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Changes in SOM composition and stability to microbial degradation over time in response to wood chip ash fertilisation

Mette Hansen [a, *], Anna Saarsalmi [b], Clément Peltre [c]

[a] Department of Geosciences and Natural Resource Management, Faculty of Science, University of Copenhagen, Rolighedsvej 23, DK-1958, Frederiksberg C, Denmark
[b] Natural Resources Institute Finland (Luke), P.O. Box 18, FI-01301, Vantaa, Finland
[c] Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, Frederiksberg C, DK-1871, Denmark

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ABSTRACT

Recirculation of nutrients from wood chip combustion by ash fertilisation of forest systems can be used to re-introduce nutrients that are otherwise lost, counteracting nutrient depletion due to whole tree harvesting. However, the effects of ash application on soil organic matter (SOM) composition, turnover and stability are unknown. The aim of the study was to investigate how ash fertilisation of forest soils affects SOM composition and stability to microbial degradation over time. O-horizon and 0–5 cm mineral soil samples were collected from two coniferous forest sites, one in Finland and one in Denmark, where ash had been spread at different times. Changes in SOM biodegradability were estimated based on an incubation experiment, expressed as percentage of initial carbon. Changes in SOM composition were characterised using thermal analysis and Fourier transform mid-infrared photoacoustic spectroscopy (FTIR-PAS) analysis of bulk soil samples. Ash fertilisation of forest soils affected SOM composition in the O-horizon, but not in the top 5 cm of the mineral soil. The pH and biodegradability of SOM were increased in the O-horizon. The changes in SOM composition consisted of enrichment of Fe- and Al-oxides/hydroxides, depletion of carboxylic and aromatic groups and lower thermal stability in soils with older and greater ash application. Ash fertilisation increased soil pH, either right after ash application or through a buffering effect of the ash on acidification caused by decomposing needles over time. The increased pH due to ash fertilisation together with the nutrient inputs from the ash most likely stimulated SOM turnover. This in turn increased the labile fraction of SOM, whereby the thermal stability of SOM decreased as simpler compounds were formed.

1. Introduction

Recirculation of nutrients from wood chip combustion by ash fertilisation in forest systems has been used to re-introduce nutrients that are otherwise lost (Karltun et al., 2008), in order to counteract depletion due to whole tree harvesting (Blanco et al., 2005; Olsson et al., 1996). It has been shown in several studies that fertilisation with wood ash can increase the nutrient status of forest soil and acts as a liming agent to decrease acidity (Brunner et al., 2004; Ingerslev et al., 2014; Jacobson et al., 2004; Ludwig et al., 2002; Saarsalmi et al., 2001). However, the effects of ash fertilisation on soil organic matter (SOM) composition and stability to microbial degradation over time are still not well understood. The ability of SOM to persist over time is a key determinant in understanding carbon (C) turnover on both local and global scale (Schmidt et al., 2011) and it is a challenge to fully understand why some SOM can persist for millennia without being decomposed, whereas other SOM is readily decomposed. Forest soils are an important C pool in Europe, containing similar amounts of C as in tree biomass and usually containing more C than similar soils under arable land and often more than soils under grassland (Smith et al., 2005). The turnover of the pool of C in the soil is controlled by various processes, as a balance between inputs and outputs. The mechanisms controlling SOM decomposition include biological decomposition via respiration, physical decomposition and movement of the SOM via erosion or leaching (Sollins et al., 1996).

Ash consists of a mixture of oxides, carbonates, sulphates, chlorides and silicates (Steenari et al., 1999) and large amounts of

* Corresponding author.
E-mail addresses: metha@ign.ku.dk (M. Hansen), anna.saarsalmi@luke.fi (A. Saarsalmi), peltre@plen.ku.dk (C. Peltre).

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both macro- and micronutrients are retained in the ash (Ingerslev et al., 2011). Application of ash to forest soil has a liming effect, as the retained Ca is primarily in the form of $CaCO_3$ because oxides in the fresh ash form hydroxides via hydration and these are further chemically stabilized via carbonation (Steenari et al., 1999). Ash application can influence the microbial community in the soil. If the pH increases to a more favourable level, an increase in microbial activity is likely to occur (Badalucco et al., 1992; Edmeades et al., 1981).

It is possible that ash can change SOM stability, as SOM can be protected from decomposition by interacting with mineral surfaces or metals applied by the ash (Kleber et al., 2015). Through ligand exchange, OM can be stabilized through strong organo-mineral association as OH groups of the mineral are exchanged with functional groups of the OM (Gu et al., 1994). This process is pH-dependent (Filius et al., 1998; Lutzow et al., 2006), and application of ash could therefore affect SOM stability both through its alkaline nature and through the increased input of minerals and metals to the soil. Conversely, the liming effect and the input of nutrients could provide more favourable conditions for soil microbial biomass, possibly leading to an increased decay of SOM.

The aim of the present study was to investigate how ash fertilisation of forest soils affects SOM composition and stability over time. Changes in SOM biodegradability were measured during a laboratory incubation experiment. Potential alteration of SOM composition due to ash application was studied using thermal analysis and Fourier transform mid-infrared photoacoustic spectroscopy (FTIR-PAS) analysis of bulk soil samples. This study was established to address the hypothesis that ash fertilisation alters SOM composition and stability over time due to its liming potential, input of nutrients and addition of metal ions.

