg (g DM)}^{-1}$ ), only the SSA Ostrau resulted in a lower plant P content ( $2.6 \text{ mg (g DM)}^{-1}$ ). Furthermore, three SSAs (Trollins2, Trollins3, Luenen) did not reach the level of the MCP control ( $4.3 \text{ mg (g DM)}^{-1}$ ). The most significant differences were found for plant P uptake and rPUE (Figure 1c) compared to the two controls. None of the SSAs exhibit values (P uptake:  $8.6\text{--}11.6 \text{ mg plant}^{-1}$ , rPUE: 35–46%) comparable to the MCP control (P uptake:  $13.9 \text{ mg plant}^{-1}$ , rPUE: 56%). Only for the SSA Grosslappen, P uptake and rPUE did not differ from those of the RockP control (P uptake:  $12.7 \text{ mg plant}^{-1}$ , rPUE: 51%).

### 3.2. Efficacy of SSA-P at pH 6.0

At a pH of 6.0 in the growing medium, all SSAs led to a significantly higher plant fresh weight ( $19.4\text{--}22.5 \text{ g plant}^{-1}$ ) than the RockP control ( $18.2 \text{ g plant}^{-1}$ ) (Figure 1d). However, none of the SSAs reached the level of the MCP control. Similar to the plant fresh weight, the P content of all SSA fertilized plants ( $1.4\text{--}1.5 \text{ mg (g DM)}^{-1}$ ) was significantly lower compared to the MCP control ( $4.0 \text{ mg (g DM)}^{-1}$ ), whereas there were no differences compared to the RockP control (Figure 1e). The most negative impact of the SSAs was observed for plant P uptake and rPUE (Figure 1f). The levels (P uptake:  $3.0\text{--}3.7 \text{ mg plant}^{-1}$ , rPUE: 12–15%) were approximately four times lower than the MCP control. Nevertheless, except for the SSA Grosslappen, plant P uptake and rPUE slightly exceeded the values of the RockP control.



**Figure 1.** Fresh weight (a,d), phosphorus (P) content (b,e) and P uptake (c,f) of marigold plants fertilized with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen), monocalcium phosphate (MCP) or rock phosphate (RockP) after cultivation for four weeks under contrasting pH conditions (4.5, 6.0). Values in the columns of subfigures c and f indicate the P use efficiency in % of applied P. Sewage sludge ashes with capital “A” did not differ significantly from MCP control, nor did those with lowercase “a” from RockP control (Dunnnett test,  $p < 0.05$ ). Error bars represent the standard error of mean ( $n = 4$ ).

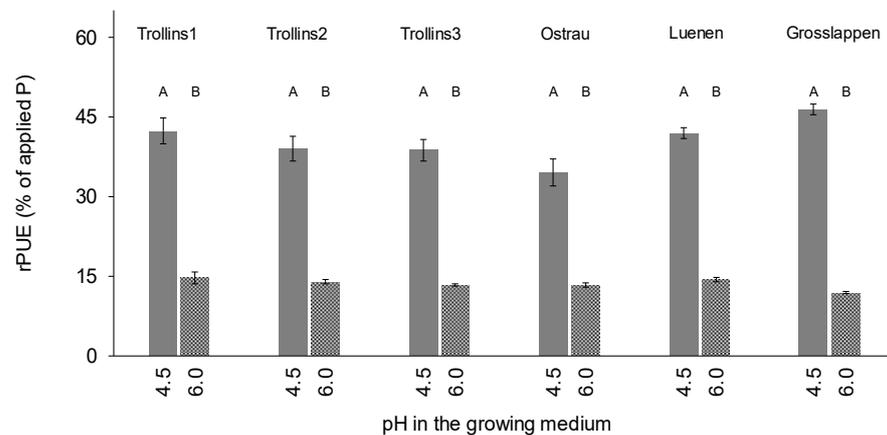
### 3.3. Effect of pH on rPUE

For all tested SSAs, the pH in the growing medium significantly effected the rPUE (Figure 2). While rPUE ranged from 11.9–14.4% at the pH of 6.0, it increased up to 35–46% at a pH of 4.5. However, the extent of this pH effect depends on the SSA type (Figure 3). The rPUE difference between pH 4.5 and 6.0 was significantly lower for the SSAs Trollins2 (25 percentage points), Trollins3 (25 percentage points) and Ostrau (21 percentage points) compared to the SSA Grosslappen (35 percentage points). The SSAs Trollins1 and Luenen showed an intermediate position and did not significantly differ from the SSA Grosslappen.

