



## Phosphorus speciation in the organic layer of two Swedish forest soils 13–24 years after wood ash and nitrogen application

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### ABSTRACT

Application of wood ash to forests can restore pools of phosphorus (P) and other nutrients, which are removed following whole tree harvesting. Yet, the mechanisms that affect the fate of ash-P in the organic layer are less well known. Previous research into the extent to which ash application leads to increased P solubility in the soil is contradictory. We combined synchrotron P K-edge XANES spectroscopy, μ-XRF microscopy, and chemical extractions to examine the speciation and solubility of P. We studied organic horizons of two long-term field experiments, Riddarhyttan (central Sweden), which had received 3, 6, and 9 Mg ash ha<sup>-1</sup>, and Rödålund (northern Sweden), where 3 Mg ash ha<sup>-1</sup> had been applied alone or combined with N every-three years since 2003. At the latter site, we also determined P in aboveground tree biomass. Overall, the ash application increased P in the organic layer by between 6 and 28 kg P ha<sup>-1</sup>, equivalent to 17–39 % of the initial P content in the applied ash. At Rödålund, there was 4.6 kg Ca-bound P ha<sup>-1</sup> (9.5 %) in the ash treatment compared to 1.6 kg ha<sup>-1</sup> in the ash + N treatment and < 0.4 kg ha<sup>-1</sup> in the N treatment and the control. At Riddarhyttan, only the treatment with the highest ash dose had residual Ca-bound P (3.8 kg ha<sup>-1</sup>). In contrast, the ash application increased Al-bound P ( $p < 0.001$ ) with up to 15.6 kg P ha<sup>-1</sup>. Moreover, the ash increased Olsen-P by up to two times. There was a strong relationship between the concentrations of Olsen-P and Al-bound P ( $R^2 = 0.83$ ,  $p < 0.001$ ) as well as Fe-bound P ( $R^2 = 0.74$ ,  $p = 0.003$ ), suggesting that the ash application resulted in an increased amount of relatively soluble P associated with hydroxy-Al and hydroxy-Fe compounds. Further, there was an 18 % increase in P uptake by trees in the ash treatment. By contrast, repeated N fertilization, with or without ash, reduced Olsen-P. The lower P extractability was concomitant with a 39 % increase in plant P uptake in the N treatment, which indicates elevated P uptake in response to higher N availability. Hence, the application of wood ash increased Al-bound P, easily available P, and P uptake. N fertilization, while also increasing tree P uptake, instead decreased easily available P and did not cause a shift in soil P speciation.

### 1. Introduction

The forest organic layer acts as a bridge between the vegetation and the mineral soil and is important for the biogeochemical cycling of macronutrients such as phosphorus (P) (e.g. Ladanai et al., 2010; Ponge,

2003; Olsson et al., 1996). In Podzols, much of the P cycling occurs in the organic layer, where there is a tight coupling between uptake/immobilization and biological decomposition (Wood et al., 1984). In the mineral soil, a large amount of phosphate (PO<sub>4</sub>) is adsorbed to poorly ordered, surface aluminum (Al) and iron (Fe) mineral phases (Prietzel

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et al., 2016; Tuyishime et al., 2022), which act as a long-term buffer of the equilibrium P concentration (Wood et al. 1984). Forest harvests remove a large amount of nutrients, which might decrease the long-term availability of P (Akselsson et al., 2008; Yanai, 1998; Yu et al., 2018). Co-limitation of P caused by excessive nitrogen (N) deposition (Hedwall et al., 2017) and increased leaching/erosion due to wildfire (Lagerström et al., 2009) may also contribute to long-term P deficiency.

In the EU, particularly in the Nordic and Baltic countries, logging residues, mainly tree tops, branches, and twigs, are used for energy production. Utilization of the residues has increased over the past decades to meet legally binding targets to reduce fossil greenhouse gas emissions (Camia et al. 2021). This has resulted in the production of hundreds of thousands of tonnes of wood ash each year, as a by-product of wood fuel combustion (Bjurström et al., 2003; Mellbo et al., 2008). In 2001, the Swedish Forest Agency issued non-binding recommendations on wood ash recycling following the harvest of logging residues to maintain long-term sustainable forest management (Swedish Forest Agency, 2019). However, only a small portion of the wood ash is brought back to the forest although the potential is much greater (Swedish Forest Agency, 2019; de Jong et al., 2017). The wood ash contains all nutrients present in the logging residues, except for N, which is lost during combustion. To reduce nutrient losses and mitigate soil acidification the wood ash can be returned back to the forest (Karlton et al., 2008; Larsson and Westling, 1998).

Prior to application, it is recommended to stabilize the loose ash (by self-hardening or formation of granules or pellets), to allow the conversion of highly reactive substances of the ash, e.g. caustic oxides, to more slowly dissolving chemical compounds (Karlton et al., 2008; Steenari and Lindqvist, 1997). To produce hardened and crushed ash, the stabilization is done by moistening the ash and allowing the mixture to harden naturally for one to three months before being crushed (Jacobson et al., 2014). Calcium (Ca), occurring mainly as  $\text{CaCO}_3$ , is the most abundant nutrient element (7–30 % by weight) in the hardened bottom or fly wood ash, whereas the P content is often between 0.17 and 2.2 % of the ash (Olsson and Westling, 2006; Augusto et al., 2008; Hannam et al., 2018; Steenari et al., 1999b). The P in the ash is expected to occur mostly as crystalline hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) (Steenari and Lindqvist, 1997), and thus, the dissolution of P from the hardened wood ash can be slow over time. In a column experiment, only between 15 and 20 % of the ash-P had dissolved over a period of five months (Eriksson, 1996). The solubilization of the ash-P may therefore be seen as a long-term remedy for the P depletion caused by forest harvest. In Sweden, the recommended dose of wood ash is two or three metric tons per hectare, depending on stand characteristics, with a minimum ash-P content of  $7 \text{ g kg}^{-1}$  (Swedish Forest Agency, 2019).

The interest in wood ash recycling is greatest in Europe and Canada, particularly in northern Europe (Hannam et al., 2018; Huotari et al., 2015; Pitman, 2006; Reid and Watmough, 2014; Augusto et al., 2008). Previous research has focused on the chemical composition and leaching properties of the ash (Larsson and Westling, 1998; Steenari et al., 1999a; Steenari and Lindqvist, 1997), on the effect of ash application on tree growth and nutrients uptake (e.g. Jacobson et al., 2014; Arvidsson and Lundkvist, 2002), and on the resulting soil and water acid-base status (Westling and Zetterberg, 2007). Yet only a few studies have focused on the chemistry of soil P. Further, the research results into the effect of wood ash application on the solubility of P in forest soils are contradictory (Augusto et al., 2008). For example, Jacobson et al. (2004) found an increase in the stocks of acid ammonium lactate-extractable P (P-AL) in the humus and top mineral soil five years after the application of 6 and  $9 \text{ Mg ha}^{-1}$  self-hardened, crushed wood ash to two forested sites at Riddarhyttan, central Sweden. Moreover, Nieminen (2009) observed an increase of the water-extractable  $\text{PO}_4 - \text{P}$  content in the humus layer following the addition of untreated wood ash ( $0.5 \text{ Mg ha}^{-1}$ ) in laboratory microcosms. In contrast, Clarholm (1994) observed no change in 'labile' P, as extracted by  $0.5 \text{ M NaHCO}_3$  at pH 8.5 ("Olsen P"), 18 months after the application of  $4 \text{ Mg ha}^{-1}$  of granulated wood ash to a

forest stand in southern Sweden. Similarly, Fransson et al. (1999) did not observe a statistically significant difference in oxalate-extractable P two years after the application of 'slightly hardened' wood ash. Results from Finnish ash fertilization experiments show significant treatment effects on extractable P in some experiments but not in others (Saarsalmi et al., 2004; Saarsalmi et al., 2010). Probably, there are different reasons for these contradictory results. The amount of wood ash (and associated P), the timescale of the study (Jacobson, 2003; Jacobson et al., 2004; Lim et al., 2020), and the dissolution rate of ash-P (Ohno, 1992), which differs between loose and different forms of hardened ash, may all be relevant factors to consider.

Since the N content in wood ash is very low, due to the losses of N during combustion (Karlton et al., 2008), N fertilizers may be applied at the same time as the wood ash (Swedish Forest Agency, 2019). N fertilization is expected to lead to an increased tree growth and to a higher P uptake, thus increasing the P demand (Braun et al., 2010; Flückiger and Braun, 1998; Heuck et al., 2018; Talkner et al., 2015; Weand et al., 2010). It might be hypothesized that the amount of soluble P would be lower in plots treated with ash and N fertilizer compared to those treated with ash only. So far, only a few studies have been carried out that allow us to test this hypothesis. Brais et al. (2015) observed an increase in Mehlich 3-extractable P in the organic layer of a jack pine stand in Canada, which was of the same magnitude in plots treated with both wood ash and N as in those plots where only wood ash was applied, suggesting that N fertilization did not bring about a decrease in P solubility in this case. Similar observations were made in a pot experiment (An and Park, 2021). However, additional evidence is needed as well as an increased understanding of the mechanisms involved.

