

Biomass ashes and their phosphorus fertilizing effect on different crops

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Abstract The reutilization of biomass ashes in agriculture is an important issue to create nutrient cycles and to save fertilizer. To analyse the P fertilization effect of crop biomass ashes (rape meal ash (RMA), straw ash (SA), and cereal ash (CA)) in interaction with different crops, two pot experiments with a poor loamy sand deficient in P were carried out. Besides the three ash treatments, other treatments included triple superphosphate (TSP) as a high soluble P source, potassium chloride (KCl) as a high soluble K source, and a control (CON) without P and K. The main crops (maize, lupin, summer barley, and oilseed rape) were cultivated in the first experiment from April to May and the catch crops (oil radish, phacelia, italian ryegrass, and buckwheat) were cultivated in the second experiment from August to September. Plant parameters (biomass and P uptake of shoots), soil pH, different P pools of the soil (total P (Pt), water soluble P (Pw), double lactate soluble P (Pdl), oxalate soluble P (Pox)), P sorption capacity (PSC), and the degree of P saturation (DPS) were investigated. The fertilization effect of biomass ashes was comparable with that of TSP. On average of all crops, the highest P uptake (86.7 mg pot^{-1}) was found after RMA application, and the lowest P uptake (66.6 mg pot^{-1}) for CON. The

readily bio-available soil P contents (Pw and Pdl) were significantly increased when P was supplied, regardless of whether P was given with ash or with high soluble TSP. The P fertilization effects also depended on the cultivated crops. The ash treatments resulted in highest increases of soil Pw values when combined with buckwheat cultivation. After buckwheat harvest the Pw content in the control was 8.0 mg kg^{-1} , and in the ash treatments between 13.9 mg kg^{-1} (CA) and 15.7 mg kg^{-1} (RMA). From the results of this study we conclude, that crop biomass ashes can be an adequate P source comparable to that of highly soluble commercial P fertilizer.

Keywords Biomass ashes · Fertilization · P sorption · P uptake · Phosphorus · Soil P · Crops

Introduction

The largest amount of phosphorus (P) in the world is used for fertilizer, and the estimates of the duration of world-wide P-reserves are linked to the development of future agricultural needs and efficiency. The global P resources, however, are limited and will probably be depleted within the next century (Haarr 2005). Therefore, solutions for P recycling by utilization of residues and wastes in agriculture become more important to save the world-wide P reserves. Ashes from combustion of biomass are the oldest mineral

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fertilizer in the world. In the context of increasing bioenergy production, the recycling of ashes in agriculture may solve the problem of ash disposal and reduce the necessity of commercial fertilizer application (Sander and Andr n 1997; Perucci et al. 2006).

Biomass ashes are nearly free of nitrogen but contain P and other nutrients needed for plant nutrition (Eti gni and Campbell 1991; Sander and Andr n 1997; Vance and Mitchell 2000; Zimmermann and Frey 2002; Patterson et al. 2004; Uckert 2004). Furthermore, biomass ashes can also be used as liming agents (Clapham and Zibilske 1992; Muse and Mitchell 1995; Mozaffari et al. 2002; Nkana et al. 2002; Odlare 2005; Mandre 2006). Ash application can stimulate the microbial activities and mineralization processes in the soil by amelioration of chemical and physical characteristics (Demeyer et al. 2001).

Nutrient composition and other properties of ashes are affected by different factors. Firstly, the kind of biomass combusted influences the quality and the nutrient values of ashes. Low available P concentrations in ash of 0.01% were found in bagasse ash (Jamil et al. 2004). About 0.5% P was found in municipal waste incinerator ash (Rosen et al. 1994) and cocoa husk ash (Onwuka et al. 2007). The P content in alfalfa stem fly ash amounted to 0.9% (Mozaffari et al. 2002). For horticulture ashes, total P concentrations between 0.04 and 1.0% were described by Zhang et al. (2002). Patterson et al. (2004) found a total P concentration of 0.6% in wood waste ash (wood, bark, and knots). In investigations by Erich and Ohno (1992), Saarsalmi et al. (2001), and Hyt nen (2003) wood ashes contained 0.9–1.7% P. In general, hardwood ash has more P than ash of softwood (Pitman 2006). P concentrations of more than 1% were detected in peat ash (1.3%, Hyt nen 2003), in saw dust ash (1.3%, Awodun 2007), and in different straw ashes: wheat straw ash (1.3%), barley straw ash (1.7%), rye straw ash (1.6%), and rape straw ash (2.1%) (Sander and Andr n 1997). For sewage sludge ashes, a total P concentration from 2 to 9% can be assumed (Jakobsen and Willett 1986; Zhang et al. 2002; Franz 2008). Poultry litter ashes also contain high P contents of about 5.0% (Yusiharni 2001; Codling et al. 2002).

The liming effect is mainly connected with the Ca content and can also differ in dependence of the combustion material. Ash from rape straw had a

higher Ca content and better liming effect than ash from cereal straw (Sander and Andr n 1997).

Beside the raw material used, the combustion process itself affects chemical composition of the ashes. In investigations of Eti gni and Campbell (1991) P concentration in wood ash varied between 1.7% (at 538 C) and 2.6% (at 1093 C) depending of combustion temperature. Furthermore, the utility of wood ash as a lime substitute also depended on boiler combustion efficiencies (Vance and Mitchell 2000).

