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Phosphorus Allocation in Surface Soil of Two Drained Peatland Forests Following Wood and Peat Ash Application – Why Effective Adsorption on Low Sorptive Soils?

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Fertilization of drained peatland forests with wood ash and different commercial phosphorus fertilizers (calcium phosphates) generally give similar stand growth responses. However, it has been shown that use of calcium phosphate fertilizers generally lead to highly increased P release to recipient water courses. On the other hand, no corresponding release has been reported after ash fertilization. Soil samples from the surface peats from a nutrient poor and a fertile drained peatland site were collected before and 1–4 years after application of five different types of ash products. The changes over time in the different chemical forms of P in the substrate were studied. The results indicated that the reason for the low liability to leaching of ash fertilizers was that significant amounts of P are adsorbed by Al and Fe during weathering of the ash fertilizers. However, further studies are needed to clarify whether the adsorption of P occurs with the Al and Fe of the ash or the native Al and Fe compounds present in soil before ash fertilization.

Keywords ash fertilization, forestry, peat, aluminium, iron, phosphorus adsorption, phosphorus fractionation
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1 Introduction

In Finland, the forest industry, together with thermal and electric power plants produce 200 000–300 000 t of ash annually. Half of this ash is from wood and bark and the other half from fuel peat and coal (Korpilahti et al. 1999). At present, almost all the ash is being disposed of as waste or used as landfill material. However, because of new environmental legislation and stricter landfill directives that have been issued during the recent years, the possibility of recycling wood ash back to the forests has raised growing interest.

It has long been known that wood ash has a liming effect and acts as a good source of plant nutrients, especially of phosphorus (P) and potassium (K) (Silfverberg and Huikari 1985, Silfverberg 1996, Moilanen et al. 2002). Usually ash fertilization does not improve tree stand production on mineral soil forests (Jacobson 2003, Saarsalmi et al. 2004), probably because on those nitrogen and not K or P limits tree growth. However, on peat soils K and P deficiency is common and may limit tree growth (e.g. Kaunisto and Paavilainen 1988, Paavilainen and Päivänen 1995). About 15 million hectares of such soils have been drained for forestry in the boreal and temperate zones (Paavilainen and Päivänen 1995). Ash fertilization improves the P and K availability of drained peatland forests and long-term growth responses (>30 years) have been documented, especially on nitrogen-rich sites (Silfverberg and Huikari 1985, Ferm et al. 1992, Silfverberg 1996). Particularly in Finland, forestry drainage has been intensive (>5 million ha) and the prospects of recycling wood ash to forests are therefore good.

Before it will be possible to increase the recycling of ash, the environmental consequences of ash fertilization need to be clarified. Many of the environmental concerns related to ash recycling, e.g., heavy metal accumulation in berries and mushrooms (Moilanen et al. 2006), accumulation of environmental pollutants in soil fauna (Lundkvist 1998) or forest fauna (Lodenius et al. 2002), potentially harmful impacts of ash on soil microbial community (Perkiömäki 2004), heavy metal leaching to water bodies (Piirainen and Domisch 2004), have not been proven to be so serious that it would be impossible to fertilize the forest sites at least once during a tree stand generation.

One concern that is also raised in connection with increased wood ash recycling is that ash fertilization may enhance P release to downstream water bodies. It has been shown that the use of commercial calcium phosphate fertilizers on drained peatlands generally leads to highly increased P-losses (Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm and Cuttle 1983, Renou et al. 2000), and that the trophic state of a recipient water body has been altered as a consequence of application of P (Lepistö and Saura 1998). However, after ash fertilization no corresponding changes in hydrological P losses from drained peatlands have been reported (Nilsson and Lundin 1996, Tulonen et al. 2003, Piirainen and Domisch 2004). Even when relatively high amounts (5000–6500 kg ha^{-1}) of powdered, unstabilized ash products were applied on a very low P-sorptive, ombrotrophic peat soil, the P leaching rates remained low (Piirainen and Domisch 2004).

The reason for the difference in liability to leaching between ash and commercial calcium phosphate fertilizers may be the high content of aluminium (Al) and iron (Fe) in ash (e.g. Steenari et al. 1998, Larsson and Westling 1998, Perkiömäki and Fritze 2003). In general, peaty soils have low contents of P-sorbing Al and Fe hydroxides and oxides (Cuttle 1983, Nieminen and Jarva 1996) and a number of studies have shown that the application of Al or Fe together with P increases adsorption and reduces leaching from organic soils (Larsen et al. 1959, Fox and Kamprath 1971, Scheffer and Kuntze 1989). However, the P adsorption capacity of the native Al and Fe present in the soil before ash application may also increase after ash fertilization because of the liming effect. The P adsorption by Al and Fe is suppressed in organic soils by the sorption of humic acids on the surfaces of Al and Fe oxides (Larsen et al. 1959) and the humus-metal complexes of this kind are broken by liming (Rannikko and Hartikainen 1980).

To be able to estimate the importance of Al-P and Fe-P formation for P adsorption and hydrological phosphate losses, information that presently is not available is needed on the trans-

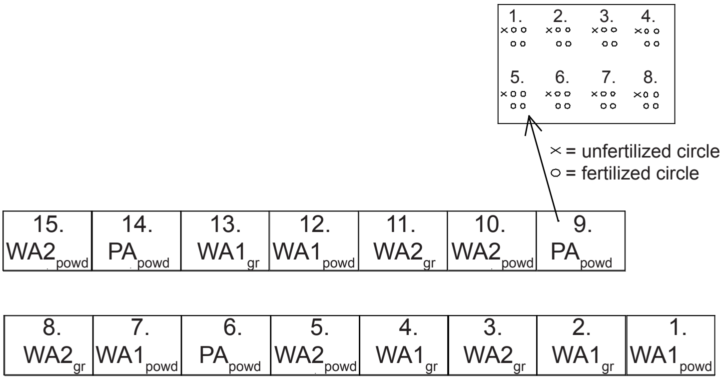

Fig. 1. Experimental layout of the two ash experiments. In each plot (10 × 10 m) eight (1–8) fertilization patches (about 1 m^2) were systematically located. In each of these patches four sampling circles (ø 14.8 cm) were fertilized and one left as an unfertilized control. For ash treatments, see Table 1.

formations of P between different chemical forms during weathering of ash fertilizes. In this study, soil samples of the surface peat from experiments on two drained peatland sites were collected 2 months–4 years after application of 5 types of ash fertilizers, and the changes over time in the different chemical forms of P were studied. The main aim was to find out if such a significant formation of Al-P and Fe-P would occur during weathering of the ash fertilizers that it may efficiently control the adsorption and leaching of P.