These dynamics could be better understood if the speciation of P in the soil was known. So far, there are only a few studies that documented changes in P speciation as a result of wood ash fertilization. When the added ash is mixed with the organic layer, e.g. by soil animals (Persson et al., 2021), or leached downward, the P in the ash (mostly apatite; Steenari and Lindqvist, 1997) interacts with organic acids or with soil constituents, e.g. metal-organic complexes (Lundström et al., 2000), causing the wood ash P to dissolve and transform into other species (Alotaibi et al., 2018; Ohno, 1992). Following the dissolution of the ash-P, the amount of P bound to Al and Fe, either as phosphates or as adsorbed surface complexes, may increase (Ohno, 1992). Moreover, the increased pH induced by the ash application stimulates the mineralization of organic matter (OM) and nitrification (Augusto et al., 2008; Cruz-Paredes et al., 2019; Lundström et al., 2003; Persson et al., 1995; Rosenberg et al., 2010). These processes are likely to affect the P speciation of the organic horizons in a complex fashion.

Synchrotron X-ray absorption near-edge structure (XANES) spectroscopy at the P K-edge is one of few available techniques to directly estimate the average composition of P species in soil (Beauchemin et al., 2003; Hesterberg, 2010; Gustafsson et al., 2020). Combining XANES spectroscopy with micro-X-ray fluorescence ( $\mu\text{-XRF}$ ) imaging offers complementary insight into the heterogeneous distribution of different P species, as the speciation and co-localization of P with other elements can be resolved on a  $\mu\text{m}$  scale (Hesterberg et al., 2017; Werner et al., 2017; Adediran et al., 2020; Vogel et al., 2021). Hence, the objective of the current study was to determine the extractability and speciation of P in the organic layer at two Swedish experimental sites in response to the application of (i) wood ash alone (at Riddarhyttan) and (ii) to ash and N application (at Rödälund). In the case of Rödälund, we further relate the P responses to P uptake by trees, as reflected in the accumulation of P in aboveground biomass.

## 2. Materials and methods

### 2.1. Study sites

Two experimental sites from managed forests, in which long-term experiments with ash fertilization have been carried out, were chosen

**Table 1**  
Characteristics of study sites.

Characteristic name	1470 Rödålund	250 Ridrarhyttan
Latitude	64°08'N	59°48'N
Longitude	19°52'E	15°32'E
Altitude (m a.s.l)	209	135
MAP (mm yr <sup>-1</sup> )	600	730
MAT (°C)	2.3	3.9
Dominant tree species	<i>Pinus sylvestris</i>	<i>Pinus sylvestris</i>
Stand density (trees ha <sup>-1</sup> )	2040 ± 151	1100
Stand age (years)	52	50
Stem volume (m <sup>3</sup> ha <sup>-1</sup> )	225	150
Parent material	Wave-washed sand	Sandy sediment
Soil order <sup>a</sup>	Albic Podzol	Albic Podzol

<sup>a</sup> Soil classification according to IUSS Working Group (2014). MAP: mean annual precipitation. MAT: mean annual temperature.

for this study, c.f. Table 1 for site characteristics. Rödålund (64°08'N, 19°52'E) is situated in northern Sweden, near Vindeln, Västerbotten County at 250 m above sea level. The mean annual temperature is 2.3 °C. The mean annual precipitation averaged over the last 30 years is about 600 mm, of which one third falls as snow on frozen ground from mid-October to early May. The site was planted with *Pinus sylvestris* (Scots pine) seedlings in 1996, later *Picea abies* (Norway spruce) (18 %) and *Betula spp.* (8 %) were naturally regenerated (Lim et al., 2020). The ground vegetation is dominated by dwarf shrubs, *Vaccinium myrtillus* and *Vaccinium vitis-idaea*, a ground layer of mosses, *Pleurozium schreberi* and *Hylocomium splendens* and lichens, *Cladonia spp.* The field experiment at this site began in autumn 2001 to study the long-term effects of whole-tree thinning, nutrient compensation on forest production and soil acidification. The soil is an Albic Podzol (IUSS Working Group, 2014) developed on a wave-washed sand deposit (Figure S1A). The organic layer is about 6 cm thick underlain by a strongly weathered E horizon, which is about 17 cm thick. The illuvial B horizon extends to 50 cm depth, below which there is a stony C parent material horizon (Tuyishime et al., 2022).

Ridrarhyttan (59° 48'N, 15° 32'E) is located in the county of Västmanland, in the south-central part of Sweden, at 135 m above the sea level. The experiment (250 Ridrarhyttan) was established in a 50-year-old pine stand. The mean annual temperature (MAT) and precipitation (MAP) are 3.9 °C and 730 mm, respectively (Table 1). The site is dominated by *P. sylvestris* and the understory vegetation is of *V. myrtillus* type (Jacobson et al., 2004). The site is a permanent recharge area for groundwater. The soil profile (Figure S1B) is classified as an Albic Podzol (IUSS Working Group, 2014) developed on sandy sediment. The organic layer is approximately 5 cm thick above a 2 cm-thick E horizon. The oxalate-extractable P, Al and Fe concentrations in this horizon are 0.03 g kg<sup>-1</sup>, 0.46 g kg<sup>-1</sup> and 0.54 g kg<sup>-1</sup>, respectively, compared to 0.25 g kg<sup>-1</sup>, 4.9 g kg<sup>-1</sup> and 2.8 g kg<sup>-1</sup> in the upper B horizon (unpublished data).

## 2.2. Field experiments and sampling

The Rödålund experiment was designed using the split-plot approach, which consists of six replicated plots (60 × 70 m<sup>2</sup>, of which 40 × 50 m<sup>2</sup> is the net plot), to which each of the following four treatments was assigned: stem-only thinning, whole-tree thinning, whole-tree thinning with compensatory fertilization (150 kg N ha<sup>-1</sup>), and whole-tree thinning with repeated fertilization (150 kg N ha<sup>-1</sup> every third year). The total dose of N applied with repeated fertilization 2005–2019 was 750 kg ha<sup>-1</sup>. The N fertilizer 'Skog-Can' was composed of ammonium-nitrate with additions of dolomite lime (5 % Ca, 2.4 % Mg) and boron (0.2 %). Each plot was split into two halves, and the wood ash (3 Mg ha<sup>-1</sup>) was added to one of the subplots within plots once in 2005. When compared to stem-only thinning, whole-tree thinning did not affect soil chemical properties or the carbon stock (Lim et al., 2020). Therefore, in the present study, we used whole-tree thinning as a

**Table 2**  
The amount and composition of wood ash.

Element	Amount and composition of wood ash							
	Rödålund <sup>a</sup>		Ridrarhyttan <sup>b</sup>					
	3 Mg ash ha <sup>-1</sup>		3 Mg ash ha <sup>-1</sup>		6 Mg ash ha <sup>-1</sup>		9 Mg ash ha <sup>-1</sup>	
	%	amount (kg ha <sup>-1</sup> )	%	amount (kg ha <sup>-1</sup> )				
Ca	14	420	13.7	411	822	1233		
Mg	1.7	51	1.4	42	84	126		
Na	0.63	18.9	1.25	37.5	75	112.5		
K	6.3	189	6.4	192	384	576		
P	1.6	48	0.8	24	48	72		
Fe	0.64	19.2	1.1	33.3	66	99		
Al	1.4	42	1.9	57	114	171		
Si	8.8	264	5.6	168	336	504		

<sup>a</sup> From Lim et al. (2020),

<sup>b</sup> From Jacobson et al. (2004) and Ring et al. (2006).

reference, and whole-tree thinning with repeated fertilization as a N fertilization treatment, focusing on the interactive effect between wood ash and the repeated N fertilization (Figure S2). The self-hardened and crushed wood ash applied at this site originated from a fly ash produced at the Falun district heating plant in 2003–2004 using a boiler with a bubbling fluidizing bed and flue gas condensation (Lim et al., 2020).

The Ridrarhyttan experiment was designed according to a randomized block design. The wood ash was applied in September 1995 to experimental plots (net size 30 × 30 m<sup>2</sup>) surrounded by a buffer strip of about 5 m (Jacobson et al. 2014). The treatments of different doses from 3, 6, and 9 Mg ash ha<sup>-1</sup> (3D, 6D, and 9D) (Table 2), including the control, were assigned to experimental plots arranged in three blocks ( $n = 4$ , c.f. Figure S2). The blocking was done based on stand parameters, the number of stems per plot, basal area, and site characteristics (e.g. soil moisture, ground vegetation, site index). For further information about the experiment, see Jacobson et al. (2004). The ash applied to this site was self-hardened, crushed wood ash, which originated from a pulp mill in Piteå, northern Sweden.

At Rödålund, sampling was done in August 2018. Ten soil cores (10 mm diameter) were collected from the organic horizon at random locations inside each subplot, excluding 2 m from the edge of the net subplot, then mixed to make a composite sample. In total, 24 composite samples from 12 plots were collected. At Ridrarhyttan, samples from the organic horizons were taken in a similar way in 2019 from plots treated with wood ash and from control plots.