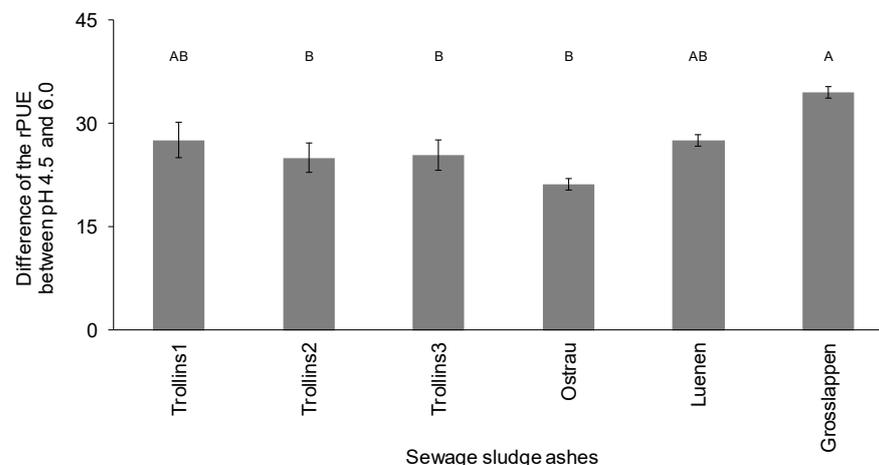
### 3.4. Effect of SSA Type on rPUE

The rPUE of the three SSA batches originating from Trollins did not differ significantly, irrespective of the pH in the growing medium (Figure 4). In contrast, variations in rPUE were found in respect of the SSA origin. At a pH of 4.5 in the growing medium, the rPUE of the SSA Ostrau (35%) was significantly lower compared to the SSA Grosslappen

(46%). The rPUE of the SSA batches originating from Trollins and the rPUE of the SSA Luenen were at a medium level. At a pH of 6.0 in the growing medium, fertilization with the SSA Grosslappen led to a significantly lower rPUE (11.9%) than the SSAs Trollins1 (14.4%), Trollins2 (13.9%) and Luenen (14.4%), whereby the latter three did not differ among themselves. An intermediate position was observed for the rPUE of the SSAs Ostrau (13.3%) and Trollins3 (13.3%).



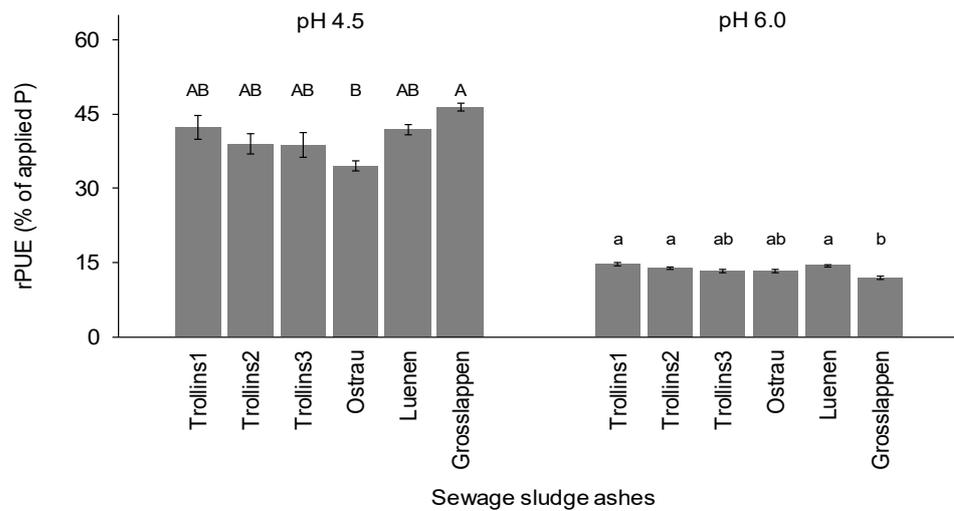
**Figure 2.** Relative phosphorus use efficiency (rPUE) at two contrasting pH levels in the growing medium for each sewage sludge ash (SSA). Different letters indicate differences between the pH levels for each SSA (Tukey,  $p < 0.001$ ), and error bars indicate the standard error of mean ( $n = 4$ ).