2 Material and Methods

The two peatland sites were located at the Kivisuo experimental field in south-central Finland (61º51' N, 25º59' E, 130 m a.s.l.). The rate of nutrient and heavy metal release from ash was studied previously at the Kivisuo experiment and more detailed description of the two study sites, the ash products and the collection of soil samples are given in Nieminen et al. (2005). The original site type of the nutrient-poor site was small-sedge pine bog (Heikurainen and Pakarinen 1982), which was dominated by a sparse Scots pine stand (*Pinus sylvestris* L.) with about 5 m mean height and 10 m^3 ha^{-1} stem volume. The site had been drained in the middle of 1940s, but no clear changes from the original pristine state could be seen neither in the ground vegetation nor the tree stand. On the more fertile site drainage had clearly transformed the site from the pristine state and was classified as an old drainage mire of the *Vaccinium vitis-idaea* type (Heikurainen and Pakarinen 1982). It was dominated by a birch stand (*Betula pubescens* Ehrh.) with 15 m mean height and 80 m^3 ha^{-1} stem volume.

The five ash products studied were: powdered ($WA1_{powd}$) and granulated ($WA1_{gr}$) wood ash from Metsä-Botnia's pulp mill at Äänekoski (south-central Finland); corresponding ashes ($WA2_{powd}$ and $WA2_{gr}$) from StoraEnso's Enocell pulp mill (east Finland); and powdered peat ash (PA_{powd}) from Fortum's Power and Heat plant at Joensuu (east Finland). The Äänekoski granulated ash ($WA1_{gr}$) was stabilized by the self-hardening method (Nilsson et al. 1996) and the Enocell ash by rolling a mixture of ash and water (2:1) in a drum. The P, K, Ca, Mg, Na, Mn, S, Zn, B, Cd and Cu contents were higher in the four wood ashes, while the Al and Fe contents were significantly higher in the peat ash (Table 1).

Both sites had a similar experimental layout. The layout had a random design with three replications per ash product; that is a total of 15 plots (10 x 10 m) per site (Fig. 1). In each of these 15 plots 8 fertilization patches (about 1 m^2) were established and, in each patch, 5 sampling circles (ø 14.8 cm) were laid out. Four of the circles were fertilized with 8.66 g of dried (60ºC) ash (= 5000 kg ha^{-1}) and one circle was left unfertilized.

Table 1. Contents of mineral nutrients and heavy metals in each ash fertilizer.

	WA1$_{powd}$	WA1$_{gr}$	WA2$_{powd}$	WA2$_{gr}$	PA$_{powd}$
P (mg g^{-1})	13.3	12.4	13.0	12.4	6.9
K (mg g^{-1})	43.3	54.8	39.0	37.5	3.9
Ca (mg g^{-1})	228.9	229.0	185.8	172.4	74.5
Mg (mg g^{-1})	24.5	23.7	24.1	22.0	10.9
Na (mg g^{-1})	10.2	10.4	6.7	6.8	2.4
Al (mg g^{-1})	11.9	11.5	12.0	12.4	29.0
Fe (mg g^{-1})	12.9	11.9	9.3	9.6	60.4
Mn (mg g^{-1})	12.3	11.6	19.7	18.5	1.6
S (mg g^{-1})	18.3	26.5	26.3	22.9	3.7
Zn (mg kg^{-1})	3280.0	3510.0	4865.0	4680.0	129.0
B (mg kg^{-1})	286.0	303.0	420.0	394.0	37.0
Cd (mg kg^{-1})	16.2	17.2	28.9	22.9	< 2.0
Co (mg kg^{-1})	23.2	21.2	21.2	20.3	23.7
Cr (mg kg^{-1})	79.2	78.1	49.6	51.9	80.0
Cu (mg kg^{-1})	93.1	101.5	112.5	124.0	65.7
Ni (mg kg^{-1})	93.6	81.2	81.5	76.7	78.4
Pb (mg kg^{-1})	241.5	137.0	54.8	44.5	63.3

WA1$_{powd}$ = powdered wood ash from Metsä-Botnia/Äänekoski; WA1$_{gr}$ = granulated wood ash from Metsä-Botnia/Äänekoski; WA2$_{powd}$ = powdered wood ash from StoraEnso/Enocell; WA2$_{gr}$ = granulated wood ash from StoraEnso/Enocell; PA$_{powd}$ = powdered peat ash from Fortum Power and Heat ltd./Joensuu

Table 2. Total P (TP) contents and the proportions of P_{H2O}, easily soluble P, Al-, Fe- and Ca-P, and residual P in each ash fertilizer.