## 2.3. General chemical properties and P solubility

Undecomposed plant litter and roots were gently removed from fresh samples and sieved through an 8-mm steel mesh. The samples were then air-dried at 30 °C for seven days and sieved again (<2 mm). The pH of fresh samples was measured in deionized water using a soil: solution ratio of 1:10 (Blakemore et al., 1987). Total organic carbon (TOC) and total N (TN) contents were determined after dry combustion according to ISO 13,878 (ISO, 1998), using an elemental CN analyzer (TruMac® CN, Leco corp, St: Joseph, MI, USA). The concentrations of oxalate-extractable Al (Alox), Fe (Feox), and P (Pox) were determined at pH 3.0 according to van Reeuwijk (1995), where Al, Fe and P were quantified with ICP-OES using a Thermo ICAP 6300 instrument. Olsen-P was determined according to Olsen (1954). Briefly, 2 g dry sample was equilibrated for 30 min with a 40 mL solution containing 0.5 M NaHCO<sub>3</sub> (with pH adjusted to 8.5). The suspension was centrifuged at 3000 rpm for 10 min and filtered before P analysis by the molybdate-blue colorimetric method using an AA500 AutoAnalyzer (SEAL analytical). Acid-digestible P or total P (TP) was determined after HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> digestion of 1 g dry material, and subsequent quantification with ICP-MS following ISO 11,466 (ISO, 1995).

### 2.3.1. Phosphorus stocks in the aboveground biomass and organic layer

P and N stocks in aboveground biomass at Rödålund in 2009 were estimated based on each component of tree biomass (stemwood, stem bark, branches, and needles) and the corresponding TP concentration in tree biomass sampled in 2008, assuming that the P concentration in 2009 were the same as in 2008. The biomass of each component (stemwood, bark, branches, and foliage) was estimated using a combination of a derived site-specific allometric function for each component and repeated measurements of tree dimensions of all trees (diameter at 1.3 m, tree height, and length of live crown; Lim et al., 2020). Milled samples of each tree fraction from 2008 were analyzed for P using  $\text{HNO}_3/\text{H}_2\text{O}_2$  digestion as above. Total N was analyzed after dry combustion as above. For Riddarhyttan, data on P stocks in biomass are not available.

For the organic horizons, the stocks of P and other elements were calculated by multiplying the element concentration ( $\text{mg kg}^{-1}$  dry mass) with the organic layer stock ( $\text{kg m}^{-2}$ ) (Table S3 and S4). For the site Rödålund, data on the organic layer stock were taken from Lim et al. (2020), while for Riddarhyttan they are presented here for the first time (Table S4).

## 2.4. Assessment of phosphorus speciation

### 2.4.1. Bulk P K-edge XANES spectroscopy

Phosphorus K-edge XANES spectroscopy was performed on bulk samples at beamline 8 (BL8) (Klysubun et al., 2020) of the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand. BL8 utilized synchrotron radiation generated from the SLRI storage ring with an electron beam energy of 1.4 GeV and beam flux was  $3 \times 10^{11}$  photons  $\text{s}^{-1}$  ( $100 \text{ mA}^{-1}$ ). The X-ray photon energy was scanned by an InSb (1 1 1) double crystal monochromator giving a beam flux of  $1.3 \times 10^9$  to  $3 \times 10^{11}$  photons  $\text{s}^{-1}$  ( $100 \text{ mA}^{-1}$ ). The scanning was done on finely milled samples ( $<50 \mu\text{m}$ ) mounted in hollow and stainless-steel sample holders (2 mm thick,  $1 \times 1.5 \text{ cm}^2$  with a sample window of  $0.5 \times 1 \text{ cm}^2$ ), and covered with P-free polypropylene X-ray film (Eriksson et al., 2016). The sample spectra were recorded in the fluorescence-yield mode in the energy range of 2100–2320 eV using a solid-state 13-element Ge detector. The step size was 2 eV between 2100 and 2139 eV, 1 eV between 2139 and 2146 eV, 0.2 eV between 2146 and 2160 eV, 0.3 eV between 2160 and 2190 eV, and 5 eV between 2190 and 2322 eV. A two-second dwell time was used per energy step. Between 4 and 8 scans were collected for each sample. Collected P K-edge XANES spectra of samples were analyzed using linear combination fitting (LCF) (Ravel, 2009) using the Athena software (version 0.9.25). The LC fits were subsequently processed for uncertainty analysis using the AthenaAut software according to Gustafsson et al. (2020). Ten standards divided into six species groups were used to provide a good representation of the solid P phase in the surface horizons of acid forest soil (Gustafsson et al. 2020): 1) soil organic P (representing generic organic P from a Spodosol organic horizon),  $\text{PO}_4$  adsorbed to Al ( $\text{PO}_4$  adsorbed to allophane,  $\text{PO}_4$  adsorbed to gibbsite, and  $\text{PO}_4$ -adsorbed to  $\text{Al}(\text{OH})_3$ ), 3)  $\text{PO}_4$  adsorbed to Fe ( $\text{PO}_4$  adsorbed to ferrihydrite,  $\text{PO}_4$  adsorbed to goethite), 4) amorphous  $\text{AlPO}_4$ , 5) amorphous  $\text{FePO}_4$ , and 6) CaP (apatite Taiba and hydroxyapatite).

To some extent, these assignments are only indicative. As previously shown, organic P species, when adsorbed to Fe and Al (hydr)oxides, result in spectra intermediate between those of soil organic P and those of  $\text{PO}_4$  adsorbed to Al or Fe (Gustafsson et al., 2020). During LCF, energy shifts were not permitted, the sum of weights (SOW) was not forced to 1, and a maximum of four standards was allowed in the output. When presenting the results from LCF, we assumed that the sum of all weights corresponded to TP.

### 2.4.2. Micro-focused X-ray fluorescence spectroscopy

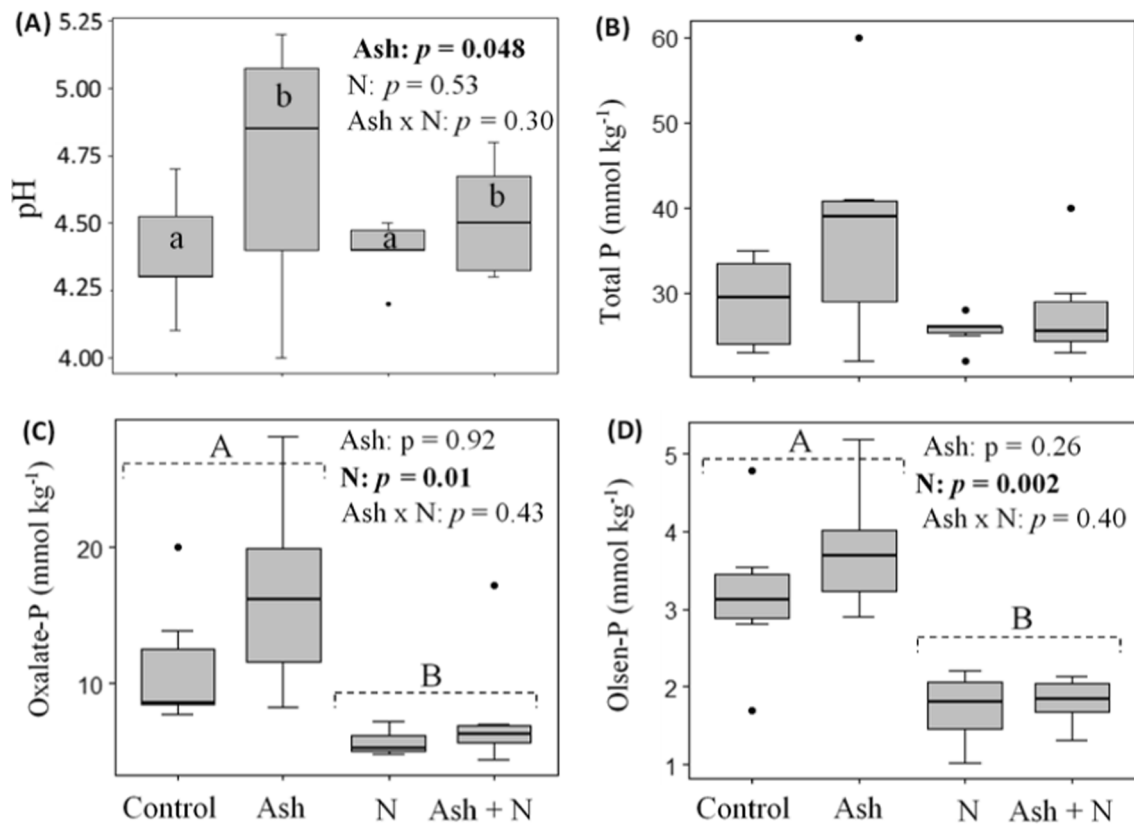
To provide additional support for bulk P K-edge XANES analysis, a replicate from each of the experimental treatments at Rödålund (Plot 1a:

Control - no fertilization, Plot 1b: ash fertilized, Plot 24a: N fertilized, Plot 24b: N and ash fertilized) was selected and subjected to micro-focused X-ray fluorescence imaging of multiple elements (e.g., Al, P, S and Ca), and X-ray atomic absorption near-edge structure ( $\mu$ -XANES) spectroscopy at the P and S K-edges. For this analysis, representative samples from each treatment were embedded in high-purity epoxy resin. Micro-polished petrographic thin sections of  $30 \mu\text{m}$  thick were prepared at TS Lab & Geoservices snc, Cascina, Italy.  $\mu$ -XRF and  $\mu$ -XANES spectra were collected on petrographic thin sections at the PHOENIX (Photons for the Exploration of Nature by Imaging and XAFS) beamline at the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland), using the PHOENIX I (X07MB) branch, which used a double crystal monochromator (Bruker, AXS GmbH) and covers energies from 0.8 to 8 keV. For the measurements, a Si (1 1 1) crystal was employed. Focusing of the X-ray beam was performed with two Kirkpatrick-Baez (K-B) mirrors. The intensity of the incoming beam was measured as a total electron yield (TEY) signal on a Ni coated polyester foil, located c. 1 m upstream of the sample, at c.  $5 \times 10^{-7}$  mbar of pressure. Fluorescence signals were collected using an energy dispersive detector with four elements of silicon drift diodes (Vortex, Hitachi, California 91311, USA). To minimize X-ray absorption by air, the analysis was performed in a vacuum environment.  $\mu$ -XRF images ( $400 \times 400 \mu\text{m}^2$ ) were acquired with a dwell time of 0.4 s per point using a step size of  $3 \times 3 \mu\text{m}^2$  at an excitation energy of 2500 eV. For each pixel, the full fluorescence spectrum was recorded, which contains the signature of all excited elements including P and some major elements known to influence its speciation (e.g. Al, Ca and S). Here the S image serves as a proxy for OM (carbon) interactions with P (Adediran et al., 2021). Although the S imaged by  $\mu$ -XRF could be both inorganic and organic, the proportion of the S that is bound by organic carbon can be resolved by S K-edge XANES analysis (Adediran et al., 2021). Further, spot-wise  $\mu$ -XANES data on P and S were collected at spots with varying concentrations according to elemental imaging. P and S K-edge  $\mu$ -XANES spectra were recorded in fluorescence mode over the 2.10–2.22 and 2.45–2.55 keV energy ranges for P and S respectively, with 0.2 eV steps. For each sample, up to 8 high-quality  $\mu$ -XANES scans from different P spots were merged to one spectrum.

The  $\mu$ -XRF spectra were dead-time-corrected and normalized to incoming beam intensities before individual elemental spectrum deconvolution. Microscale-resolution elemental maps were obtained after fitting each pixel  $\mu$ -XRF spectrum using the PyMca X-ray Fluorescence Toolkit (Solé et al., 2007). The P  $\mu$ -XANES spectra were subjected to probabilistic LCF analysis as described above in section 2.4.1. The S K-edge  $\mu$ -XANES spectrum consists of distinct resonance peaks, whose energy positions are linearly correlated to the oxidation state of the S species (Vairavamurthy, 1998). These peaks were decomposed by Gaussian curve fitting as described in Prietzel et al. (2011), using the software package PeakFit (version 4.12, Systat Software, Inc.). The areas of the best-fitting peaks were calculated and multiplied by a weighting factor (Prietzel et al., 2011), which accounts for the variation in the absorption cross-section per unit mass with the S oxidation state (Veronesi et al., 2013; Prietzel et al., 2011).

## 2.5. Statistical analyses

For Rödålund, a two-factor analysis of variance was used to determine the effects of wood ash and repeated N fertilization on P speciation and solubility. A split-plot ANOVA model (Kenward-Roger's method) was applied, which consists of N as whole-plot factor and ash as sub-plot factor. Thus, the wood ash and N were added in a factorial way such that the levels of N factor (corresponding to N and no N addition) are ordered in six replicates ( $n = 6$ ) randomly assigned to experimental plots, whereas the ash factor levels (for ash and no ash addition;  $n = 12$ ) are randomly arranged within the N-factor in the sub-plots. The model also includes the "Ash  $\times$  N" interaction between the two treatment factors, the whole-plot random error, and the regular residual error (sub-plot error). With the split-plot design, the precision of the measurement of



**Fig. 1.** pH (A), total P (B), acid oxalate-extractable P (Pox) (C), and alkaline NaHCO<sub>3</sub>-extractable P (Olsen-P) (D) at Rödålund. The data are presented based on the interactive treatments of wood ash and N. Dissimilar upper case letters (A and B) indicate a significant difference (at  $p \leq 0.05$ ) in the variables between repeated N-fertilized and control ( $n = 6$ ). Dissimilar lower case letters (a and b) indicate a significant difference (at  $p \leq 0.05$ ) in the variable among ash treatments ( $n = 12$ ) within N fertilization treatment (N and no N). Boxplots without letters indicate no significant difference between or among the treatments.

**Table 3**  
General chemical properties (mean values) of the investigated organic horizons.

Study site	Treatment	pH	Alox	Feox	TOC	N	C:Porg	N:Porg
			mmol kg <sup>-1</sup>			g kg <sup>-1</sup>	mol mol <sup>-1</sup>	
Rödålund	Control	4.38 ± 0.1	44.1 ± 14.3	14.2 ± 4.5	332 ± 21.7	9.67 ± 0.4	1247.9 ± 94	31.5 ± 2
	Ash	4.72 ± 0.2	40.1 ± 17.7	17.8 ± 4.6	337 ± 27.6	9.50 ± 0.7	2192 ± 1045	50.7 ± 22
	N	4.4 ± 0.0	42.0 ± 14.4	14.2 ± 3.1	404 ± 14.9	14.5 ± 0.4	1621 ± 106	49.8 ± 2
	Ash + N	4.52 ± 0.1	51.4 ± 16.5	16.5 ± 4.9	399 ± 17.8	14.7 ± 0.9	1627.1 ± 136	50.7 ± 4
Riddarhyttan	0 Ash	3.93 ± 0.1	42.7 ± 11.6	18.9 ± 6.7	430 ± 9.6	11.0 ± 0.1	1835.3 ± 145	40.1 ± 2
	3 Ash	3.93 ± 0.0	50.7 ± 11.6	26.5 ± 6.7	387 ± 4.8	10.8 ± 0.3	1541.9 ± 111	36.6 ± 2
	6 Ash	4.13 ± 0.0	46.7 ± 11.6	22.0 ± 6.7	372 ± 13.8	10.5 ± 0.7	1703.9 ± 80.5	41.2 ± 1
	9 Ash	4.97 ± 0.2	64.8 ± 11.6	29 ± 6.7	284 ± 7.6	8.3 ± 0.5	1035.1 ± 121	25.9 ± 3

the sub-plot factor is increased (there are more observations) at the expense of the whole-plot factor (Gomez and Gomez, 1984). Therefore, this model fits well with the data from Rödålund as it is robust for testing the effects of wood ash. Moreover, the Tukey method (with  $p = 0.05$ )

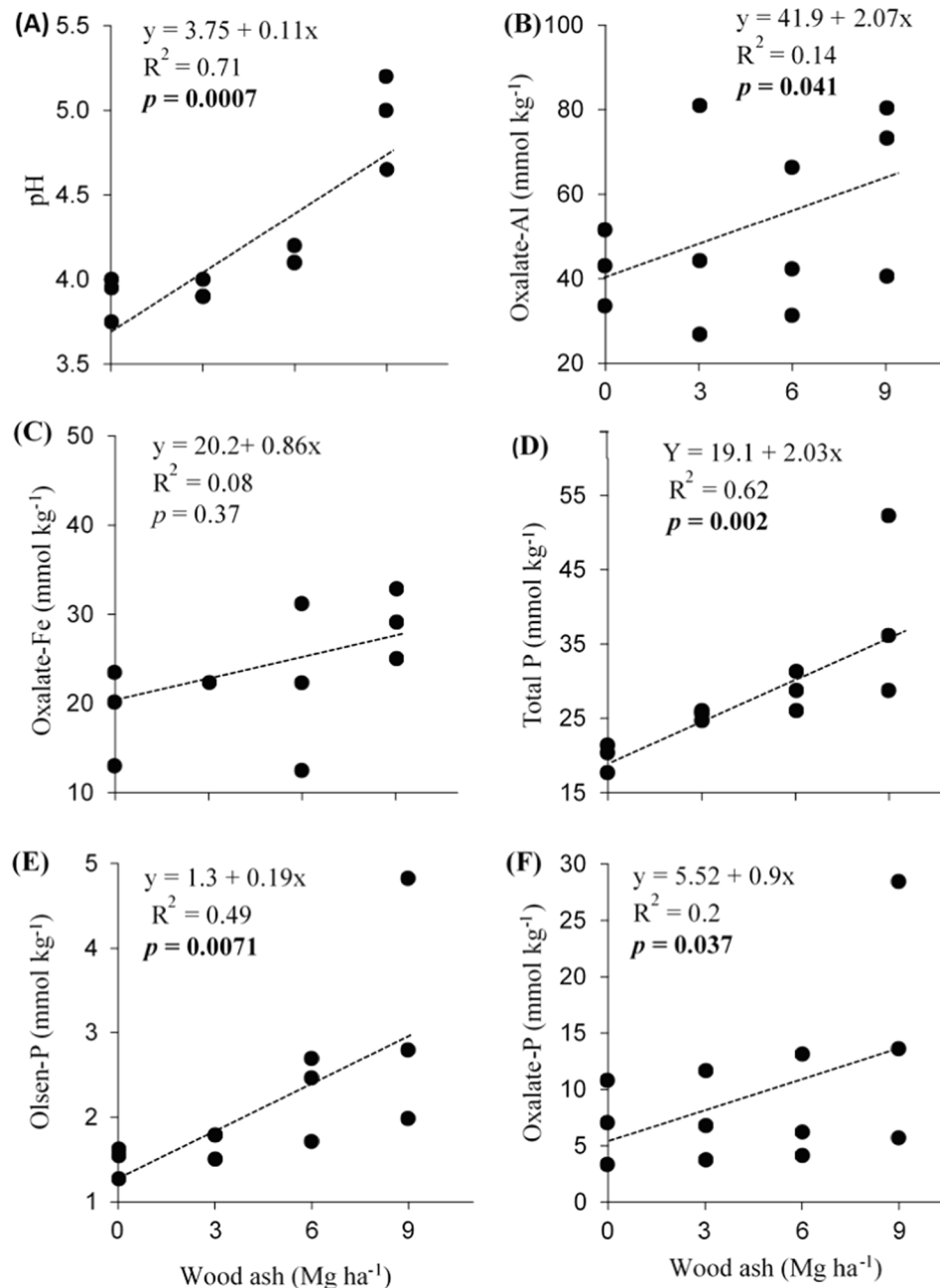
using Least Squares Means (emmeans) function was used to compare estimated means of different groups of ash and N treatments.