The availability of nutrients in ashes can vary. According to Ohno and Erich (1990), only a small part of P added with wood ash appeared to be extractable and available for plants. A poor solubility of P in biomass ashes was also described by Pels et al. (2005). In contrast, positive effects of alfalfa stem ash on Olsen P in loamy soil (extracted with NaHCO₃) were detected by Mozaffari et al. (2002). They found the relationship between ash application rate and extractable P content in soil could be described by a linear regression. Increased available P contents in soil and better growth of maize due to fertilization with cocoa husk ash were reported by Onwuka et al. (2007). Results of Van Reuler and Janssen (1996) showed significantly increased yields and P uptakes of upland rice fertilized with wood ash.

Other positive crop yield effects of ashes were also found for winter wheat (*T. aestivum* L.), spinach (*S. oleracea* L.), oat (*A. sativa* L.), and bean (*P. vulgaris* L.) (Clapham and Zibilske 1992; Krejzl and Scanlon 1996). Investigations of Patterson et al. (2004) showed an increase of 50% for barley yield (*H. vulgare* L.) and up to 124% for oilseed yield of canola (*B. rapa* L.) due to wood ash application. In the tropics, Phongpan and Mosier (2003) found positive effects of rice hull ash on rice yield in Thailand, and Ikpe and Powell (2002) reported positive impacts of millet ash on millet yields.

Although these investigations showed a general potential of biomass ashes to increase crop growth and nutrient uptake, research concerning interactions of different kind of biomass ashes and various crops are rarely available. However, nutrient uptake efficiency and mobilization mechanisms of crops are important for high utilization of applied P (Schilling et al. 1998; Neumann 2007).

In our study we investigated three different crop biomass ashes and eight crop species within two experiments. In order to comprise a broad spectrum

of ashes, based on different combustion materials, we selected straw ash, cereal ash and rape meal ash.

The objectives of this work were to

- compare the P fertilizing effect of different crop biomass ashes in comparison to a high soluble mineral P source, TSP,
- evaluate the ability of different main and catch crops to utilize P from biomass ashes for plant nutrition, and
- investigate possible interactions between the effects of fertilizing treatments and cultivated crops.

Materials and methods

Soil

In 2007 two pot experiments with a sandy soil (Table 1) were carried out in order to investigate the effect of biomass ashes on soil P pools and plant parameters. The soil used was taken from a long term field experiment located in Northern Germany (Rostock) which did not receive any P supply for 10 years. The double lactate soluble P content (Pdl)

of about 39 mg kg^{-1} soil indicated a suboptimal P supply (Table 1). Contents of double lactate soluble K (about 115 mg kg^{-1}) and Mg (about 120 mg kg^{-1}) were optimal.

Treatments and experimental design

Different crop ashes derived from rape meal, straw and cereal were used to cover a broad spectrum of plant raw materials (Table 2). The rape meal ash (RMA) was produced at the *University of Rostock, Faculty of Mechanical Engineering and Marine Technology* (Germany) in a fluidized bed combustion at a temperature of 860°C . The rye straw ash (SA) was produced via grate firing at 750°C and delivered by the *Leibniz Institute for Agricultural Engineering in Potsdam-Bornim* (Germany). The rye cereal ash (CA) was produced at the *Agricultural Technical School of Tulln* (Austria) also via grate firing at $650\text{--}850^\circ\text{C}$. The biomass ashes varied in their nutrient composition (Table 2). The heavy metal contents of the biomass ashes are shown in Table 3.

Mitcherlich pots were filled with 6 kg air-dried and sieved soil and irrigated with 600 ml distilled water. The ashes/fertilizer were applied on the soil surface and mixed into the upper 5 cm of soil. For the

Table 1 Soil properties at the beginning of the pot experiments

Experiment	pH CaCl ₂	Pw (mg kg ⁻¹)	Pdl (mg kg ⁻¹)	Pox (mmol kg ⁻¹)	DPS (%)	PSC (mmol kg ⁻¹)	Pt (mg kg ⁻¹)
1. Main crops	5.65	10.7	38.9	11.96	38.92	30.77	505.6
2. Catch crops	5.72	10.4	38.9	11.82	39.23	30.14	501.8

Pw water soluble P, Pdl double lactate soluble P, Pox oxalate soluble P, DPS degree of P saturation, PSC P sorption capacity, Pt total P; main crops maize, blue lupin, summer barley, oilseed rape; catch crops oil radish, phacelia, italian ryegrass, buckwheat

Table 2 Treatments of the pot experiments and the amount of nutrients given (g pot⁻¹; 6 kg soil per pot)

Treatments	Abbr.	Nutrient concentrations ^a (%)			Fertilizer application rates (g pot ⁻¹)	Nutrient amounts (g pot ⁻¹)			
		P	K	Mg		N	P	K	Mg
Control	CON	–	–	–	–	0.5	–	–	–
Phosphorus (TSP)	TSP	20.2	–	–	1.0	0.5	0.2	–	–
Rape meal ash	RMA	8.0	7.3	5.5	2.5	0.5	0.2	0.2	0.1
Straw ash	SA	1.0	5.3	1.0	9.8	0.5	0.1	0.5	0.1
Cereal ash (from the seeds)	CA	10.5	10.8	3.3	1.9	0.5	0.2	0.2	0.1
Potassium (KCl)	KCl	–	52.4	–	1.0	0.5	–	0.5	–