	Total P, %	P_{H2O}	Soluble P	Al-P	Fe-P	Ca-P	Residual P
				% of Total P			
WA1$_{powd}$	1.33	< 0.1	0.9	3.9	0.4	71.8	23.0
WA1$_{gr}$	1.24	< 0.1	0.9	3.0	0.3	70.0	25.8
WA2$_{powd}$	1.30	< 0.1	0.6	5.2	0.3	71.0	22.9
WA2$_{gr}$	1.24	< 0.1	0.9	3.9	0.2	71.7	23.3
PA$_{powd}$	0.69	< 0.1	7.9	8.0	0.3	53.4	30.4

At the beginning of the experiment in August 2000, peat samples were taken from the unfertilized circles; samples from the fertilized circles were collected about 2, 9, 21, and 45 months after the ash application. On each sampling occasion, an undisturbed 10 cm thick core was taken from one systematically chosen sampling circle from each of the eight fertilization patches. The samples were combined by plot. Before taking the sample the field layer vegetation was cut away to a height of 2–3 cm above the soil surface. The bottom layer vegetation was, however, included in the peat sample. This was to ensure that no residues of the added ash fertilizers, if present in the bottom layer vegetation, would be removed.

The chemical analyses of the soil samples taken from the sampling circles showed that, at the beginning of the experiment, the pH and Al, Fe and Ca concentrations were higher on the fertile site than on the nutrient-poor site (Tables 3 and 4), but the pH and Al, Fe and Ca concentrations increased more at the nutrient-poor site after fertilization. The peat bulk density was about 0.04 g cm^{-3} at the nutrient-poor site compared with 0.10 g cm^{-3} at the fertile site. Based on the Al and Fe contents in peat, the P adsorption capacity of both the nutrient-poor and the fertile site should be low (Cuttle 1983, Nieminen and Jarva 1996, Nieminen 2000).

To determine the different P fractions, the peat samples from the sampling circles were first dried at 60 °C to constant mass, weighed for bulk density calculations and homogenized in a stainless steel mill (sieve mesh diameter 0.25 mm). The

Table 3. pH and Ca, Al and Fe concentrations of surface peat (0–10 cm) from the nutrient-poor site at the beginning of the experiment (time 0) and 2, 9, 21 and 45 months after ash application. For explanation, see Table 1 and Fig. 1.

	Time	WA1$_{\text{powd}}$	WA1$_{\text{gr}}$	WA2$_{\text{powd}}$	WA2$_{\text{gr}}$	PA$_{\text{powd}}$
pH	0	3.56 ± 0.08	3.51 ± 0.01	3.51 ± 0.03	3.52 ± 0.04	3.49 ± 0.02
	2	6.30 ± 0.25	6.49 ± 0.14	6.04 ± 0.20	5.70 ± 0.23	4.16 ± 0.03
	9	–	–	–	–	–
	21	–	–	–	–	–
	45	5.12 ± 0.08	5.66 ± 0.05	4.98 ± 0.11	5.20 ± 0.05	3.76 ± 0.08
Ca, mg g^{-1}	0	1.42 ± 0.17	1.48 ± 0.08	1.41 ± 0.10	1.49 ± 0.04	1.39 ± 0.20
	2	30.53 ± 4.40	33.10 ± 6.71	24.40 ± 2.31	18.63 ± 5.45	8.84 ± 0.70
	9	25.73 ± 2.69	24.10 ± 5.24	20.60 ± 0.95	20.97 ± 3.76	8.86 ± 0.44
	21	22.13 ± 2.06	22.10 ± 2.07	19.63 ± 0.06	15.33 ± 0.31	7.35 ± 0.78
	45	18.14 ± 1.19	19.93 ± 2.26	14.40 ± 1.31	20.00 ± 1.22	4.73 ± 0.90
Al, mg g^{-1}	0	0.52 ± 0.03	0.55 ± 0.03	0.50 ± 0.06	0.55 ± 0.05	0.56 ± 0.08
	2	2.14 ± 0.13	2.00 ± 0.19	2.06 ± 0.08	1.80 ± 0.40	3.55 ± 0.29
	9	2.26 ± 0.18	1.93 ± 0.27	1.96 ± 0.11	2.03 ± 0.29	3.80 ± 0.27
	21	2.07 ± 0.09	1.91 ± 0.02	2.00 ± 0.04	1.59 ± 0.06	3.73 ± 0.22
	45	2.16 ± 0.26	1.92 ± 0.07	1.92 ± 0.07	2.11 ± 0.18	3.50 ± 0.16
Fe, mg g^{-1}	0	1.09 ± 0.17	1.23 ± 0.18	1.07 ± 0.18	1.18 ± 0.21	1.20 ± 0.19
	2	2.64 ± 0.36	2.77 ± 0.33	2.29 ± 0.13	2.20 ± 0.18	7.40 ± 0.65
	9	2.66 ± 0.11	2.58 ± 0.07	2.30 ± 0.23	2.40 ± 0.31	7.63 ± 0.31
	21	2.62 ± 0.22	2.66 ± 0.17	2.40 ± 0.12	2.10 ± 0.24	8.00 ± 0.38
	45	2.59 ± 0.39	2.52 ± 0.27	2.17 ± 0.14	2.19 ± 0.21	6.60 ± 0.25

– not measured

Table 4. pH and Ca, Al and Fe concentrations of surface peat (0–10 cm) from the fertile peatland site at the beginning of the experiment (time 0) and 2, 9, 21 and 45 months after ash application. For explanation, see Table 1 and Fig. 1.