**Figure 3.** Difference of relative phosphorus use efficiency (rPUE) in percentage points between pH 4.5 and 6.0 for each sewage sludge ash (SSA). Different letters indicate differences between the SSAs (Tukey test,  $p < 0.05$ ), and error bars indicate standard error of mean ( $n = 4$ ).

### 3.5. Growing Media Analyses and Estimated Plant P Availability

Analyses of the growing media (Table 4) showed that  $P_{CAL}$  was consistently higher than  $P_{CAT}$ , whereby the difference was more evident at the higher growing medium pH of 6.0. At the beginning of the experiment, all SSAs except Luenen resulted in extremely low values ranging for  $P_{CAL}$  and  $P_{CAT}$ , ranging from 6 to 20% and 0 to 14% of applied P, respectively. For the SSA Luenen,  $P_{CAL}$  and  $P_{CAT}$  were much higher compared to the other SSAs and partly exceeded the value of the RockP control. However, the level of MCP was not reached by far. At the end of the study, only small differences in  $P_{CAT}$  and  $P_{CAL}$  were found between the SSAs.

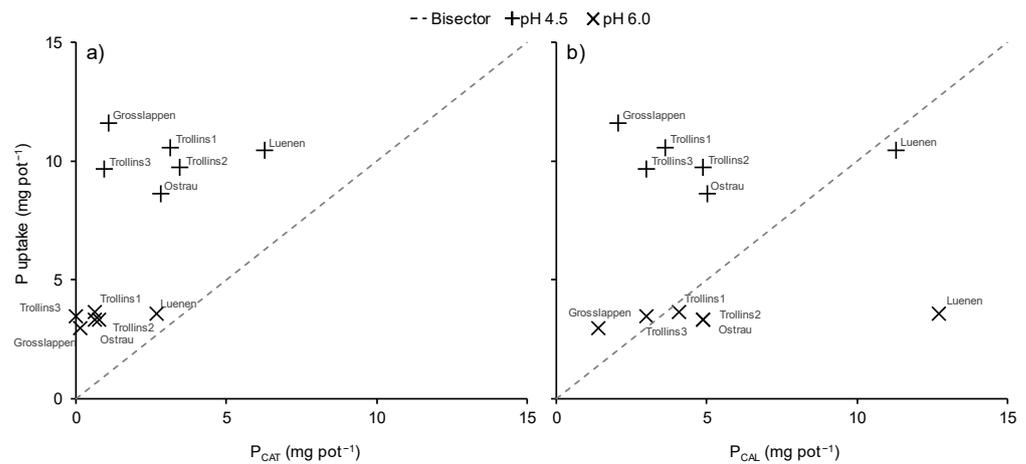


**Figure 4.** Relative phosphorus use efficiency (rPUE) of different types of sewage sludge ashes (SSA) at two contrasting pH levels in the growing medium. Different capital letters indicate differences (Tukey,  $p < 0.05$ ) between the SSAs at pH 4.5, and lowercase letters indicate differences between the SSA at pH 6.0. Error bars represent the standard error of mean ( $n = 4$ ).