For Riddarhyttan, a linear mixed-effect regression analysis with block and wood ash treatment (as a continuous variable) was used to

**Table 4**  
Analysis of variance for the main effects of wood ash and N treatments and their interaction (ash × N) on soil chemical properties in organic layer at the site Rödålund. Quantitative relationship between wood ash treatment levels and soil chemical properties in the organic layer at Riddarhyttan. All effects were statistically analysed at the 0.05 significance level.

Study site	Treatment	Alox	Feox	TOC	TN	C:Porg	N:Porg
Rödålund	Ash	$p = 0.85$	$p = 0.45$	$p = 0.98$	$p = 0.91$	$p = 0.38$	$p = 0.40$
	N	$p = 0.77$	$p = 0.88$	$p = 0.039$	$p = 0.0005$	$p = 0.86$	$p = 0.46$
	Ash × N	$p = 0.64$	$p = 0.85$	$p = 0.82$	$p = 0.80$	$p = 0.38$	$p = 0.44$
Riddarhyttan	R <sup>2</sup>	0.14	0.08	0.86	0.55	0.36	0.38
	p value	<b>0.041</b>	0.37	< <b>0.001</b>	<b>0.006</b>	<b>0.038</b>	<b>0.033</b>

Alox and Feox: acid oxalate-extractable Al and Fe (mmol kg<sup>-1</sup>). TOC and TN: total organic carbon and nitrogen (g kg<sup>-1</sup>). C:Porg and N:Porg: molar C to organic P ratio (mol/mol). N:Porg: molar N to organic P ratio (mol/mol).



**Fig. 2.** Relationships between the amount of wood ash added and pH (A), acid oxalate-extractable Al (Alox) (B) and Fe (Feox) (C), total P (D), alkaline NaHCO<sub>3</sub>-extractable P (Olsen-P) (E), and acid oxalate-extractable P (Pox) (F), in the organic layer of the Riddarhyttan site, ( $n = 4$ ).

determine the effects of ash on extractable P and the P speciation in the organic horizon. The regression model was chosen because the ash treatments are different treatment levels of a numeric variable, i.e. the levels describe a measurable quantity of the ash. The random normality was checked by plotting the final residuals. All statistical analyses were performed using R (v.4.02).

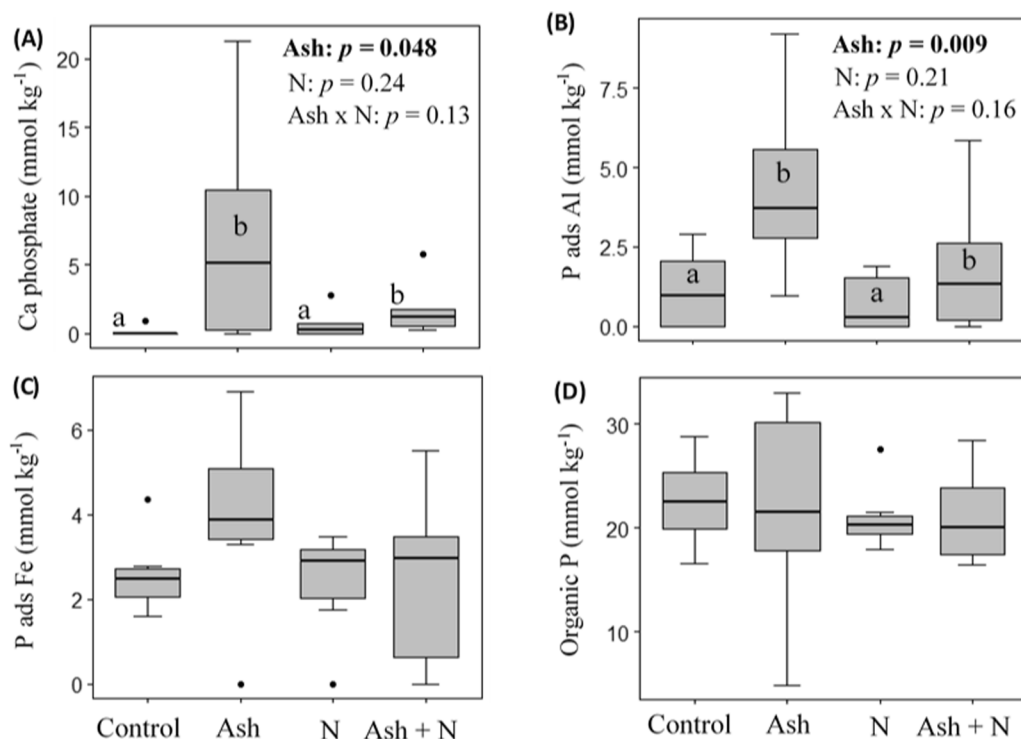
### 3. Results

#### 3.1. Soil chemical properties and P extractability as affected by treatment

At Rödälund, the application of 3 Mg ash ha<sup>-1</sup> to the organic horizon increased the pH by 0.22 units compared to the control ( $p = 0.048$ ) (Fig. 1A). Other main properties, e.g. TOC, TN, Alox, Feox, and the molar N:Porg and C:Porg ratios were not significantly affected by the ash

application (Table 3 and Table 4). The same was true for Pox and for Olsen-P, although the averages were higher in the ash treatment by a factor of approximately 1.5 and 1.2, respectively (Fig. 1). In contrast, the N fertilization of the organic horizon increased the concentrations of TOC ( $p = 0.039$ ) and TN ( $p < 0.001$ ) significantly (Table 3 and Table 4), but the effect on the molar N:Porg and C:Porg ratios were not significant. The concentrations of Pox and Olsen-P decreased significantly in response to N addition (Fig. 1C and 1D;  $p = 0.016$  and  $p = 0.002$ , respectively). When considering interactive treatment groups, the Pox concentration increased from 5.6 mmol kg<sup>-1</sup> in the N-only treatment to 7.8, 11.2, and 16.6 mmol kg<sup>-1</sup> in the ash + N, control, and ash-only treatments, respectively (Table S2). Likewise, Olsen-P increased from 1.72 mmol kg<sup>-1</sup> in the N-only treatment to 1.81, 3.18, and 3.78 mmol kg<sup>-1</sup> in the ash + N, control, and ash-only treatments.

At Riddarhyttan, the pH of the organic horizon increased as a



**Fig. 3.** Ca-bound P (A), P adsorbed on Al (B), P adsorbed on Fe (III) (C), and organic P (C) at the Rödålund site (organic layer). The data are presented based on the interactive treatments of wood ash addition and N fertilization. Dissimilar lowercase letters (a and b) indicate a significant difference (at  $p \leq 0.05$ ) in the variable among ash treatments ( $n = 12$ ) within N fertilization treatments (N and no N). Boxplots without letters indicate no significant difference between or among the treatments.

function of the ash dose ( $R^2 = 0.71$ ,  $p < 0.001$ ; Fig. 2A), whereas the concentrations of TOC and TN decreased ( $p < 0.001$  and  $p = 0.006$ , respectively) (Table 3 and Table 4). Similarly, the molar C:Porg and N:Porg decreased significantly with increasing ash dose, but the effect was not strong;  $R^2 = 0.36$  and  $0.38$  (Table 4). The concentrations of TP, Olsen-P, and Pox increased with increasing wood ash application rate ( $p = 0.002$ ,  $p = 0.007$ , and  $p = 0.037$ , respectively; Fig. 2D, 2E, and 2F). The increase of the concentration of Pox was concomitant with that of Alo<sub>x</sub> ( $p = 0.047$  (Fig. 2B)).