	Time	WA1$_{\text{powd}}$	WA1$_{\text{gr}}$	WA2$_{\text{powd}}$	WA2$_{\text{gr}}$	PA$_{\text{powd}}$
pH	0	3.68 ± 0.14	3.68 ± 0.17	3.58 ± 0.08	3.65 ± 0.12	3.57 ± 0.08
	2	5.26 ± 0.13	5.73 ± 0.06	4.84 ± 0.07	4.56 ± 0.17	3.93 ± 0.01
	9	–	–	–	–	–
	21	–	–	–	–	–
	45	4.82 ± 0.12	5.47 ± 0.08	4.55 ± 0.14	4.60 ± 0.19	3.93 ± 0.04
Ca, mg g^{-1}	0	4.23 ± 0.68	3.80 ± 0.83	3.60 ± 0.25	3.64 ± 1.13	3.61 ± 0.60
	2	16.23 ± 2.20	15.90 ± 1.35	12.77 ± 1.77	12.17 ± 2.14	7.10 ± 1.10
	9	17.10 ± 2.98	18.57 ± 0.45	16.20 ± 1.56	12.70 ± 0.66	8.84 ± 0.20
	21	14.63 ± 1.90	16.00 ± 2.40	13.23 ± 1.19	10.68 ± 1.25	7.35 ± 0.45
	45	15.73 ± 2.44	19.00 ± 0.50	12.77 ± 1.05	14.97 ± 1.60	7.43 ± 0.85
Al, mg g^{-1}	0	0.99 ± 0.22	1.21 ± 0.12	1.17 ± 0.13	1.42 ± 0.38	1.26 ± 0.28
	2	1.96 ± 0.12	1.82 ± 0.13	1.69 ± 0.04	2.04 ± 0.29	2.69 ± 0.17
	9	2.07 ± 0.11	2.14 ± 0.22	2.06 ± 0.27	2.19 ± 0.39	3.41 ± 0.33
	21	1.81 ± 0.03	1.95 ± 0.19	1.81 ± 0.11	2.03 ± 0.31	2.80 ± 0.32
	45	2.08 ± 0.17	2.10 ± 0.15	1.87 ± 0.11	2.23 ± 0.36	3.00 ± 0.25
Fe, mg g^{-1}	0	1.81 ± 0.31	1.88 ± 0.37	1.85 ± 0.21	2.23 ± 0.15	1.99 ± 0.30
	2	2.74 ± 0.11	2.59 ± 0.19	2.28 ± 0.24	2.78 ± 0.03	5.05 ± 0.44
	9	2.91 ± 0.22	2.83 ± 0.24	2.53 ± 0.22	2.88 ± 0.19	6.10 ± 0.55
	21	2.67 ± 0.08	2.65 ± 0.30	2.42 ± 0.46	2.80 ± 0.08	5.23 ± 0.38
	45	2.69 ± 0.20	2.76 ± 0.32	2.38 ± 0.22	2.77 ± 0.05	5.19 ± 0.06

– not measured

total P in the peat was determined using microwave destruction with a mixture of HNO_3 and HCl and inductively coupled plasma emission spectrometry (ICP/AES, ARL 3580). The easily soluble, and Al-, Fe-, and Ca-bound P forms were determined according to the procedure of Chang and Jackson (1957). This involved sequential extraction of 1.0 g peat with 50 ml of 1 M NH_4Cl, 0.5 M NH_4F, 0.1 M NaOH, and 0.25 M H_2SO_4. The pH of the NH_4F reagent was adjusted to 8.5 according to Fife (1959). The P content of each extract was analysed by ICP/AES, ARL 3580. In addition to the easily soluble, and Al-, Fe-, and Ca-bound forms, the residual (insoluble) P-fraction was determined. The residual P was calculated as the difference between the total P and the P extracted by the fractionation procedure (easily soluble + Al-, Fe- and Ca-P).

With regard to the P fractionation procedure Qualls and Richardson (1995) point out, "it is doubtful whether any extraction procedure for soil can give a precise separation of the complex components of soil. Individual fractions may contain more than one component". Generally, the different fractions are therefore referred to in terms of the extractant (e.g. H_2SO_4-P) rather than in terms of the form of P that occur in them (e.g. Ca-P). However, like Qualls and Richardson (1995), we here refer to different fractions in terms of hypothetic P-forms so that they will be more familiar to the reader. Nevertheless, it is important to be aware of the methodological qualifications of the fractionation procedure.

The five ash fertilizers used in the present study were also analyzed for their different forms of P and the procedure of fractionation was the same as described above for the peat samples. In addition to total P and the different P fractions, the water soluble P (P_{H2O}) in the ash fertilizers was determined. P_{H2O} was analyzed by ICP/AES, ARL 3580 after boiling (10 min) the ash sample in deionized water using an initial fertilizer:solution ratio of 1:25.

The changes over time of the different P fractions both as total pools (kg ha^{-1}) and as percentages of the total P store in peat in the 0–10 cm layer are presented. The total pool of each P-fraction in the soil at the beginning of the experiment (Time 0, see Tables 5 and 6) was calculated as the sum of the P added in the soil in the ash and the native P in the peat in the control circles. The effect of ash fertilization on the pools of the different P-fractions was tested using repeated measures ANOVA (Wilks' Lambda test statistics). The grouping factors were peatland site type (2 levels) and fertilizer treatment (5 levels), and the repeated or within factor was the sampling time (5 levels: 0, 2, 9, 21, and 45 months after application).

3 Results

31 Forms of P in Ash Fertilizers

The total P content of the four wood ashes was 1.24–1.33%, and in the peat ash, 0.69%. Most of the P in the ash fertilizers occurred in the form of Ca-P (Table 2). About 70% of total P in the four wood ashes, and 53% in the peat ash, occurred as Ca-P. The proportion of insoluble residual was also high in all five ash fertilizers (20–30%). The peat ash differed from the wood ashes in that its total P concentration and the proportion of Ca-P were significantly lower, but the proportions of residual P, Al-P, and especially soluble P, were higher. The proportions of Fe-P were very low (0.2–0.4%) and no water soluble P occurred in any of the five ash fertilizers.