**Table 4.** CAT and CAL extractable amount of phosphorus ( $P_{CAT}$ ,  $P_{CAL}$ ) in the growing media ( $mg\ pot^{-1}$ ) of contrasting pH (4.5, 6.0) at the start and end of the trial, fertilized with sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen), water-soluble monocalcium phosphate (MCP), and rock phosphate (RockP), respectively. Details of the sewage sludge ashes are summarized in Tables 1 and 2. Values at the end of the experiment are presented as the mean  $\pm$  standard deviation ( $n = 4$ ).

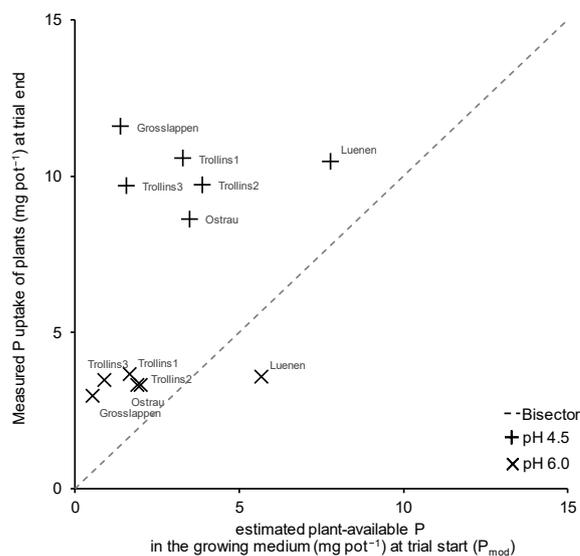
Treatments		Trial Start		Trial End			
pH in Growing Medium	SSA	$P_{CAT}$	$P_{CAL}$	$P_{CAT}$		$P_{CAL}$	
4.5	Trollins1	3.1	3.6	1.4	$\pm 0.1$	2.5	$\pm 0.2$
	Trollins2	3.5	4.9	1.6	$\pm 0.2$	2.6	$\pm 0.2$
	Trollins3	1.0	3.0	1.6	$\pm 0.3$	2.6	$\pm 0.4$
	Ostrau	2.8	5.0	1.9	$\pm 0.3$	2.3	$\pm 0.4$
	Luenen	6.3	11.3	2.1	$\pm 0.2$	3.0	$\pm 0.2$
	Grosslappen	1.1	2.0	1.3	$\pm 0.1$	2.4	$\pm 0.3$
	MCP	23.9	28.9	3.1	$\pm 0.6$	4.7	$\pm 0.7$
	RockP	7.2	7.5	2.9	$\pm 0.2$	2.6	$\pm 0.2$
6.0	Trollins1	0.6	4.1	0.3	$\pm 0.1$	1.4	$\pm 0.2$
	Trollins2	0.8	4.9	0.6	$\pm 0.1$	2.2	$\pm 0.1$
	Trollins3	0.0	3.0	0.3	$\pm 0.1$	1.7	$\pm 0.3$
	Ostrau	0.6	4.9	0.7	$\pm 0.2$	2.1	$\pm 0.1$
	Luenen	2.7	12.7	1.5	$\pm 0.2$	6.2	$\pm 0.6$
	Grosslappen	0.2	1.4	0.2	$\pm 0.2$	1.0	$\pm 0.1$
	MCP	18.4	25.7	2.9	$\pm 1.3$	4.7	$\pm 0.7$
	RockP	0.3	5.5	0.7	$\pm 0.4$	2.6	$\pm 0.2$

As shown in Figure 5, neither  $P_{CAT}$  nor  $P_{CAL}$  could predict plant P uptake. While  $P_{CAT}$  generally underestimated P uptake (5 to 74%), the relationship between P uptake and  $P_{CAL}$  was less clear. If the SSA Luenen is disregarded,  $P_{CAL}$  reflected plant P uptake quite well at a growing medium pH of 6.0. However, there was an underestimation at the lower pH of 4.5, similar to with  $P_{CAT}$ .



**Figure 5.** Relationship of phosphorus (P) uptake of marigold plants four weeks after fertilization with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen) and cultivation in growing media of contrasting pH to  $P_{CAT}$  (a) and  $P_{CAL}$  (b) at the trial start in the growing medium.

