Is wood ash amendment a suitable mitigation strategy for N\textsubscript{2}O emissions from soil?

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HIGHLIGHTS

- Wood ash amended to different soil types affected the emission of N\textsubscript{2}O.
- The final resulting soil pH was the most important factor affecting N\textsubscript{2}O emissions.
- Wood ash applied at low rates (<9 t ha\textsuperscript{-1}) may mitigate N\textsubscript{2}O emissions from soils with low pH and high SOM.

GRAPHICAL ABSTRACT

ABSTRACT

Wood ash, the by-product of biomass combustion to energy, can return important nutrients back to the soil and counteract acidification. However, the application of wood ash may affect the emission of greenhouse gases. Here, the effect of wood ash application on nitrous oxide (N\textsubscript{2}O) emissions from different soil environments were investigated in a 40 days incubation experiment comprising ten different soil types amended with five different wood ash concentrations (0, 3, 9, 20, and 54 t ash ha\textsuperscript{-1}). The emitted N\textsubscript{2}O was measured continuously, and initial soil properties without ash application (carbon (C), nitrogen (N), ammonium (NH\textsubscript{4}\textsuperscript{+}), nitrate (NO\textsubscript{3}\textsuperscript{-}), and pH) and resulting soil properties (pH, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{3}\textsuperscript{-}) were measured prior and after the incubation period, respectively. The Random Forests (RF) model was used to identify which factors (initial and resulting soil properties, vegetation, management, wood ash dose, and respiration rate) were the most important to predict the development of emitted N\textsubscript{2}O after ash application. Wood ash either increased, decreased, or had no effect on the amount of emitted N\textsubscript{2}O depending on soil type and ash dose. The RF model identified the final resulting pH as the most important factor for the prediction of emitted N\textsubscript{2}O. The results suggest that wood ash can mitigate N\textsubscript{2}O emissions from soil, however, this effect depends on soil type where a mitigating effect of wood ash application was observed mainly in low pH soils with high soil organic matter whereas an increase in N\textsubscript{2}O emissions was observed in mineral soils that had previously received N fertilization. This study emphasises the importance of pH manipulation in regards to N\textsubscript{2}O emissions from soil.

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1. Introduction

Nitrous oxide (N₂O) is a potent greenhouse gas contributing to radiative forcing. N₂O has a global warming potential 300 times that of carbon dioxide (CO₂), and it is now considered the third most influential greenhouse gas (Stocker et al., 2013). Today, emissions from agricultural and natural soils contribute 60% of the total N₂O emitted globally (Clais et al., 2013).

The primary N₂O producing processes in soil are microbial nitrification and denitrification; which both utilize inorganic N compounds, ammonium (NH₄⁺) and nitrate (NO₃⁻), respectively (Firestone and Davidson, 1989). (Supplementary material one (S1), Fig. A). Nitrification is the most important source of N₂O fluxes from well-aerated soils (water-filled pore space <60%), while N₂O production in wet soils (water-filled pore space 60–90%) is predominantly derived from anaerobic denitrification (Skiba et al., 1997; Bateman and Baggs, 2005; Mathieu et al., 2006). Denitrification is the major biological process in soils that returns fixed nitrogen to the atmosphere, where N₂O is an obligatory intermediate and may under certain conditions also be the end product. N₂O from nitrification is formed during ammonia oxidation, where N₂O is formed by chemical decomposition of hydroxylamine (Hooper and Terry, 1979; Wragge et al., 2005; Frame and Casciotti, 2010). However, the formation of nitrite (NO₂⁻) is always the main pathway, and levels of nitric oxide (NO) and N₂O produced are several orders of magnitude lower (103–106) than those of NO₂⁻ (Arp and Stein, 2003). The NO₂⁻ produced by nitrification of NH₄⁺ is often directly denitrified. The process of denitrification coupled to nitrification involves distinct microorganisms (Arth et al., 1998; Avrahami and Conrad, 2002; Carrasco et al., 2004; Kool et al., 2010), and a patchy environment with mixed aerobic and anaerobic microsites. However, some ammonia oxidisers have the ability to perform nitrification and denitrification in one process called nitrifier denitrification (Wrage-Mönning et al., 2018). The rate and end products of the N₂O-producing processes are affected by soil properties and conditions such as soil organic matter (SOM), nitrogen (N) substrate form and availability, pH, and oxidative conditions. In S1 (Table A), soil conditions favouring N₂O production from different N₂O producing processes are summarized.

Previously, soil pH management has been proposed as a strategy to mitigate N₂O emissions from soils (Liu et al., 2010; Barton et al., 2013). Thus far, several authors have investigated the relationship between N₂O emissions and soil pH (Goodroad and Keeney, 1984; Yamulki et al., 1997; Stevens et al., 1998; Feng et al., 2003; Baggs et al., 2010; Cuhel et al., 2010; Barton et al., 2013) however, with conflicting results. Soil pH can be managed by applying different soil amendments (e.g. lime) or wood ash. Increasing amounts of wood ash are being produced as a by-product of biomass combustion to energy (Silva et al., 2019). Wood ash consists of the inorganic compounds from the harvested biomass, sand residues, and a very small fraction of not fully combusted organic material (Ingerslev et al., 2011). Hence, wood ash contains all inorganic plant macro- and micronutrients from the biomass except N (Rosenberg et al., 2010). During combustion different oxides develop and subsequent aeration will lead to the formation of carbonates in the wood ash, making the ash very alkaline with a pH between 8 and 13 (Augusto et al., 2008). As opposed to disposing of the ash in landfills, recycling the ash as a soil amendment will return important nutrients to the soil, and counteract acidification (Brunner et al., 2005; Pitman, 2006).