32 Forms of P in the Peat

At the beginning of the experiment (Time 0, Table 5) the total P store (P in peat + P added through ash) in the uppermost 0–10 cm peat layer at the nutrient poor site was 75–80 kg ha^{-1} in the wood ash plots and about 49 kg ha^{-1} in the peat ash plots. The total P stores at the more fertile site were 122–141 kg ha^{-1} for the wood ash plots and 95 kg ha^{-1} for the plots fertilized with peat ash (Table 6). At time 0, about 80% of the total P store of the nutrient poor site was accounted for by the P added in the ash in the wood ash plots, and 70% in the peat ash plots. At the fertile site the corresponding proportions were 44–52% for the wood ash plots and about 36% for the peat ash treatments.

Ca-P and residual P were the main P-fractions

Table 5. Pools (kg ha^{-1}) of different P fractions ± S.D. in the surface peat (0–10 cm) of the nutrient-poor site at time 0 and 2, 9, 21 and 45 months after application. Total pool of each P fraction at time 0 calculated as the sum of the added P (Ash-P) and the native (Peat-P) in the peat at the beginning of the experiment. For ash characteristics, see Table 1.

		Initial		After			
		0		2	9	21	45
	Peat-P	Ash-P	Total				
WA1$_{powd}$							
Soluble P	3.3 ± 0.2	0.6	3.9	30.3 ± 2.4	27.2 ± 2.0	19.2 ± 2.8	17.9 ± 2.7
Al-P	1.6 ± 0.1	2.6	4.2	9.1 ± 2.3	11.7 ± 4.4	11.1 ± 1.8	10.9 ± 0.7
Fe-P	6.3 ± 0.8	0.3	6.6	6.3 ± 1.2	9.3 ± 1.8	14.6 ± 3.0	14.7 ± 0.3
Ca-P	0.2 ± 0.0	47.8	48.0	19.6 ± 0.9	15.6 ± 2.6	14.9 ± 2.2	6.9 ± 1.0
Residual P	2.3 ± 1.0	15.1	17.4	14.0 ± 2.5	14.8 ± 2.8	5.5 ± 1.8	4.4 ± 1.2
Total	**13.7**	**66.4**	**80.1**	**79.3**	**78.6**	**65.3**	**54.8**
WA1$_{gr}$							
Soluble P	3.2 ± 0.1	0.6	3.8	20.1 ± 1.5	20.6 ± 3.1	17.3 ± 2.2	19.2 ± 2.4
Al-P	1.6 ± 0.1	1.9	3.5	12.0 ± 1.4	16.4 ± 2.5	14.3 ± 1.9	14.2 ± 1.5
Fe-P	6.4 ± 0.5	0.2	6.6	6.3 ± 0.6	8.5 ± 1.9	13.0 ± 1.4	14.5 ± 0.7
Ca-P	0.2 ± 0.0	43.5	43.7	26.0 ± 1.0	25.3 ± 12.8	17.8 ± 1.7	12.3 ± 2.6
Residual P	2.7 ± 0.3	15.7	18.4	11.8 ± 7.0	8.9 ± 12.0	8.4 ± 4.4	6.3 ± 1.4
Total	**14.1**	**61.9**	**76.0**	**76.2**	**79.7**	**70.8**	**66.5**
WA2$_{powd}$							
Soluble P	3.2 ± 0.2	0.4	3.6	22.5 ± 1.0	21.9 ± 3.0	16.7 ± 2.2	22.9 ± 1.1
Al-P	1.6 ± 0.1	3.4	5.0	8.6 ± 1.2	10.5 ± 1.0	12.1 ± 1.3	11.0 ± 1.7
Fe-P	6.2 ± 1.0	0.2	6.3	6.4 ± 1.0	9.2 ± 0.5	14.5 ± 0.8	15.3 ± 0.7
Ca-P	0.2 ± 0.0	46.2	46.4	27.2 ± 1.9	23.0 ± 3.1	19.7 ± 1.3	10.1 ± 0.6
Residual P	3.0 ± 0.4	14.9	17.9	12.6 ± 3.4	11.6 ± 2.7	6.9 ± 1.8	6.0 ± 4.1
Total	**14.2**	**65.1**	**79.3**	**77.3**	**76.2**	**69.9**	**65.3**
WA2$_{gr}$							
Soluble P	2.9 ± 0.4	0.6	3.5	16.8 ± 3.2	18.4 ± 2.7	17.8 ± 2.1	21.0 ± 1.0
Al-P	1.5 ± 0.2	2.4	3.9	12.6 ± 2.3	14.0 ± 2.5	13.1 ± 0.7	15.4 ± 0.9
Fe-P	6.2 ± 0.8	0.1	6.3	8.1 ± 2.2	9.8 ± 1.7	12.8 ± 1.8	12.9 ± 0.6
Ca-P	0.2 ± 0.0	44.4	44.6	25.3 ± 3.8	21.7 ± 12.5	17.3 ± 0.6	20.9 ± 4.7
Residual P	2.5 ± 0.3	14.2	16.7	14.6 ± 0.5	16.3 ± 4.9	4.0 ± 2.9	4.9 ± 2.0
Total	**13.3**	**61.7**	**75.0**	**77.4**	**80.2**	**65.0**	**75.1**
PA$_{powd}$							
Soluble P	3.2 ± 0.1	2.7	5.9	12.9 ± 0.9	12.7 ± 0.2	9.7 ± 0.3	9.1 ± 0.5
Al-P	1.7 ± 0.1	2.8	4.5	4.1 ± 0.2	4.4 ± 0.2	4.6 ± 0.2	5.9 ± 0.5
Fe-P	6.5 ± 0.5	0.1	6.6	7.5 ± 1.0	8.5 ± 0.7	11.7 ± 0.6	12.9 ± 1.2
Ca-P	0.2 ± 0.0	18.4	18.6	8.4 ± 0.2	9.4 ± 1.7	6.4 ± 0.5	5.3 ± 0.7
Residual P	3.3 ± 0.4	10.5	13.8	10.1 ± 2.3	9.8 ± 2.6	8.5 ± 1.3	6.4 ± 1.6
Total	**14.9**	**34.5**	**49.4**	**43.0**	**44.8**	**40.9**	**39.6**