The amount of plant available P estimated by the prediction model of Hauck et al. [23] combining  $P_{CAT}$  and  $P_{CAL}$  also did not match the P uptake of plants (Figure 6). At a growing medium pH of 4.5, an underestimation of more than 50% was observed for most of the SSAs. At pH 6.0, the underestimation was less serious, but there was also an overestimation for the SSA Luenen.



**Figure 6.** Relationship of the measured phosphorus (P) uptake of marigold plants four weeks after fertilization with different sewage sludge ashes (Trollins1, Trollins2, Trollins3, Ostrau, Luenen, Grosslappen) and cultivation in growing media of contrasting pH to the estimated amount of plant-available P by the model according to Hauck et al. [23] in the growing medium at the trial start based on  $P_{CAT}$  and  $P_{CAL}$ .

## 4. Discussion

### 4.1. Plant P Availability of Sewage Sludge Ashes

Concerning the investigated plant parameters, none of the tested sewage sludge ashes (SSAs) could compete with the water-soluble reference fertilizer monocalcium phosphate (MCP) at a growing medium pH of 6.0 (Figure 1). This was also the case for plant phospho-

rus (P) uptake at a growing medium pH of 4.5 (Figure 1c). Hence, our first hypothesis that plant availability of SSA-P cannot compete with that of MCP-P can be accepted.

At a growing medium pH of 6.0, which is common for most horticultural crops, plant uptake of SSA-P was only approximately one-fifth of the water-soluble MCP-P, but was slightly higher compared to rock phosphate (RockP)-P for most of the products (Trollins batches 1–3, Ostrau, Luenen) (Figure 1f). This poor plant availability of SSA-P has already been demonstrated for Trollins1 in a peat-based growing medium [23,34]. It agrees with the observations for soil-based plant production [15]. As outlined in the literature, poor P availability is mainly caused by the P-bearing phase. In addition to calcium phosphates (CaPs) of higher crystallinity (e.g., whitlockite ( $\text{Ca}_3(\text{PO}_4)_2$ ) [35], hydroxylapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) [36]), SSA might contain further P compounds such as aluminum phosphates (e.g., variscite ( $\text{AlPO}_4$ ) [35]), iron phosphates (e.g., strengite ( $\text{FePO}_4$ ) [12]), and other heavy metal-associated phosphates (e.g., lead phosphate [37]) as well as magnesium phosphate (farringtonite ( $\text{Mg}_3(\text{PO}_4)_2$ ) [36]). According to the findings of Römer [13] in sand culture, aluminum phosphates (AlP) showed, in contrast to iron phosphates (FeP), a higher plant P availability than apatite present in RockP. In this light, a certain proportion of AlP could explain the slightly higher plant availability of SSA-P compared to RockP-P. Another explanation might be that not all Ca-associated P compounds in SSA are fully transformed into apatitic structures during the combustion. In addition, magnesium phosphates are reported to be highly plant-available [13].

In contrast to a growing medium pH of 6.0, SSA-P was more plant-available in a growing medium of higher acidity (Figure 1). At pH 4.5, the plant fresh weight of the SSA treatments even reached the level of the water-soluble reference fertilizer MCP (Figure 1d). However, for plant P content (Figure 1b), only two SSA treatments (Trollins1, Grosslappen) resulted in a level comparable to the MCP treatment, and for plant P uptake (Figure 1c), no SSA treatment attained the MCP value. The higher plant availability of SSA-P under acidic conditions agrees with the results of our previous study [38] and those in soil-based plant production [39,40]. The observed increase in plant availability of SSA-P at a low pH could be attributed to a high proportion of P compounds of higher crystallinity, such as Ca- and Pb-associated phosphates, releasing plant-available P into the aqueous phase under acidic conditions [41,42]. However, the presence of AlP and FeP in the P-bearing phase of SSA is also evident at pH 4.5, as most of the SSA treatments (Trollins batches 1–3, Ostrau, Luenen) led to a lower plant P uptake and thus to a lower relative phosphorus use efficiency (rPUE) than RockP (Figure 1c). According to common knowledge, the solubility of FeP and AlP is poor under acidic conditions [15,43]. However, this result contrasts with the findings of Lohr et al. [25]. In their study, a growing medium pH of 5.5 compared to 6.5 resulted in a slight increase in plant P availability for AlP and in a high increase for FeP. The authors attribute this result to a high chelating effect of fulvic and humic acids in growing media under acidic conditions. Due to the contrasting effect of a low pH on plant availability of AlP and FeP, the role of these P compounds in SSAs used in growing media-based production systems remains unclear, and consequently, additional investigations are needed.