^a Total amount, aqua regia extraction

Table 3 Heavy metal contents (mg kg⁻¹) of the used biomass ashes

Biomass ash	Cd	Cr	Cu	Hg	Ni	Pb	Zn
RMA	0.5	227.9	77.1	0.02	273.6	11.9	348.9
SA	0.1	4.7	24.5	0.02	3.7	<1.5	80.9
CA	1.3	13.7	170.9	0.04	13.1	2.6	750.5

RMA and CA treatment, 2.5 g ash and 1.9 g ash, respectively, were added per pot. These amounts corresponded to a nutrient supply of 0.2 g P and 0.2 g K per pot. Due to the much lower P content in SA, an application of 9.8 g SA per pot contained only 0.1 g P but 0.5 g K. Higher amounts of SA would have probably resulted in a too strong liming effect. To compare the P and K effect of ashes, treatments with high soluble TSP and KCl were also established (Table 2). Furthermore, a control (CON) without P and K supply was set up. Each pot received a nutrient solution with 1.4 g NH₄NO₃ and 1.5 g MgSO₄ to supply N, Mg, and S.

Depending on the favorable growing time of cultivated main crops and catch crops this study was split into two experiments. For both experiments the same soil and fertilization treatments were used. Only the cultivated crops differed (Table 4). The main crops (maize, blue lupin, summer barley, and oilseed rape) were seeded in April and the catch crops (oil radish, phacelia, italian ryegrass, and buckwheat) were seeded in August. After germination, the pots were placed outside in a cage under natural weather conditions. Distilled water was used for irrigation according to crop demands. Pots could drain freely to field capacity. Percolated water was collected in

bowls below the pots and recirculated to avoid leaching losses. Plants grew until beginning of flowering and were harvested after a growing time of 46–66 days. Ryegrass was cut 3 times (after 31, 57, and 88 days) within the growing period.

All treatments were replicated four times.

Analyses

Plant and soil samples were taken from each pot for analyses. Harvested shoots were dried in an oven at 60°C, weighed and ground with a plant mill. The P content in plant tissue was measured after dry ashing using the vanadate-molybdate method (Page et al. 1982). Plant P uptake was calculated by multiplying P content of the shoots and shoot biomass yield.

The soil samples were air-dried and sieved (2 mm) before analysis. Soil pH value was measured in 0.01 M CaCl₂ using a 1:2.5 soil to solution ratio. For characterisation of soil P pools different methods were applied. The method described by Van der Paauw (1971) was used to determinate water-extractable P (Pw) with a soil:water ratio of 1:25. The P concentrations in the extracts were measured by the phosphomolybdate blue method via flow-injection analysis. Content of double lactate soluble P (Pdl) (photometric method) was quantified according to Blume et al. (2000). By means of ammonium oxalate method (Schwertmann 1964) the extractable amount of P (Pox) allows the estimation of inorganic P being adsorbed on amorphous Fe and Al oxides in the soil. Pox and oxalate-soluble Al and Fe content in soil (Alox, Feox) were analysed by shaking 2 g of soil in acid oxalate solution (100 ml) for 1 h in the dark.

Table 4 Cultivated crops in the pot experiments

Crop species	Variety	Number of plants per pot (time of harvest)
<i>1. Main crops</i>		
Maize (<i>Zea mays</i> L.)	Abakus	8
Blue lupin (<i>Lupinus angustifolius</i> L.)	Borlu	8
Summer barley (<i>Hordeum vulgare</i> L.)	Barke	15
Oilseed rape (<i>Brassica napus</i> L.)	Landmark	10
<i>2. Catch crops</i>		
Oil radish (<i>Raphanus sativus</i> L.)	Rutina	10
Phacelia (<i>Phacelia tanacetifolia</i> Benth.)	Boratus	NA
Italian ryegrass (<i>Lolium multiflorum</i> Lam.)	Gordo	NA
Buckwheat (<i>Fagopyrum esculentum</i> Moench)	Lifago	6

Concentrations of P, Al, and Fe were determined by inductively coupled-plasma optical emission spectroscopy (ICP-OES, JY 238, Jobin–Yvon, France) at 214.914 nm (P), 396.152 nm (Al), and 259.940 nm (Fe) wave length. Using these data, the P-sorption capacity (PSC [mmol kg⁻¹] = (Alox + Feox)/2 and the degree of P saturation (DPS [%] = Pox/PSC × 100) could be calculated according to Lookman et al. (1995) and Schoumans (2000). Total P (Pt) was analysed after aqua regia dissolution in a microwave oven (Mars Xpress, CEM GmbH, Kamp-Lintfort, Germany) followed by ICP spectroscopy.

Statistics

Soil and plant data corresponding to four spatial replications were subjected to analysis of variance (General linear model, GLM). The results are reported as main effects and interactions. The means of soil and plant parameters were compared by the Duncan multiple range test. Significance was determined at $P < 0.05$, and significantly different means were indicated by using different letters.