### 3.2. Bulk P K-edge XANES speciation

At the Rödålund site, the concentration of Ca-bound P (probably apatite) was found to be  $4.4 \text{ mmol kg}^{-1}$  in the wood ash treatment, which is statistically ( $p = 0.048$ ) higher than the  $0.4 \text{ mmol kg}^{-1}$  found in the organic layers without ash (Fig. 3A). The highest Ca-bound P concentration was measured in the ash-only treatment,  $7.1 \text{ mmol kg}^{-1}$ , which was 18.7 % of the TP. In the other treatment, Ca-bound P was much lower, i.e.  $1.8 \text{ mmol kg}^{-1}$  (6.4 % of TP),  $0.68 \text{ mmol kg}^{-1}$  (2.7 % of TP), and  $0.15 \text{ mmol kg}^{-1}$  (0.5 % of TP) in the ash + N, N-only, and control treatments, respectively. It should be noted that the N fertilizer used at Rödålund contained some Ca and other base cations. The LCF of the bulk XANES spectra also showed the relative contribution of total P associated with Al and Fe not to exceed, on average, 20 % of the TP for all organic horizons from Rödålund (Fig. S3). The wood ash treatment significantly ( $p = 0.009$ ) increased the concentration of P adsorbed on Al (P ads Al) in the ash-fertilized subplots (Fig. 3B). Considering different interactive treatment groups, the concentration of this P species decreased from  $4.4 \text{ mmol kg}^{-1}$  in the ash-only treatment to 1.9, 1.2, and  $0.7 \text{ mmol kg}^{-1}$  in the ash + N, control, and N-only treatment, respectively (Table S2). No significant difference was found for the P adsorbed on Fe (P ads Fe) concentration (Fig. 3C). Organic P (Porg) species accounted for, on average, 73.4 % of the TP concentration, thus, being the main P fraction (Fig. S3). However, there was no change in this P form caused by either treatment (Fig. 3D).

At Riddarhyttan, fertilization with wood ash did not change the contribution of Porg, which accounted for an average of 73 % of the TP

of the organic horizon (Fig. 4A and Table S4). Bulk XANES results showed that on average,  $2.3 \text{ mmol kg}^{-1}$  of Ca-bound P, which represents only 4 % of the TP, was found in the O horizons treated with  $9 \text{ Mg ha}^{-1}$ , while no Ca-bound P was measured in the remaining samples (Table S2). However, a strong quantitative relationship ( $R^2 = 0.72$ ,  $p < 0.001$ ) between the amount of wood ash and the concentration of P ads Al was found (Fig. 4B). Similarly, the concentration P ads Fe in the organic layer increased significantly ( $p = 0.044$ ) with increasing ash dose although the slope was not strong ( $R^2 = 0.35$ ) (Fig. 4C). Furthermore, there was a strong relationship between the concentration of Olsen-P and that of P ads Al ( $R^2 = 0.83$ ,  $p < 0.001$ ) as well as with the concentration of P-ads Fe ( $R^2 = 0.74$ ,  $p < 0.001$ ) (Fig. 5) in the organic layers of Riddarhyttan.

### 3.3. Microscale distribution and speciation of P at Rödålund

In the control (un-fertilized treatment), P was mainly co-localized with S (cyan color in Fig. 6a). Analysis of the S K-edge  $\mu$ -XANES showed S to be predominantly organic-S (Fig. S5). This was further supported by P K-edge  $\mu$ -XANES showing P in this treatment to be mainly organic-P (Fig. 6b). Apart from the P and S co-localizations, there was evidence of the presence of some Ca-bearing P particles in the N fertilized treatment. These micro-sized P particles were more prominent in the treatments fertilized with only ash and under combined ash and N fertilization.  $\mu$ -XRF imaging of multiple elements in these treatments shows P at these particles to be co-localized with Al and Ca. Again, this observation was further supported by P K-edge  $\mu$ -XANES results. The ash and ash + N fertilization treatments influenced P speciation in the organic layer by increasing the proportion of inorganic P species (mainly as Al and to a lesser extent Ca bound P) from ~ 3 % in control (unfertilized) and N fertilized treatments, to ~ 51 % and 13 % in treatments fertilized with only ash, and ash + N, respectively. Although only one replicate from the experimental treatments at Rödålund was subjected to these detailed  $\mu$ -XRF and  $\mu$ -XANES analyses, the result is in general agreement with the results of P speciation by bulk P K-edge analysis across all the plots at the two sites.

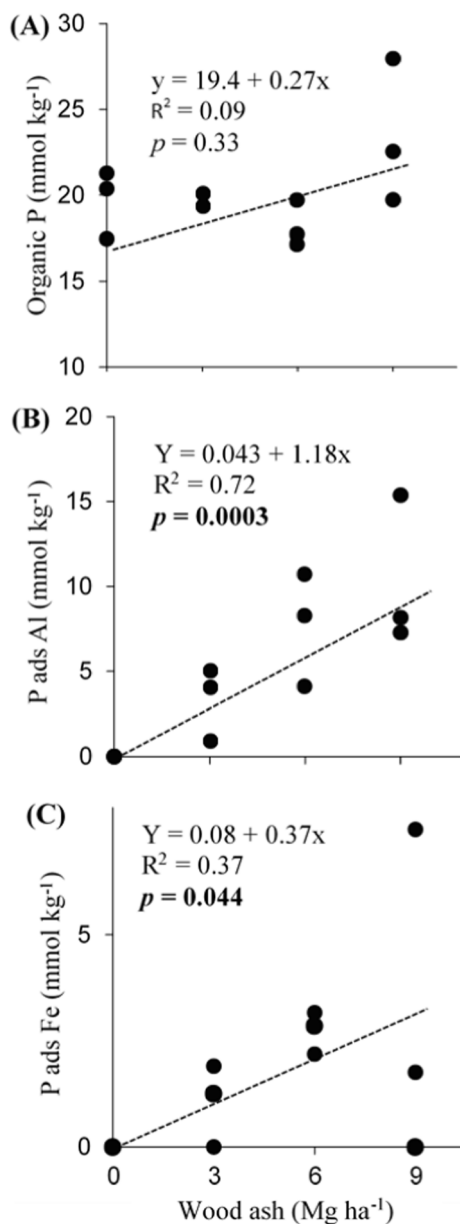


Fig. 4. Relationships between amount of added wood ash and organic P (A), P adsorbed to Al (B), and P adsorbed to Fe (C) at the Riddarhyttan site ( $n = 4$ ).

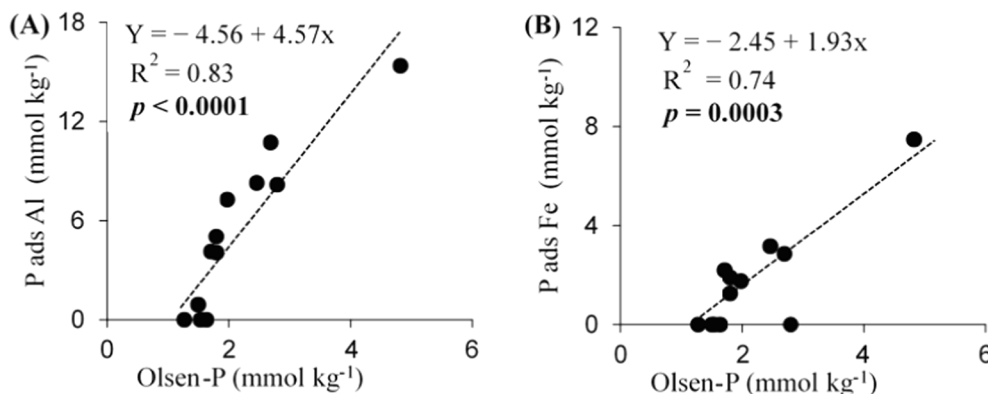


Fig. 5. Concentration of P adsorbed to Al (A) and Fe (B) as a function of the concentration of Olsen-P at Riddarhyttan across all rates of wood ash addition ( $n = 4$ ).