at time 0, Ca-P accounting for about 60% of the total P store in the wood ash plots of the nutrient poor site, and 30–40% at the more fertile site (Figs. 2 and 3). The pools of Ca-P originated almost exclusively from the P added in the ash since the native Ca-P pools were 0.2 kg ha^{-1} at the nutrient poor site and 0.3–0.4 kg ha^{-1} at the fertile site. At both sites the proportion of residual P at time 0 was 20–30% of the total P store for all five treatments. The P added in the ash was the main source of residual P at the nutrient poor site, but at the fertile site, the native P sources were equal to or slightly higher than the amounts of residual P added in the ash fertilizers. The ash fertilization was only a minor source of soluble P and Fe-P as the contents of these P fractions added in the ash fertilizers were quite small (0.1–0.3 kg ha^{-1} for Fe-P and 0.6–2.7 kg ha^{-1} for soluble P). The extra

Table 6. Pools (kg ha^{-1}) of different P fractions ± S.D. in the surface peat (0–10 cm) of the fertile site at time 0 and 2, 9, 21 and 45 months after application. Total pool of each P fraction at time 0 calculated as the sum of the added P (Ash-P) and the native P (Peat-P) in the peat at the beginning of the experiment. For ash characteristics, see Table 1.

	Initial			After			
		0		2	9	21	45
	Peat-P	Ash-P	Total				
$\mathrm{WA1}_{\mathrm{powd}}$							
Soluble P	12.2 ± 1.3	0.6	12.8	33.3 ± 2.5	29.4 ± 1.8	27.4 ± 1.5	28.8 ± 1.4
Al-P	8.7 ± 2.5	2.6	11.0	21.2 ± 3.1	18.9 ± 7.1	15.3 ± 3.1	13.3 ± 2.8
Fe-P	27.7 ± 5.6	0.3	28.0	32.3 ± 7.2	33.2 ± 7.2	36.2 ± 3.4	38.1 ± 6.5
Ca-P	0.3 ± 0.1	47.8	48.1	11.4 ± 3.3	10.4 ± 2.1	7.8 ± 1.0	8.1 ± 0.6
Residual P	12.9 ± 4.8	15.1	30.0	21.2 ± 5.0	21.9 ± 3.3	11.2 ± 4.9	12.9 ± 0.8
Total	**61.5**	**66.4**	**127.9**	**119.4**	**113.8**	**97.9**	**101.2**
$\mathrm{WA1}_{\mathrm{gr}}$							
Soluble P	11.6 ± 9.7	0.6	12.2	26.1 ± 0.7	24.9 ± 0.5	24.1 ± 4.5	27.0 ± 1.9
Al-P	8.8 ± 2.2	1.9	10.7	24.8 ± 4.9	27.9 ± 2.9	24.6 ± 3.9	22.2 ± 3.1
Fe-P	27.2 ± 7.4	0.2	27.4	33.1 ± 9.5	34.2 ± 7.5	35.6 ± 5.5	40.0 ± 6.8
Ca-P	0.3 ± 0.0	43.5	43.8	15.0 ± 0.7	14.0 ± 1.0	11.9 ± 1.3	14.8 ± 1.8
Residual P	12.2 ± 0.8	15.7	27.9	15.5 ± 6.9	20.7 ± 8.8	13.9 ± 7.1	15.3 ± 2.7
Total	**60.1**	**61.9**	**122.0**	**114.5**	**121.7**	**110.1**	**119.3**
$\mathrm{WA2}_{\mathrm{powd}}$							
Soluble P	11.7 ± 1.0	0.4	12.1	32.4 ± 2.1	29.6 ± 1.4	29.5 ± 2.5	32.9 ± 6.2
Al-P	10.0 ± 1.6	3.4	13.4	15.3 ± 2.0	13.6 ± 0.2	14.1 ± 3.1	12.1 ± 3.1
Fe-P	28.5 ± 4.5	0.2	28.7	31.2 ± 8.1	29.3 ± 2.2	36.0 ± 5.6	36.6 ± 7.0
Ca-P	0.4 ± 0.0	46.2	46.6	10.5 ± 3.7	16.6 ± 2.9	15.2 ± 1.0	12.0 ± 2.1
Residual P	17.0 ± 3.3	14.9	31.9	20.7 ± 13.6	25.1 ± 0.3	18.0 ± 8.6	14.9 ± 2.1
Total	**67.6**	**65.1**	**132.7**	**110.1**	**114.2**	**112.8**	**108.5**
$\mathrm{WA2}_{\mathrm{gr}}$							
Soluble P	12.9 ± 1.3	0.6	13.5	28.1 ± 2.9	24.3 ± 2.3	26.7 ± 0.6	31.7 ± 4.4
Al-P	14.1 ± 3.4	2.4	16.5	22.9 ± 4.3	20.8 ± 6.5	21.7 ± 2.9	23.1 ± 3.8
Fe-P	33.9 ± 4.5	0.1	34.0	39.3 ± 1.6	36.2 ± 2.7	38.5 ± 4.9	42.9 ± 3.8
Ca-P	0.4 ± 0.0	44.4	44.8	10.2 ± 1.0	15.2 ± 7.0	8.3 ± 2.2	16.8 ± 2.5
Residual P	18.4 ± 1.5	14.2	32.6	26.1 ± 5.0	22.6 ± 3.3	18.1 ±7.9	17.2 ± 3.9
Total	**79.7**	**61.7**	**141.4**	**126.6**	**119.1**	**113.3**	**131.7**
$\mathrm{PA}_{\mathrm{powd}}$							
Soluble P	11.3 ± 0.9	2.7	14.0	19.1 ± 0.3	15.6 ± 0.2	15.0 ± 0.1	16.9 ± 1.9
Al-P	8.6 ± 2.8	2.8	11.4	9.1 ± 1.7	8.3 ± 1.0	9.3 ± 2.5	10.7 ± 2.9
Fe-P	27.2 ± 5.2	0.1	27.3	28.5 ± 6.0	22.9 ± 1.4	31.0 ± 4.5	32.2 ± 3.1
Ca-P	0.4 ± 0.1	18.4	18.8	8.8 ± 1.2	7.6 ± 2.4	7.5 ± 0.9	10.7 ± 0.8
Residual P	13.4 ± 4.5	10.5	23.9	16.8 ± 1.1	22.6 ± 2.6	17.2 ± 3.9	15.1 ± 2.4
Total	**60.9**	**34.5**	**95.4**	**82.3**	**77.0**	**80.0**	**84.8**