Results and discussion

Effect of biomass ashes and cultivated crops on P uptake and shoot biomass

In general, P uptake was affected positively by P supply, independently of whether P was given as TSP or with ashes (Tables 5 and 6).

In comparison to CON the average crop P uptake increased up to 32% by the RMA treatment which was comparable to the TSP treatment. The effects of SA and CA were smaller, however they increased the P uptake in comparison to the control by 15 and 19%, respectively. The plant P uptake in the KCl treatment was comparable to the CON (absolute values shown in Table 6).

Especially, the P uptakes of maize, oilseed rape, phacelia, and italian ryegrass were increased when ash was applied, with increases up to 47% compared to CON. Since ashes consist of different nutrients the measured ash effect regarding P uptake was most probably also related to liming and/or effects of other nutrients.

The fertilizing effects of the ashes differed in dependence of the cultivated crops. P uptake from RMA into oilseed rape and ryegrass was very efficient with an increase of 39 and 47% compared to CON, whereas no significant increase in comparison to the CON occurred for oil radish and buckwheat. For CA, P uptake into maize increased by 34% compared to CON, whereas lupin and summer barley did not show any significant increase. The raise of P uptake from SA into phacelia was high (36% compared to CON), but not existent for oil radish and negligible for lupin (absolute values in Table 6). The SA effect on the P uptake of phacelia was even comparable to the RMA effect, although the P content in SA was much lower.

The fertilization effect on crop yield was found to be lower than on crop P uptake. Although, on average, the P supply (TSP or ash) increased the yields of the

Table 5 Effect of fertilizer treatments, crop species and interactions of both factors on shoot biomass, plant P uptake, pH, soil P pools, and P sorption parameters (two-factor analysis of variance)

Source of variation	Shoot biomass	P uptake	pH	Pw	Pdl	Pox	DPS	PSC	Pt
Experiment with main crops (maize, lupin, summer barley, and oilseed rape)									
Fertilizer	0.001***	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***	0.004**	0.000***
Crop species	0.000***	0.000***	0.000***	0.000***	0.000***	0.006**	0.001***	0.022*	0.000***
Fertilizer × Crop species	0.024*	0.000***	0.288 ns	0.048*	0.003**	0.401 ns	0.224 ns	0.000***	0.064 ns
Experiment with catch crops (oil radish, phacelia, italian ryegrass, and buckwheat)									
Fertilizer	0.790 ns	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***	0.694 ns	0.000***
Crop species	0.000***	0.000***	0.000***	0.000***	0.000***	0.001***	0.004**	0.000***	0.000***
Fertilizer × Crop species	0.124 ns	0.172 ns	0.097 ns	0.000***	0.004**	0.016*	0.006**	0.149 ns	0.072 ns

Pw water soluble P, Pdl double lactate soluble P, Pox oxalate soluble P, DPS degree of P saturation, PSC P sorption capacity, Pt total P

* $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns = not significant

Table 6 Shoot biomass (dry matter, g pot⁻¹) and P uptake of the shoots (mg pot⁻¹) as affected by fertilization and crops species

Fert.	Main crops				Catch crops			
	Maize	Lupin	Summer barley	Oilseed rape	Oil radish	Phacelia	Italian ryegrass	Buckwheat
Shoot biomass								
	0.040*	0.024*	0.225 ns	0.066 ns	0.146 ns	0.271 ns	0.016*	0.440 ns
CON	46.2 ab ^D	11.6 ab ^A	26.4 ^C	15.3 ^B	16.8 ^B	25.9 ^C	10.8 ab ^A	35.9 ^D
TSP	49.5 b ^D	13.4 b ^A	28.1 ^C	16.7 ^B	16.2 ^A	25.5 ^B	12.4 bc ^A	30.6 ^B
RMA	48.7 b ^D	13.4 b ^A	27.8 ^C	17.3 ^B	16.1 ^A	29.2 ^B	13.2 c ^A	30.1 ^B
SA	48.4 b ^D	12.0 ab ^A	27.7 ^C	16.7 ^B	13.3 ^A	32.6 ^B	12.3 bc ^A	32.2 ^B
CA	49.1 b ^D	11.1 a ^A	27.9 ^C	15.2 ^B	17.6 ^B	28.1 ^C	11.6 abc ^A	34.7 ^D
KCl	42.2 a ^D	10.2 a ^A	28.7 ^C	15.4 ^B	16.5 ^B	27.9 ^C	10.0 a ^A	36.7 ^D
P uptake of the shoots								
	0.000***	0.057 ns	0.000***	0.000***	0.004**	0.039*	0.000***	0.587 ns
CON	75.6 a ^D	25.3 ^A	59.1 a ^C	43.8 a ^B	64.2 abc ^A	99.8 a ^B	61.1 b ^A	103.8 ^B
TSP	109.2 d ^D	32.5 ^A	79.3 d ^C	62.4 d ^B	77.5 c ^A	127.2 b ^C	86.1 e ^{AB}	116.2 ^{BC}
RMA	99.9 bc ^D	35.8 ^A	75.1 cd ^C	60.9 cd ^B	75.0 bc ^A	136.1 b ^B	89.5 e ^A	121.5 ^B
SA	91.4 b ^D	27.2 ^A	70.1 bc ^C	55.2 bc ^B	54.6 a ^A	135.9 b ^C	70.2 c ^A	111.0 ^B
CA	101.0 cd ^D	25.9 ^A	61.7 a ^C	49.3 ab ^B	77.0 c ^A	129.5 b ^B	78.6 d ^A	127.7 ^B
KCl	70.8 a ^C	27.5 ^A	66.1 ab ^C	43.5 a ^B	62.6 ab ^A	116.4 ab ^B	51.8 a ^A	113.1 ^B