### 3.4. Phosphorus stocks in aboveground biomass

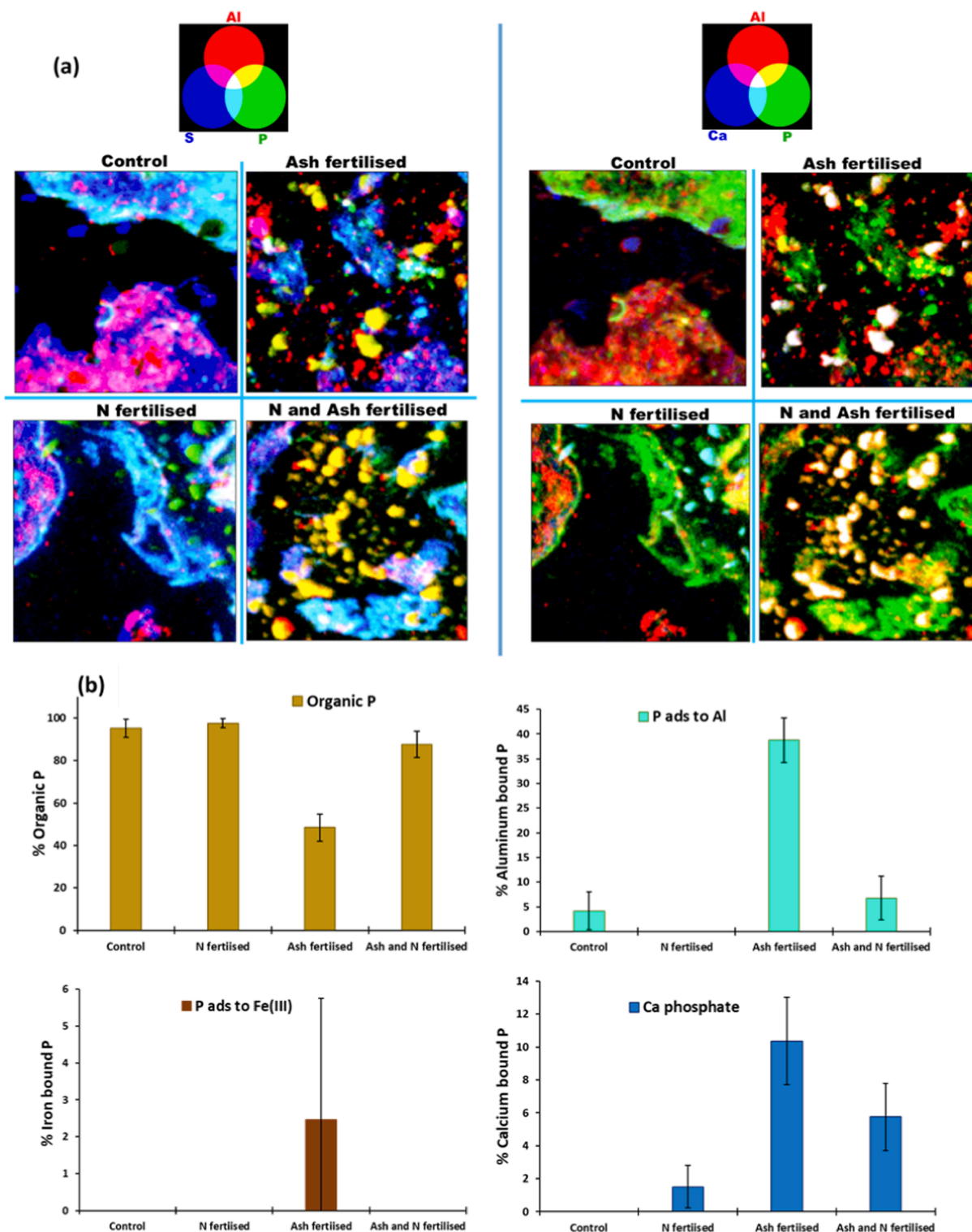
The results on above ground biomass at Rödålund are reported in Fig. 7. Repeated N fertilization resulted in a significant ( $p = 0.012$ ), 39 % higher P stock in the aboveground tree biomass in 2009 compared to the control (30.4 compared to 21.9 kg P ha<sup>-1</sup>). The response was due both to an increased P concentration ( $p = 0.004$ ) in biomass and to an increased tree biomass stocks ( $p = 0.015$ ). The P stock following ash treatment was 16 % higher than that in the control (28.0 compared to 24.2 kg P ha<sup>-1</sup>,  $p = 0.032$ ). The ash application did not affect tree biomass. There was no significant interaction between N fertilization and ash treatment ( $p = 0.77$ ). The P-to-N ratio (by mass) of the total needle biomass was significantly increased by the P-containing ash treatment ( $p = 0.002$ ) compared to the control under unfertilized conditions, from 10.2 % to 12.5 % (Fig. 7B). The interaction between N fertilization and ash treatment was also significant ( $p = 0.01$ ). However, repeated N fertilization had no effect on the P-to-N ratio ( $p = 0.349$ ; 11.6 % in N treatment, 11.1 % in control) contrary to the expected decrease in the P-to-N ratio.

## 4. Discussion

Application of wood ash influenced P speciation and resulted in increased P concentrations in the organic horizon. By contrast, repeated N fertilization resulted in the opposite effect on extractable P concentrations, although no effect on P speciation was found. To our knowledge, this is the first study describing the long-term effects of wood ash application on the soil P speciation at the micro- and molecular scales. Essentially, our results reinforced previous research on soil solution P chemistry, which showed that wood ash increased the P concentrations in soil solution, resulting in increased sorption of P (Ohno, 1992). Our study focused on the effects on the organic layers, as they are the most likely to be affected by forest management. A combination of  $\mu$ -XRF/ $\mu$ -XANES and P K-edge bulk-XANES spectroscopy revealed distinct changes in P speciation after ash application, as Al-bound P accumulated, while most of the ash-P dissolved, except for some residual Ca-bound P at high ash loads. P associated with Al and Ca was more prominent in the ash treatments, especially when ash was added alone. The presence of residual Ca-bound P is also evident from the normalized P K-edge XANES spectra of the ash treatment, which appeared to have broader white-line features and post-edge characteristics typical of Ca-bound P (Fig. S3).

The increased soil P concentrations after ash application at Riddarhyttan might have resulted from the added P in the ash. The addition of 6 and 9 Mg ash ha<sup>-1</sup> (6D and 9D) corresponded to 48 and 72 kg P ha<sup>-1</sup>. This led to an increase in TP in the organic layer of 10 and 28 kg P ha<sup>-1</sup>, respectively (Table 5), which is equivalent to 21 and 39 % of the P content in the applied ash. At Rödålund, the application of 3 Mg ha<sup>-1</sup> corresponded to 48 kg P ha<sup>-1</sup>, while the organic horizon P increased

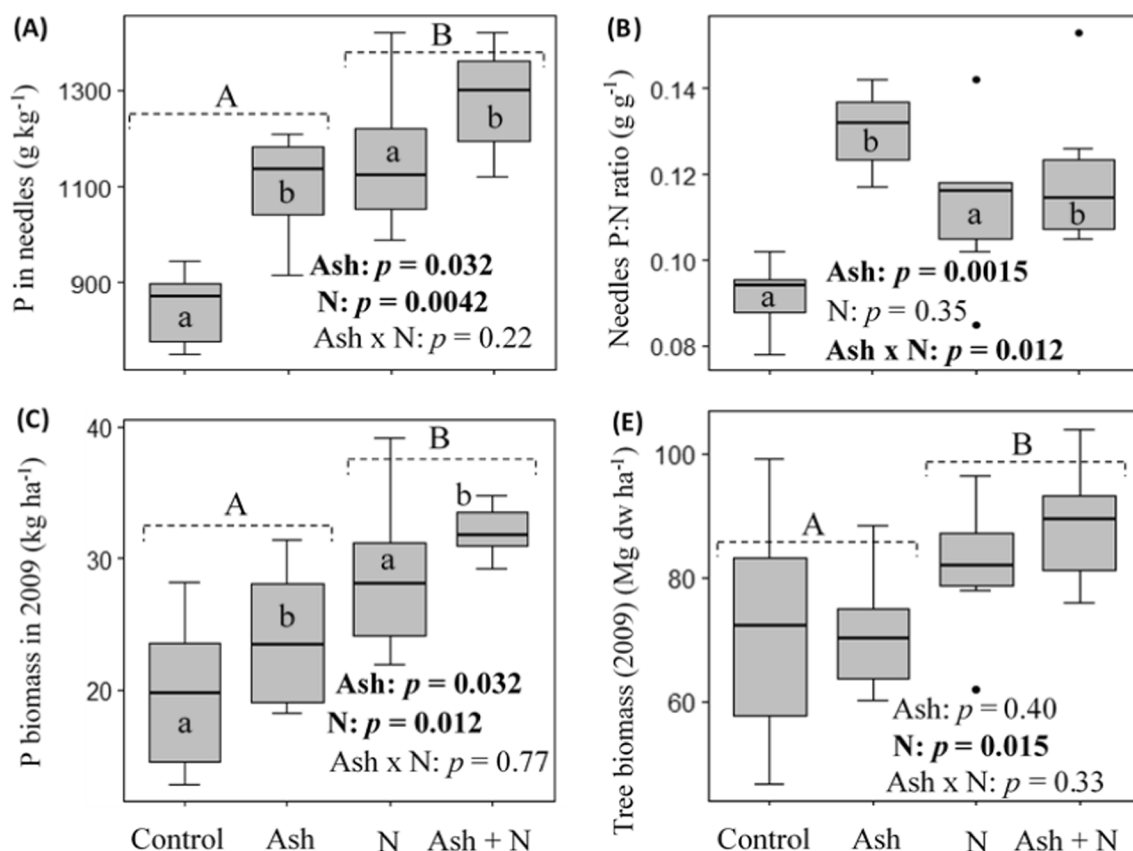




**Fig. 6.** (a) Synchrotron  $\mu$ -XRF imaging of P (green) co-localisation with Al (red), S and Ca (blue), and (b) molecular speciation of P as found by linear combination fitting of P K-edge  $\mu$ -XANES in selected experimental plots at Rödålund. The % on y-axis indicate the contribution of P species to the total P weight according to the LCF of spectra.

with  $8 \text{ kg P ha}^{-1}$ , equivalent to 17 % of the P in the applied ash. Although these percentages were similar at the two sites, XANES spectroscopy showed that the ash dissolution patterns differed at the two sites. At Rödålund, the presence of  $4.6 \text{ kg P ha}^{-1}$  as Ca-bound P in the ash-treated plots (compared to  $0.1 \text{ kg P ha}^{-1}$  in the control plots), together with the above-mentioned evidence from  $\mu$ -XRF/ $\mu$ -XANES, showed that the increased P concentration of the organic horizon was

partly due to the presence of undissolved ash particles in the ash-treated Rödålund plots. By contrast, Ca-bound P was absent from the plots treated with  $6 \text{ Mg ash ha}^{-1}$  at Riddarhyttan and only  $3.8 \text{ kg P ha}^{-1}$  in those treated with the highest dose, showing that the Ca-bound P of the ash had dissolved more completely at this site, perhaps due to different characteristics of the ash that was used (Table 2), and/or the longer time that had passed since ash application (24 years in Rödålund vs 13 years



**Fig. 7.** The concentrations of TP in needles (A), needle P:N ratio (B), P stock in biomass in 2009 (C), and tree biomass in 2009 (D), at the site Rödålund. Dissimilar upper case letters (A and B) indicate a significant difference ( $p \leq 0.05$ ) in the variables among the N and no N treatment ( $n = 6$ ). Dissimilar lowercase letters (a and b) indicate a significant difference in the variable among ash treatments ( $n = 12$ ) within N fertilization treatment (N and no N). Boxplots without letters indicate no significant difference between or among the treatments.