Al-P added in the ash fertilizers was 54–68% of the total Al-P pool in the 0–10 cm peat layer at the nutrient poor site, but only 15–25% at the fertile site.

Soon after the ash application the pools of Ca-P and residual P decreased. In the samples collected two months after application, the pools of Ca-P were 10–37 kg ha^{-1} lower than the initial pools (at time 0). Respectively the pools of residual P were 2–12 kg ha^{-1} lower. By the end of the four-year study period, the pools of Ca-P had decreased by 50–85% and those of residual P by 35–75%. Compared to their pools at time 0 the decreases in Ca-P and residual P were lower in the plots treated with peat ash than in those treated with wood ash fertilizers.

Along with the decrease in Ca-P and residual P, the pools of the other P fractions increased.

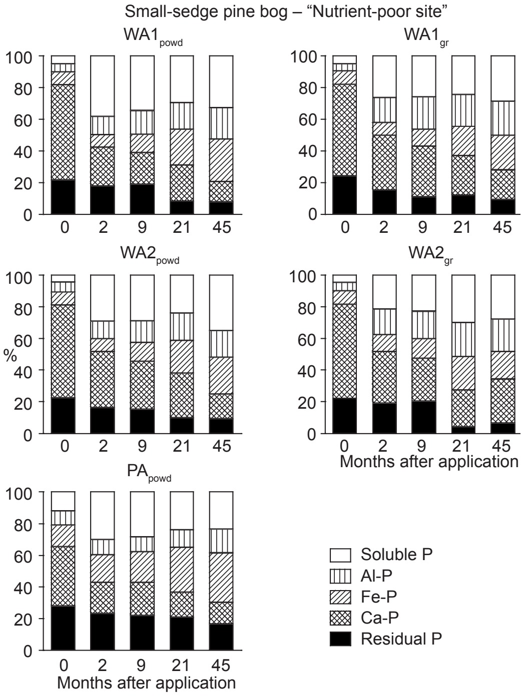

Fig. 2. Changes in the proportions (%) of soluble P, Al-P, Fe-P, Ca-P and residual P of the total P in the surface peat (0–10 cm) of the nutrient poor site 1–4 years after ash fertilization. For ash treatments, see Table 1.

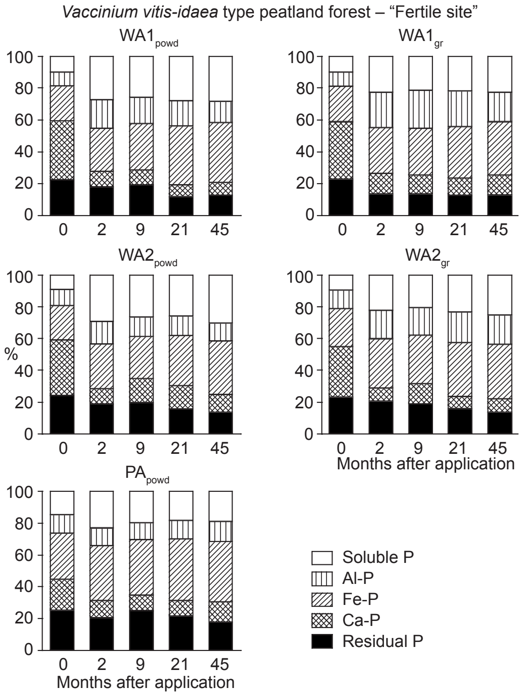

Fig. 3. Changes in the proportions (%) of soluble P, Al-P, Fe-P, Ca-P and residual P of the total P in the surface peat (0–10 cm) of the fertile site 1–4 years after ash fertilization. For ash treatments, see Table 1.

The total pools of Fe-P at time 0 were only 6–7 kg ha^{-1} at the nutrient poor site, and 27–34 kg ha^{-1} at the more fertile site. By the end of the study period, the pools of Fe-P had increased to a level of 13–15 kg ha^{-1} at the nutrient poor site. A similar increase by 5–9 kg ha^{-1} occurred at the more fertile site.

At time 0 the total pools of Al-P were low too: 3–5 kg ha^{-1} at the nutrient poor site, and 11–16 kg ha^{-1} at the more fertile site. However, a high increase in Al-P occurred soon after the application. The samples collected from the wood ash plots 2 months after application indicated that the formation of new Al-P complexes had increased the pools of Al-P by 70–240% at the nutrient poor site, and by 15–130% at the more fertile site. Although the pools of Fe-P gradually increased towards the end of the study, the pools of Al-P remained relatively stable or decreased ($WA1_{powd}$ and $WA2_{powd}$, the fertile site) after an initial increase soon after the fertilization. At the $WA2_{powd}$ plots at the fertile site, the pools of Al-P decreased even below the initial levels (at time 0). No increases in Al-P occurred after peat ash fertilization.

The pools of easily soluble P also increased substantially soon after ash application (2 months), but later during the four year study period no significant changes generally occurred. At the $WA1_{powd}$ plots at the nutrient-poor site, however, the pools decreased clearly towards the end of the study period.