CON control, TSP TripleSuperP, RMA rape meal ash, SA straw ash, CA cereal ash, KCl potassium chloride

* $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns = not significant; $P < 0.05$ (Duncan); different small letters indicate significant differences between the fertilization treatments within a column; different capital letters indicate significant differences between main crops or catch crops within a line

crops, this effect was only found to be significant for the monocotyl crops maize and italian ryegrass (Table 6). Positive yield effects of maize after fertilization with wood ash of up to 100% increasing rates were also found by Erich and Ohno (1992). In experiments of Adu-Dapaah et al. (1994) maize shoot biomass increased when cocoa pod husk ash was applied. Nkana et al. (1998) described yield increases of ryegrass of 244% compared to control when fertilized with wood ash. And Yusiharni (2001) found yield increasing effects of ash (chicken litter ash) for ryegrass cultivated on acid lateric soil.

Buckwheat and oil radish did not show any positive yield effect after P fertilization (ash or TSP), and had comparably high yields even without P supply. This reflects a high P efficiency. Probably buckwheat could mobilize sufficient P from soil reserves (see also below). A special adaptation of buckwheat on P deficient soils has previously been shown by Amann and Amberger (1989) and Suzuki et al. (2009).

The diverse effects of fertilization on yield and P uptake in dependence of cultivated crops can be explained with crop specific adaptation and mobilization mechanisms. Generally, crop plants have various strategies to influence either the spatial or the chemical availability of P in soil. Some plants adapt to low-P soil by changing their root morphology to explore a large soil volume, other excrete P-solubilizing compounds like organic acids, organic and inorganic ions, sugars, vitamins, nucleosides, and enzymes (Staunton and Leprince 1996; Dakora and Phillips 2002; Nuruzzaman et al. 2006).

Green fertilizer catch crops may enhance the P nutrition of succeeding crops by increasing the P availability in soil. This can be by direct P mobilization during the plant growth and/or after it, when decomposed catch crop biomass releases P (Eichler-Löbermann et al. 2007). High P uptake of catch crops provides a high potential for P supply of the succeeding crops. According to our results buckwheat and

Table 7 Effect of fertilizer treatments on pH, Pt, Pw, Pdl, Pox, and P sorptions parameters on average of main crops and catch crops

Fert.	Experiment with main crops (maize, lupin, summer barley, and oilseed rape)						
	pH 0.002**	Pw 0.000*** (mg kg ⁻¹)	Pdl 0.000*** (mg kg ⁻¹)	Pox 0.000*** (mmol kg ⁻¹)	DPS 0.000*** (%)	PSC 0.031* (mmol kg ⁻¹)	Pt 0.000*** (mg kg ⁻¹)
CON	5.60 ab	8.4 a	33.7 a	12.3 a	40.8 a	30.1 c	503.8 a
TSP	5.57 a	12.3 c	41.9 b	13.4 b	44.9 b	29.9 bc	527.2 bc
RMA	5.61 ab	11.5 bc	42.2 b	13.1 b	45.3 b	29.0 a	532.2 c
SA	5.72 c	11.2 bc	42.4 b	12.4 a	42.6 a	29.2 ab	515.8 ab
CA	5.68 bc	10.5 b	42.2 b	12.5 a	42.6 a	29.3 abc	516.3 ab
KCl	5.58 a	8.2 a	33.5 a	12.3 a	41.2 a	29.8 abc	502.5 a
Fert.	Experiment with catch crops (oil radish, phacelia, italian ryegrass, and buckwheat)						
	pH 0.024*	Pw 0.000*** (mg kg ⁻¹)	Pdl 0.000*** (mg kg ⁻¹)	Pox 0.000*** (mmol kg ⁻¹)	DPS 0.000*** (%)	PSC 0.876 ns (mmol kg ⁻¹)	Pt 0.003** (mg kg ⁻¹)
CON	5.31 a	8.6 a	30.3 a	11.9 a	40.1 a	29.8	516.3 ab
TSP	5.30 a	13.0 b	39.0 b	12.6 bc	41.8 bc	30.1	533.7 c
RMA	5.41 ab	12.5 b	38.8 b	12.8 cd	42.5 c	30.2	534.5 c
SA	5.52 b	12.8 b	41.6 b	12.4 bc	41.9 bc	29.7	526.9 bc
CA	5.34 ab	12.8 b	39.7 b	13.0 d	43.3 c	30.2	530.7 bc
KCl	5.22 a	8.2 a	31.6 a	12.2 ab	40.6 ab	30.0	509.8 a

CON control, TSP TripleSuperP, RMA rape meal ash, SA straw ash, CA cereal ash, KCl potassium chloride, Pw water soluble P, Pdl double lactate soluble P, Pox oxalate soluble P, DPS degree of P saturation, PSC P sorption capacity, Pt total P

* $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns = not significant, different letters within a column indicate significant differences between the treatments; $P < 0.05$ (Duncan)

phacelia, which had high P uptakes when fertilized with ashes, could be suitable to utilize P from ashes and to provide it to the following main crop.