2. Methods

2.1. Site description

Soil samples were collected from two coniferous forest sites: Valkeala (Exp. 402), Finland (60°54.4782′/27°1.2162′ Lat/Lon) and Thy, Denmark (56°59.553′/8°30.105′ Lat/Lon), in August 2014. The Finnish experiment was established in a 64-year-old Scots pine stand 23 years prior to soil sampling (Saarsalmi et al., 2004). The experiment was laid out in a randomised plot design including an unfertilised control treatment (FI_0) and a treatment with 3 Mg ha^{-1} of loose wood ash (FI_23) (Table 1), replicated three times on 0.09 ha plots. The ash was applied manually and not incorporated into the soil. Soil was sampled from all plots in August 2014. The Danish experiment was established in a 28-year-old Norway spruce stand 14 years prior to soil sampling (Ingerslev et al., 2005). That experiment was also laid out in a randomised plot design with three replicates of each treatment including a control without ash application. A dose of 4.3 t ha^{-1} of loose wood ash (Table 1) was applied manually to the treated sites in 2000, without incorporation into the soil. In all plots in Denmark, an additional 3 t ha^{-1} of loose wood ash were applied in 2011, as part of a general fertilisation regime (Table 1). Soil was sampled in 2014 from the plots that received ash on one occasion (DK_3) and those that received ash on two occasions (DK_14 + 3). Particle size distribution of parent material and thickness and nutrient status of the O-horizon at the time of establishment of the two experiments in Finland and Denmark are shown in Table 2, while a detailed description of establishment of the sites and stand characteristics can be found in Saarsalmi et al. (2004) and Ingerslev et al. (2005). Particle size distribution was determined after sampling in 2014 using a Malvern Mastersizer 2000 following the DS/ISO 13320 standard.

Table 1
Concentrations of elements applied with the ash at the sites in Finland and Denmark. All three ash products were characterised with ICP-MS following Saarsalmi et al. (2004) and Ingerslev et al. (2005). Denmark 3 refers to the second ash application in Denmark.

	Finland	Denmark	Denmark 3
P (g kg^{-1})	6.8	22.1	25.8
K (g kg^{-1})	18.2	60.1	56.2
Ca (g kg^{-1})	232	163.0	
Mg (g kg^{-1})	14.4	37.9	
Al (g kg^{-1})	50.1	17.2	
Fe (g kg^{-1})	9.1	28.1	
Mn (g kg^{-1})	8.4	8.6	
S (g kg^{-1})	15.2	7.27	
Cu (g kg^{-1})	0.08	0.264	
Zn (g kg^{-1})	2.2	0.836	
Cd (mg kg^{-1})	6.2	18.0	11.8
Pb (mg kg^{-1})	27.2	299.0	28.6
Hg (mg kg^{-1})		0.3	0.3
Ni (mg kg^{-1})		39	17.7
Cr (mg kg^{-1})		30	17.5

At both sites, the O-horizon and the top 5 cm of the mineral soil were collected with a 60 mm diameter auger. For each plot, 16 samples were collected in a systematic grid of two rows of eight samples, with 3 m between rows and 1 m between samples. The O-horizon and mineral soil were separately bulked and thoroughly mixed. The soil was kept cold (4 °C) until further analysis. The soil was sieved to <2 mm and <4 mm for the mineral and organic soil, respectively, without prior drying.

2.2. Soil analysis

The soil was dried at 50 °C and a subsample was milled to <1 mm and analysed for C and nitrogen (N) concentration by dry combustion using a FLASH 2000 EA NC Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The soil pH was determined in a 1:2.5 and 1:10 soil:water ratio for the mineral and organic soil, respectively, with a Metrohm 827 laboratory pH meter. Subsamples of the soil samples were finely milled to <1 mm, digested in a nitric acid/hydrogen peroxide solution at 250 °C and diluted to 3.5% v/v HNO with ultrapure Milli-Q water. Multi-elemental analysis was performed on the samples using ICP-MS Agilent 7900 (Agilent Technologies, Manchester, UK). Elimination of spectral interferences was achieved using an octopole 182 ion guide with the cell gases helium or hydrogen. A total of 16 elements were analysed: Fe, Al, Ca, K, Mg, P, Mn, Na Cd, Mo, Cu, Co, Zn, Cr, Ni and Pb.

2.3. Mineralisation rate

Three replicate samples of undried soil (10 g wet wt.) were placed in respirometric jars and incubated at 15 °C for 78 days in an automatic respirometer (Respicond V, Nordgreen Innovations AB, Sweden) (Nordgren, 1988) to estimate changes in SOM biodegradability. The soil water content was adjusted to 100% water-holding capacity (WHC) (Ahn et al., 2009; Mutuo et al., 2006). The CO_2 evolution was measured automatically once an hour as the accumulation of CO_2 in the KOH solution (0.3 M; 10 mL) by measuring changes in the conductivity. The mineralisation rate was calculated by linear regression of accumulated CO_2 versus time and SOM biodegradability was expressed as cumulated C mineralised as a percentage of initial C.