According to repeated measures ANOVA the changes over time in the pools of all five P-fractions were significant ($p<0.001$). The overall differences between the two sites were also significant ($p<0.001$) for all P fractions. The differences between the five fertilizers and the interaction between time and fertilizer treatment were significant ($p<0.001$) for easily soluble P, Al-P and Ca-P, but not for Fe-P (fertilizer; $p=0.203$, time × fertilizer; $p=0.087$) and residual P (fertilizer; $p=0.349$, time × fertilizer; $p=0.092$).

4 Discussion

The results showed significant adsorption of P by Al and Fe during weathering of the ash fertilizers. This adsorption may largely explain the negligible leaching losses that have been obtained with ash fertilizers on low P-sorptive peat soils (e.g. Piirainen and Domisch 2004). Whether the adsorption occurred with the Al and Fe added in soil through ash or with the native Al and Fe present in the substrate prior to fertilization is not known, however. As the non-Al and non-Fe phosphorus fertilizers are poorly adsorped by Al- and Fe-poor peat soils (Harriman 1978, Ahti 1983, Renou et al. 2000), as were the soils in the present study, the extra Al and Fe added in the soil would be the most probable sink for P. Korpilahti (2004) studied the solubility of a number of different ash products with a number of different types of extracts and found that the Al of ash was generally in a more soluble form than Fe. This would explain the greater formation of Al-P than Fe-P compounds during the early stages of ash fertilizer weathering. Because of the liming effect of ash, however, the P adsorption of the native Al and Fe in peat may increase (Rannikko and Hartikainen 1980), and given that most of the Al and Fe of ash are in the very insoluble fractions (Österbacka 2001, Korpilahti 2004, Nieminen et al. 2005), the native Al and Fe may be more important in P adsorption than the compounds in the ash. Thus, to asses the relative importance of the ash-derived and the native Al and Fe compounds in P adsorption, further studies are needed.

Although the contents of Al and Fe were considerably higher in the peat ash than in the four wood ashes, the adsorption of P by Fe and especially Al remained lower in the peat ash treatment. This lower adsorption in the peat ash plots may be because the P content of peat ash was low (Table 1) and the rate of dissolution of P was slower than for the four wood ashes. Owing to the poor liming effect of peat ash (Tables 3–4), it may also be that the P adsorption of the native Al and Fe in peat increases less after peat ash fertilization than after different wood ash treatments.

Although the formation of Al- and Fe-P compounds was significant after the ash fertilization, the increases in Al- and Fe-P were relatively low compared with the pools of P that were simultaneously dissolved from the ash. The formation Al- and Fe-P may thus be a relatively small sink for the P dissolved from ash compared with the other potential sinks, as for example, the accumulation of P in the forest vegetation. However, the formation of Al-P and Fe-P may be a sufficient sink from the viewpoint of water quality protection. This is because the total losses of P from fertilized peatlands, reported in earlier studies (Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm and Cuttle 1983, Nieminen and Ahti 1993, Renou et al. 2000) are much smaller than the extent of adsorption of P by Al and Fe in this study. However, the liming effect of ash may cause an overestimation of the P adsorption by Al because the ammonium fluoride supposed to extract Al-P also dissolves some calcium phosphates in recently limed soils (Kaila 1961). It should also be noted that in soils with an abundance of calcium carbonate, as there probably is after ash fertilization, the fractionation may not be effective in separating P bound by Al and Fe (Williams et al. 1971).

At first, the substantially increased pools of easily soluble P (NH_4Cl extractable) after ash fertilization may seem surprising, since high contents of easily soluble P in the peatlands of a catchment often imply a high risk of P leaching to recipient water courses (Nieminen 2000) and, as mentioned earlier, in earlier studies no losses have been reported after ash fertilization. However, as stated by Nieminen and Penttilä (2004), the extracts that are supposed to dissolve easily soluble P in the soil/water matrix most likely also release the weakly adsorped P in the plant roots and the other living organisms of the soil samples. Most of the NH_4Cl extractable P may actually represent "plant/micro-organisim releasable P" and the actual content of the free, rapidly moving P in the soil water, susceptible to leaching, may be very small.

Although the formation of Al- and Fe-P after ash fertilization is important from the viewpoint of water protection, a negative impact may be involved in that the P adsorbed by Al and Fe remains unavailable to trees and other forest vegetation. However, the increases in wood production after ash fertilization are generally equal, and occasionally even larger, than those with commercial fertilizers without Al and Fe (Silfverberg 1996, Moilanen et al. 2004). This indicates that a considerable part of the P in Al- and Fe-P complexes remains plant-available, but the mechanisms that control the bioavailability of these are still poorly understood. Because of the increasing solubility with decreasing acidity, the liming effect of ash (Tables 3–4) may be one reason why Al-P and Fe-P, which generally is believed to be highly insoluble in acid peat soils, would remain plant available after ash fertilization. In the case of perennial species with mycorrhizal fungi, such as trees, there are indices that another important mechanism for the bioavailability of Al-P and Fe-P is the excretion of organic acids or anions from the tree roots (Hinsinger 2001), but the importance of these root exudates in P bioavailability in peat soils is not known.

5 Conclusion

The changes over time in the different chemical forms of P in soil were studied at two drained peatland sites 2 months–4 years after application of five different types of ash products. A significant decrease occurred in the soil pools of Ca-P and residual P as a result of the dissolution of the ash fertilizers. Along with this decrease, the pools of Al-P and Fe-P increased. It was concluded that the negligible leaching losses that have occurred with ash on drained peatlands may be because significant amounts of the P dissolved from ash are adsorped by Al and Fe. However, further studies are needed to clarify whether the adsorption of P occurs with the Al and Fe of the ash or the native Al and Fe compounds that are present in the soil before ash fertilization.

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