Effect of biomass ashes and cultivated crops on soil characteristics

Generally, the fertilizer treatments as well as the crop species had a significant effect on pH value and soil P pools (Tables 5 and 7). For some parameters interactions could be found.

From the three applied ashes in the experiments, only SA caused significantly increased pH of the soil in comparison to the treatments without ash (Table 7), which is probably related to the high application rate of SA and the connected liming effect.

Among all crops, phacelia lead to the lowest pH values in the soil (Table 8). This was probably caused by a high cation:anion ratio of the nutrient uptake linked to an excretion of H_3O^+ ions, as detected in

former experiments (Eichler-Löbermann and Schnug 2006).

The bio-availability of P in the soil is not directly correlated to the absolute amount of P, but depends on subsequent delivery from the soil P pools into soil solution. This delivery depends mainly on chemical soil characteristics like pH. The better solubility of Ca phosphates under lower pH values can increase the effect of biomass ashes on more acid soils.

The P supply with ashes or with TSP resulted in a significant increase in readily plant available P forms Pw and Pdl (Table 7), whereas the effect of the crops was rather indifferent (Table 8). Remarkably, there were no differences in Pw contents of the soil between the P fertilizing treatments, even though commercial TSP fertilizer contain 80–93% water-soluble P (Mullins and Sikora 1995) and the water solubility of P in crop ashes is usually lower than 1% (Eichler-Löbermann et al. 2008). Also concerning Pdl, the same increasing effects of ashes and TSP

Table 8 Chemical properties of soil (pH, Pw, and Pdl) in dependence of crop species and type of fertilization

Fert.	Main crops				Catch crops			
	Maize	Lupin	Summer barley	Oilseed rape	Oil radish	Phacelia	Italian ryegrass	Buck-wheat
pH								
	0.005**	0.036*	0.408 ns	0.336 ns	0.001***	0.240 ns	0.002**	0.006**
CON	5.49 ab ^A	5.54 ab ^A	5.67 ^B	5.71 ^B	5.36 b ^B	5.04 ^A	5.57 a ^C	5.27 a ^B
TSP	5.43 a ^A	5.51 a ^{AB}	5.69 ^C	5.65 ^{BC}	5.36 b ^B	5.04 ^A	5.59 a ^C	5.19 a ^B
RMA	5.54 ab	5.53 a	5.69	5.67	5.47 bc ^B	5.10 ^A	5.71 bc ^C	5.37 a ^B
SA	5.70 c	5.67 b	5.77	5.72	5.63 c ^B	5.06 ^A	5.80 c ^C	5.61 b ^B
CA	5.58 bc ^A	5.68 b ^{AB}	5.69 ^{AB}	5.77 ^B	5.43 b ^B	4.94 ^A	5.65 ab ^C	5.33 a ^B
KCl	5.44 ab ^A	5.51 a ^{AB}	5.73 ^C	5.65 ^{BC}	5.15 a ^{AB}	4.94 ^A	5.57 a ^C	5.20 a ^B
Pw (mg kg ⁻¹)								
	0.000***	0.018*	0.000***	0.000***	0.000***	0.000***	0.025*	0.000***
CON	7.5 a ^A	10.4 ab ^B	7.8 a ^A	8.0 a ^A	8.7 a ^{AB}	8.1 a ^A	9.6 a ^B	8.0 a ^A
TSP	10.7 bc ^A	15.3 c ^B	11.5 c ^A	11.9 b ^A	12.8 b	11.3 b	12.3 b	15.5 b
RMA	10.8 bc	12.7 abc	10.0 b	12.5 b	12.5 b ^A	11.0 b ^A	10.9 ab ^A	15.7 b ^B
SA	9.5 b ^A	13.5 bc ^B	10.1 b ^A	11.5 b ^{AB}	15.5 c ^B	10.9 b ^A	10.6 ab ^A	14.4 b ^B
CA	11.9 c ^B	11.7 abc ^B	7.5 a ^A	11.1 b ^B	12.7 b	12.3 b	12.2 b	13.9 b
KCl	7.5 a ^A	9.2 a ^C	7.9 a ^{AB}	8.1 a ^B	8.4 a ^B	7.7 a ^{AB}	9.3 a ^C	7.6 a ^A
Pdl (mg kg ⁻¹)								
	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***	0.000***
CON	33.0 a	34.7 a	33.3 a	33.8 a	31.7 a ^C	26.4 a ^A	33.7 a ^D	29.5 a ^B
TSP	39.5 b ^A	44.9 b ^B	41.9 b ^{AB}	41.2 b ^A	39.2 b ^B	32.1 bc ^A	40.8 b ^{BC}	43.8 b ^C
RMA	39.3 b	44.7 b	41.2 b	43.5 b	38.6 b ^B	32.1 bc ^A	42.0 b ^B	42.5 b ^B
SA	40.1 b	45.8 b	41.5 b	42.0 b	44.7 c ^B	34.4 cd ^A	42.0 b ^B	45.2 b ^B
CA	42.2 b ^B	48.3 b ^B	34.6 a ^A	43.5 b ^B	40.7 bc ^B	35.5 d ^A	41.2 b ^B	41.5 b ^B
KCl	32.8 a	34.9 a	34.1 a	32.2 a	30.6 a ^A	30.4 b ^A	34.2 a ^B	31.3 a ^A