As indicated by the relatively uniform differences in plant P availability between SSAs and the controls, the comparison among SSAs revealed only a few significant differences in rPUE (Figure 4). At a growing medium pH of 6.0, the rPUE ranged from 11.9% to 14.7%. This small range at a low level is of minor practical relevance regarding adequate plant nutrition. In contrast, at the lower pH of 4.5, acid-soluble phosphates in SSAs resulted in a higher rPUE, varying markedly between 34.5% (Ostrau) and 46.4% (Grosslappen). The low rPUE observed for Ostrau might be linked to the particle size distribution. As revealed by laser diffraction analyses, Ostrau was the only SSA with particles  $>630 \mu\text{m}$  (numerically 27%, Table 2), and thus the coarsest product. Therefore, in addition to the P-bearing phase, particle size seems to be a key factor for plant P availability. This assumption is supported by previous studies [34] and the findings of other authors [44].

However, the importance of particle size distribution on plant P availability depends on the pH of the growing medium. At a low pH, the dissolution of acid-soluble P compounds is diminished by a high amount of coarse particles due to a small reaction surface [45]. This particle size and pH interaction is causative for Ostrau having the lowest rPUE difference between pH 4.5 and 6.0 of the growing medium (Figure 3). Although there is no significant difference in rPUE between Ostrau and the other SSAs, except Grosslappen, the rPUE at a growing medium pH of 4.5 was positively correlated ( $R^2 = 0.77$ ) with the number of particles  $<160 \mu\text{m}$  of the SSAs. This further underlines the role of particle size in plant P availability.

#### 4.2. Prediction of Plant P Uptake by Growing Media Analyses

To predict plant P uptake, a growing medium extractant must reflect the P concentration in the aqueous phase of the growing medium, as plants take up only dissolved P. The concentration of dissolved P in growing media made of peat depends entirely on the chemical equilibrium constant of the fertilized P compounds. The release of sorbed P into the aqueous phase is negligible due to its low P buffer capacity [20].

As shown in Figure 5, for most SSA treatments, plant P uptake did not match the P amounts in the growing medium extractable by calcium chloride + diethylenetriamine-pentaacetate ( $P_{\text{CAT}}$ ) and calcium-acetate-lactate ( $P_{\text{CAL}}$ ). In addition, the plant P uptake differentiation did not fit both extractants. Therefore, the second hypothesis that a solvent on its own is not suitable for assessing the plant availability of SSA-P is confirmed. An underestimation of plant P uptake was generally observed for the CAT method, especially with a growing medium pH of 4.5 (Figure 5a). This underestimation might be attributed to the chelation of Fe and Al from non-CAT-soluble FeP and AlP [25] by humic acids releasing plant-available orthophosphates into the aqueous phase [46]. This effect is more pronounced with a growing medium pH of 4.5, since the chelating effect of humic acids is generally promoted under acidic conditions [47] and was shown in detail for Fe(III) by Van Dijk [48].