**Table 5**

Phosphorus stocks of the investigated organic horizons.

Study site	Treatment	TP	Olsen-P	Pox	Porg	P ads Al	P ads Fe	AlPO <sub>4</sub>	FePO <sub>4</sub>	CaP
		kg ha <sup>-1</sup>								
Rödålund	Control	16.8 ± 2.2	1.97 ± 0.4	6.5 ± 1.1	13.2 ± 1.9	0.8 ± 0.4	1.5 ± 0.2	0.7 ± 0.7	0.4 ± 0.4	0.1 ± 0.1
	Ash	20.5 ± 2.7	2.2 ± 0.4	9.6 ± 2.1	10.6 ± 1.3	2.1 ± 0.5	2.9 ± 1.3	0.0 ± 0.0	0.3 ± 0.3	4.6 ± 2.2
	N	14.3 ± 0.7	0.95 ± 0.1	3.2 ± 0.3	11.8 ± 0.8	0.3 ± 0.2	1.3 ± 0.3	0.1 ± 0.1	0.2 ± 0.2	0.4 ± 0.3
	Ash + N	17.9 ± 1.6	1.17 ± 0.1	4.97 ± 1.2	13.5 ± 1.1	1.3 ± 0.6	1.6 ± 0.6	0.0 ± 0.0	0.3 ± 0.4	1.6 ± 0.5
Riddarhyttan	Control	30.2 ± 3.0	2.3 ± 0.2	10.1 ± 2.3	30.0 ± 2.9	0.0 ± 0.0	0.0 ± 1.9	n.d	n.d	0.0 ± 0.0
	3 Ash	36.1 ± 7.0	2.4 ± 0.5	11.6 ± 5.3	29.1 ± 4.2	5.1 ± 2.1	1.73 ± 1.0	n.d	n.d	0.0 ± 0.0
	6 Ash	40.2 ± 5.7	3.3 ± 0.7	11.2 ± 4.2	25.1 ± 1.6	11.2 ± 3.5	3.9 ± 1.9	n.d	n.d	0.0 ± 0.0
	9 Ash	58.8 ± 14.1	4.8 ± 1.6	24.5 ± 11.7	34.3 ± 2.5	15.6 ± 4.9	5.0 ± 3.8	n.d	n.d	3.8 ± 3.8

n.d: not detectable by the bulk P K-edge XANES.

in Riddarhyttan). Instead at Riddarhyttan, the concentration of P bound to Al and to Fe increased, with 15.6 and 5.0 kg P ha<sup>-1</sup> respectively, in the highest ash dose treatment. Increased dissolved P concentrations and a higher pH, allowing hydrolysis of organically complexed Al and Fe, could have shifted the chemical equilibrium towards P adsorption, as shown by a strong relationship between Olsen-P and P ads Al/Fe. Although Al- and Fe-bound P increased also at Rödålund after ash treatment, the increase was much smaller (Table 5). Apart from the difference in ash quality, the variations of P responses between the two sites may also be explained by the higher content of oxalate-extractable Fe and Al in the Riddarhyttan organic horizons, in combination with the higher Fe and Al content of the applied ash. This may have provided a larger number of adsorption sites for P. Taken together, our results show that the wood ash application increased the P levels in the organic

horizons and that the increase was mainly due to labile P bound to Al and Fe phases, which may be a source of plant-available P (Amadou et al., 2022).

We observed a decrease in TOC, TN as well as molar N:Porg and C:Porg ratios in response to ash application at the site Riddarhyttan. A reason for this might be increased OM decomposition by the pH-raising effect of the ash (Persson et al., 2021; Rosenberg et al., 2010). By contrast, Porg was unaffected by ash application, at both sites. There could be different reasons for this. It might be that the ash application increased decomposition, but that the turnover time of phosphorylated organic compounds is longer than that of non-phosphorylated organic compounds, and hence no effect on Porg is visible yet. Second, and more likely, it could be that the formation of Porg increased in response to ash application as the soil biota formed Porg from ash-derived P stimulated

by the pH in the ash-amended organic horizons (Augusto et al., 2008; Persson et al., 2021; Persson et al., 1995). It may also be that apatite dissolution from the ash resulted in increased fungal biomass (Forsmark et al., 2021; Mahmood et al., 2003), which likely contributed to Porg, and thus kept this pool unaffected. The lack of an effect of N application on Porg can also be explained by an increased demand for P by biota in response to N addition, which favors P immobilization by ectomycorrhizal fungi (Forsmark et al., 2021; Heuck et al., 2018). This is consistent with the molar N:Porg and C:Porg (based on organic P fraction), which were unaffected by the long-term, repeated N fertilization (c.f. Table 3 and Table 4).

The TP, Pox, and Olsen-P stocks all declined in response to repeated N fertilization, which confirms previous studies about the effect of N addition on organic horizons in temperate regions, including Scandinavian coniferous forests (Heuck et al., 2018). The increased N availability due to N addition is expected to enhance P uptake by plants and potentially microorganisms, which reduces easily available P. Hence, any available P from organic sources is likely efficiently immobilized by microorganisms (Heuck et al., 2018; Pistocchi et al., 2018). The combination of ash and N fertilizers also nearly halved the easily available P stock (Olsen-P) compared to the organic horizons that only received ash (Table 5), despite the additional input of P from the ash. This emphasizes the effect of N fertilizer on plant P uptake.

The results concerning P stocks in aboveground biomass demonstrated that both N fertilization and ash addition increased tree P uptake (based on the 2009 data). The ash treatment also increased the foliage P/N ratio in contrast to the N treatment, where this ratio remained unaffected. The ratio increased from 9.2 % in the control to 13 % in ash treatment. In both cases, the P concentration was near or above the optimum level (Knecht and Göransson, 2004). The effect of the ash treatment was expected owing to the high P content of the ash. Despite the increase in P uptake, the ash treatment had no effect on tree growth (Fig. 7D), regardless of N fertilization. This suggests, first, that the increased P stocks in biomass of this treatment reflected a higher P availability, not a higher demand, and second, that the tree growth was not limited by P at the site. On the other hand, the significantly higher P uptake and tree growth following N fertilization likely explain the reduced concentrations of available P. The maintained P/N ratio of foliar biomass in N treatment indicates a strong capacity of the Rödålund stand to increase P acquisition in parallel with increased N uptake. This finding deviates to some extent from the results of other long-term fertilization experiments in Nordic forests, including sites that are very close to Rödålund (Palmqvist et al., 2020; Tamm et al., 1999; Binkley and Högbom, 2016). According to the latter findings, the N addition increased tree growth and P uptake (as in Rödålund) but resulted in lowered P/N ratios in needles, and hence complementary additions of P and other elements were needed for sustained production. From a forest production perspective, the addition of P from the wood ash in Rödålund showed no additive effect. However, wood ash treatment in combination with N resulted in higher P uptake (+12.4 kg ha<sup>-1</sup> increase) than in N-only treatment (+9 kg ha<sup>-1</sup>), indicating that adding hardened wood ash can ameliorate N-induced P deficiency while maintaining tree growth, more so after multiple forest cycles. Hence, one important result of this study is that wood ash did increase plant-available P forms in the soil and increased P uptake in trees regardless of the N fertilization treatment. This result is probably general to a wide group of soil and forest conditions.

## 5. Conclusion

This study provides in-depth insights into the fate of added P from self-hardened wood ash to the forest organic horizon and how this influences soil P, organic carbon, and nitrogen as well as P uptake by trees. Decades after wood ash applications, there were still undissolved Ca phosphates, albeit in small quantities, which very likely were derived from the ash. As the ash dissolved, the P solubility and P bound to Al and

Fe increased, while the organic P pool remained unchanged. The high solubility of P in the ash-fertilized plots increased the P uptake by plants, as reflected by the higher P stock in aboveground biomass. The ash application may also have resulted in a P availability that was higher than required by the trees. Long-term, repeated N fertilization significantly increased P uptake by trees and decreased levels of available P in the organic horizon. In summary, the application of wood ash increased Al-bound P and increased the levels of easily available P as well as P uptake by trees.

## CRedit authorship contribution statement

**J.R. Marius Tuyishime:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Gbotemi A. Adediran:** Software, Investigation, Writing – review & editing, Visualization. **Bengt A. Olsson:** Conceptualization, Methodology, Validation, Resources, Formal analysis, Writing – review & editing, Supervision. **Therese Sahlén Zetterberg:** Validation, Writing – review & editing, Supervision. **Lars Högbom:** Validation, Resources, Writing – review & editing. **Marie Spohn:** Validation, Writing – review & editing, Supervision. **Hyungwoo Lim:** Validation, Formal analysis, Writing – review & editing. **Wantana Klysubun:** Resources, Writing – review & editing. **Camelia N. Borca:** Resources, Writing – review & editing. **Thomas Huthweller:** Resources, Writing – review & editing. **Jon Petter Gustafsson:** Conceptualization, Methodology, Software, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

We are committed to allowing an open access publishing option.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foreco.2022.120432>.

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