CON control, TSP TripleSuperP, RMA rape meal ash, SA straw ash, CA cereal ash, KCl potassium chloride; Pw water soluble P, Pdl double lactate soluble P

* $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns = not significant; $P < 0.05$ (Duncan); different small letters indicate significant differences between the fertilization treatments within a column; different capital letters indicate significant differences between main crops or catch crops within a line

were found. A strong correlation was measured between Pw and Pdl in soil ($r = 0.83^{***}$).

Since the P cycle in soil is a very complex system and may be influenced by chemical, physical as well as by biological processes, changes in Pw and Pdl cannot only be explained by balancing the P input with fertilizer and the P output via crops harvest. However, oil radish and lupin which had rather low P uptakes (see above) resulted in relative high Pw and Pdl values after harvest, and phacelia which had the

highest P uptake of all crops led to lower Pw and Pdl values. In contrast to this, the highest Pw values in the soil were found after buckwheat cultivation in the ash and TSP treatments (about 15.0 mg kg⁻¹ soil), although buckwheat had high P uptakes. Also for Pdl, high values of about 43 mg kg⁻¹ soil were found after buckwheat cultivation in the ash and TSP treatments (Table 8). These were comparable to those after oilseed rape cultivation, although the P uptake of buckwheat was double as high as for oilseed rape

Table 9 Chemical properties of soil (Pox, DPS, PSC, and Pt) in dependence of crop species and type of fertilization

Fert.	Main crops				Catch crops			
	Maize	Lupin	Summer barley	Oilseed rape	Oil radish	Phacelia	Italian ryegrass	Buck-wheat
Pox (mmol kg ⁻¹)								
	0.005**	0.033*	0.360 ns	0.016*	0.001***	0.022*	0.570 ns	0.001***
CON	12.5 ab	12.4 a	11.8	12.4 ab	11.8 a	12.0 a	11.7	12.2 a
TSP	13.3 c	14.5 b	12.7	13.3 c	12.3 ab ^A	12.8 b ^{AB}	12.2 ^A	13.0 bc ^B
RMA	13.5 c	13.1 a	12.8	13.2 bc	13.0 bc ^B	12.6 b ^{AB}	12.1 ^A	13.4 c ^B
SA	12.8 abc	12.3 a	12.3	12.3 a	12.4 ab	12.4 ab	12.3	12.5 ab
CA	13.0 bc ^B	12.8 a ^B	11.9 ^A	12.2 a ^{AB}	13.9 c ^B	13.0 b ^{AB}	12.3 ^A	13.0 bc ^{AB}
KCl	12.2 a	12.5 a	12.3	12.1 a	12.2 ab	12.6 b	12.1	11.9 a
DPS (%)								
	0.002**	0.032*	0.071 ns	0.002**	0.005**	0.002**	0.439 ns	0.018*
CON	40.6 a	41.0 a	39.2	42.5 ab	39.7 a ^{AB}	38.0 a ^A	41.7 ^B	41.0 ab ^B
TSP	44.7 c	47.7 b	42.6	44.4 bc	42.7 a	41.1 b	41.0	42.4 bc
RMA	45.7 c	46.4 b	43.4	45.7 c	42.6 a	40.9 b	42.2	44.3 c
SA	44.2 bc ^B	41.5 a ^A	42.8 ^{AB}	42.0 ab ^A	42.1 a	41.6 b	43.4	40.5 ab
CA	41.8 ab	43.7 ab	40.7	44.1 bc	46.2 b ^B	42.3 b ^A	42.6 ^A	42.0 bc ^A
KCl	41.9 ab	43.2 ab	39.7	40.1 a	41.6 a ^B	40.3 b ^{AB}	41.7 ^B	38.8 a ^A
PSC (mmol kg ⁻¹)								
	0.031*	0.033*	0.024*	0.018*	0.213 ns	0.056 ns	0.345 ns	0.752 ns
CON	30.8 bc	30.2 b	30.2 bc	29.1 b	29.8 ^{AB}	31.6 ^B	28.1 ^A	29.9 ^{AB}
TSP	29.7 abc	30.4 b	29.8 abc	29.9 b	28.7 ^A	31.2 ^C	29.8 ^B	30.6 ^C
RMA	29.5 ab ^B	28.2 a ^A	29.5 ab ^B	28.8 ab ^{AB}	30.6 ^B	31.0 ^B	28.8 ^A	30.2 ^{AB}
SA	29.1 a	29.7 b	28.7 a	29.2 b	29.3	29.9	28.4	31.0
CA	31.1 c ^C	29.2 ab ^B	29.4 ab ^B	27.6 a ^A	30.0 ^{AB}	30.7 ^B	28.9 ^A	31.0 ^B
KCl	29.1 a	29.0 ab	31.1 c	30.1 b	29.4 ^{AB}	31.2 ^C	29.0 ^A	30.6 ^{BC}
Pt (mg kg ⁻¹)								
	0.037*	0.150 ns	0.002**	0.027*	0.000***	0.844 ns	0.619 ns	0.090 ns
CON	521 b ^B	487 ^A	493 ab ^A	514 a ^B	529 b ^C	511 ^{AB}	523 ^{BC}	502 ^A
TSP	519 b	526	523 c	541 ab	555 c	523	536	520
RMA	526 b	518	525 c	560 b	548 bc	521	526	543
SA	512 ab	509	513 bc	529 a	545 bc ^C	522 ^{AB}	531 ^{BC}	509 ^A
CA	534 b ^{BC}	507 ^{AB}	483 a ^A	541 ab ^C	553 c ^B	517 ^A	532 ^{AB}	519 ^A
KCl	492 a ^A	505 ^{AB}	497 ab ^A	517 a ^B	504 a ^A	522 ^B	524 ^B	489 ^A