The positive effect of Fe and Al chelation on plant P availability might also explain the underestimation of plant P uptake by  $P_{\text{CAL}}$  with a growing medium pH of 4.5 for all SSAs except Luenen, where  $P_{\text{CAL}}$  nearly matched plant P uptake (Figure 5b). The differing behavior of Luenen might be due to a higher proportion of acid-soluble P compounds, such as CaP of higher crystallinity, compared to the other SSAs. This is supported by the overestimation of plant P uptake by  $P_{\text{CAL}}$  at the higher pH of 6.0 of the growing medium, according to Alt and Peters [49], typically for CaP of higher crystallinity. In addition to CaP, we assume that other highly acid-soluble P compounds are present in Luenen due to higher  $P_{\text{CAL}}$  values compared to RockP (Table 3), which consists of highly crystalline CaP. As such, lead phosphates (PbP) of higher crystallinity are possibly present in the SSA Luenen, which was the only industrial sewage sludge, for the following reasons: (i) PbP appears in industrial sewage sludges [37], (ii) PbP of higher crystallinity is more acid-soluble than CaP of higher crystallinity [42], and (iii) Pb ions are known to substitute Ca ions in apatites [50], which are formed during sewage sludge combustion.

The limitations of CAT and CAL show that these extractants can hardly characterize P's plant availability from secondary sources such as SSA differing in P compounds [14,15,23,51]. In this light, Hauck et al. [23] suggested improving the prediction of plant availability of P from secondary sources in growing media by combining  $P_{\text{CAT}}$  and  $P_{\text{CAL}}$  to  $P_{\text{mod}}$ :  $P_{\text{mod}} = P_{\text{CAT}} + (P_{\text{CAL}} - P_{\text{CAT}}) \times 0.3$ . As shown by the comparison of Figures 5 and 6, the highest difference between  $P_{\text{mod}}$  and  $P_{\text{CAT}}$  and  $P_{\text{CAL}}$  was observed for Luenen. However, the estimation of plant-available P in the growing medium by  $P_{\text{mod}}$  was also not satisfactory since plant P uptake from Luenen was underestimated by  $P_{\text{mod}}$  at a growing medium pH of 4.5 and still overestimated at a pH of 6.0 (Figure 6). For the rest of the SSAs,  $P_{\text{mod}}$  did not improve plant P uptake prediction. At a growing medium pH of 6.0, the prediction power of  $P_{\text{mod}}$  and  $P_{\text{CAL}}$  for plant P uptake was nearly the same. The observed underestimation at a growing medium pH of 4.5 is not surprising, as  $P_{\text{mod}}$  is derived from

an additive combination of  $P_{CAL}$  and  $P_{CAT}$ , which both strongly underestimate plant P uptake. This could be because  $P_{CAT}$  and  $P_{CAL}$  cannot comprehensively reflect the presumed chelation of Fe and Al from FeP and AlP.

The positive effect of chelation on plant availability of FeP and AlP could potentially be included in  $P_{mod}$  by an increased concentration of the chelator DTPA in the CAT extractant or by choosing another chelating agent (e.g., EDTA). Alternatively, an additional alkaline solvent (e.g., sodium bicarbonate) might be helpful to assess plant-available SSA-P by extracting FeP-P and AlP-P [52], which was indicated for growing media by Handreck [53].

## 5. Conclusions

The rPUE of SSA depends highly on the pH of the growing medium. At a commonly used pH of 6.0 in soilless plant production, the rPUE of SSAs ranged from 12 to 15% compared to 58% for the water-soluble reference fertilizer (MCP). This low level contradicts the use of SSA as base fertilizer for soilless growing media in the horticultural production of non-acidophilic crops. In contrast, at a pH of 4.5, a higher rPUE level from 35 to 46% was observed for SSAs compared to 56% for MCP. Consequently, SSA seems to be a promising substitute for primary P sources such as MCP for crops requiring low growing medium pH. However, several points must be considered before establishing SSAs in horticultural practice. An adequate quantity of SSA fertilizer cannot be generalized, since rPUE among SSAs varies at a pH of 4.5 of the growing medium. Furthermore, the required SSA quantity could not be derived by growing media analyses based on CAT and CAL, as extractable P in the growing medium did not reflect the plant uptake of SSA-P. To improve the prediction of plant-available SSA-P, solvent modifications or additional extractants might be promising and should be studied in further research. Overall, economic feasibility as another important factor for SSA establishment should be subjected to further investigation.

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