CON control, TSP TripleSuperP, RMA rape meal ash, SA straw ash, CA cereal ash, KCl potassium chloride, Pox oxalate soluble P, DPS degree of P saturation, PSC P sorption capacity, Pt total P

* $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns = not significant; different small letters indicate significant differences between the fertilization treatments within a column; different capital letters indicate significant differences between main crops or catch crops within a line; $P < 0.05$ (Duncan)

(116 mg pot⁻¹ and 53 mg pot⁻¹, respectively). Probably buckwheat could mobilize P additionally to its own need. In investigations by Bekele et al. (1983), buckwheat has demonstrated high Ca-uptake rates followed by H⁺ release which might be responsible for a shift in mass-action equilibrium favoring the solubility of poor soluble P sources. A very high P uptake efficiency from Ca phosphates was also reported for buckwheat by Zhu et al. (2002).

Specific effects of other crops on soil P contents became visible e.g. for the CA treatment. The combination of CA and barley resulted in very low Pw values of 7.5 mg kg⁻¹ soil, which were comparable to the CON, whereas a combination of CA and maize resulted in Pw values of 11.9 mg kg⁻¹ soil, which tended to be the highest found for maize (Table 8).

For Pdl the cultivation of blue lupin in combination with CA resulted in about 40% higher values compared to CON (48.3 mg kg⁻¹ soil and 34.7 mg kg⁻¹ soil, respectively), whereas the combination of summer barley and CA lead to very low Pdl content (34.6 mg kg⁻¹ soil) (Table 8).

High Pdl values found for lupine are in accordance with the lower P uptake of lupine, and consequently lower exhaustion of P in soil. However, additional mobilizing effects could also have contributed to this high Pdl values. For lupin, a P mobilizing effect was found in many studies, albeit mainly for white lupin (*L. albus*) (Gilbert et al. 1999; Shen et al. 2003; Kania 2005) due to its cluster roots and an intense expression of root-induced chemical changes in the rhizosphere. According to results of Egle et al. (2003) and Pearse et al. (2007), blue lupin (*L. angustifolius*), which was used in our study, does not form root clusters, but does have a high solubilising effect related to efflux of carboxylates and excessive cation uptake.

The decrease of the readily available P contents directly after phacelia harvest is probably just a temporary process. In a long term field experiment with different catch crops used as green fertilizer, phacelia resulted in the highest increase of bio-available P contents in soil (Eichler-Löbermann et al. 2007).

Application of P resulted in an increase of Pox contents in soil (Table 7), although this effect was lower than on Pw and Pdl. Increasing effects were mainly found for RMA and TSP. Differences in contents of Pox also depended on cultivated crops (Table 5). For the main crops after cultivation of lupin and maize the highest Pox contents were

measured up to 14.5 mmol kg⁻¹ (Table 9). For the catch crops, again buckwheat but also oil radish cultivation resulted in high Pox contents.

The DPS is related to what proportion the sorption sites in soil are occupied by Pox (Breeuwsma et al. 1995). Therefore, DPS values were closely related to Pox values and were affected by crop cultivation and fertilization (Table 5). The application of TSP or ashes generally caused the higher DPS values in comparison to the control (Table 7). The combination of lupin and TSP or RMA and oil radish combined with CA lead to the highest values of DPS (Table 9). By desorption processes, the sorbed P can be delivered into the soil solution and can contribute to plants P nutrition.

Fertilization effects on Pt were low in both experiments (Tables 7 and 9).

Conclusions

The utilization of biomass ashes as fertilizer can be an important strategy to create nutrient cycles in agriculture and to save nutrient resources. Based on our results, crop biomass ashes can be used as effective source for P fertilization on loamy sand. Generally, the ashes increased the crop P uptake as well as the readily plant available P pools in soil in comparison to the control.

The interactive effects of biomass ashes and cultivated crops may have an additional effect on P utilization from ashes. The crop effect on ash P utilization is probably related to specific adaptation and mobilization processes and needs further consideration. High P uptakes of green fertilizer catch crops can guarantee high P release after decomposition. Since catch crops additionally supply the soil with organic material, an application of crop biomass ashes to catch crops seems very promising. According to our results, a combination of ash fertilization with phacelia or buckwheat cultivation could be very positive in this sense.

Provided that ashes do not contain harmful concentrations of heavy metals or other toxic substances, biomass ashes can be applied in agriculture as a valuable fertilizer.

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