So far, only a few studies have investigated the effect of wood ash application on N₂O emissions from soil. Klemmedtsen et al. (2010) found a decrease of 40–46% emitted N₂O, in the first year after wood ash application in a spruce forest on drained organic soil. They assigned the reduction of emitted N₂O to increased soil pH. Limmatainen et al. (2014) also found that granulated wood ash reduced N₂O production in peat soil. However, these authors assigned the reduced N₂O emissions to changes in the ion strength inhibiting N₂O production. Similarly, Royer-Tardif et al. (2019) found that wood ash decreased N₂O production in a sugar maple forest two years after application. Contrarily, Maljanne et al. (2006a) found no effect of wood ash amendment on N₂O production in a podzolized spruce forest soil. However, in another study, the same authors observed a tendency towards both increased or decreased N₂O production from different long-term field experiments with peat soil (Maljanne et al., 2006b). Thus, depending on the N₂O producing processes dominating in the specific soil environment and initial soil properties, wood ash application may affect N₂O emissions differently. Thus, coupling specific soil properties to the effect of wood ash application on N₂O production is important to predict the potential effects of wood ash amendment to soil.

Here, the mitigating effect of wood ash application on N₂O production from a range of different soils was investigated. The aim was to examine the relative importance of different inherent and induced soil properties (SOM, pH, total C, total N, NH₄⁺, and NO₃⁻ content) and factors such as vegetation and fertilizer management to predict the development of N₂O production from soils amended with wood ash at different concentrations. Accordingly, an incubation study, including ten different temperate soils, was conducted. The soils differed in vegetation and land use (woodland, heath, and agriculture), fertilizer management (manure, NPK, or unfertilized), and basic soil properties. We hypothesized that the effect of wood ash application on N₂O production from soil depends on the initial soil properties where the initial and induced soil pH is an important factor.

2. Methods and materials

2.1. Wood ash

The wood ash was collected from Galten district heating plant, Galten, Denmark. The ash is a mix of bottom and fly ash originating from the combustion of wood chips of Norway spruce. To determine the chemical composition of the ash, samples were digested with nitric acid (HNO₃) and P, K, Ca, Mg, Na, Mn, Zn, Cu, Cd, Pb, Cr, and Ni were measured by inductively coupled plasma atomic emission spectrometry ICP-OES (PerkineElmer, optima 3000 XL). pH was measured using a glass electrode in a 1:2.5 water to wood ash solution on a Phm240 pH/ION Meter (Meterlab, Radiometer Copenhagen). Wood ash properties are presented in S1 (Table B).

2.2. Soil sampling and analysis

Ten different soil types comprising plantation forests, peat, and agricultural soils were collected from various locations in Zealand, Denmark. Three woodland soils (W1, W2, and W3), three peat soils (P1, P2, and P3), and four agricultural soils (A1, A2, A3, and A4) were sampled from the top 1–8 cm beneath the litter layer and stored at 5 °C. More detailed descriptions of all soils are presented in S1 (Table C).

Soil bulk densities were determined using 100 cm² volumetric rings on field soil. Estimates of field capacity were made as follows: Soils were air-dried for 48 h at 20 °C, sieved through a 2 mm mesh or homogenized by hand if the SOM content was high and subsequently compressed gently into 175 ml plastic cups with holes in the bottom. The samples were saturated with water, and the water content of the soil collected from 2 to 4 cm depth in the container was determined after 24 h. Soil pH was measured using a glass electrode in a 1:2.5 soil water extraction on a Phm240 pH/ION Meter (Meterlab, Radiometer Copenhagen). SOM was determined by loss of ignition as the weight % difference between samples oven-dried at 105 °C and samples combusted at 550 °C. Total C and N were determined by infrared absorption spectroscopy (IR) on a LECO TruSpec Carbon Nitrogen Determinator (Michigan, USA). Particle size distributions for the mineral soils (A1, A2, A3, and A4) were determined by laser diffraction using a Hydro 2000GC, Malvern Mastersizer 200G. NH₄⁺ and NO₃⁻ were determined in a 1:5 soil water extraction and analysed colourimetrically on a 5000 FIASTAR flow injection analyser.
The soils were sieved using a 2 mm sieve or homogenized by hand if the content of organic material was too high. Soil samples equivalent to 10 cm$^3$ field soil were mixed with five different wood ash concentrations equivalent to 0, 3, 9, 20 and 54 t ash ha$^{-1}$, assuming that the wood ash was mixed in the top 5 cm soil. Mixed soil and wood ash samples were supplied with sterilized distilled water to obtain field capacity in 116-ml serum bottles and closed with airtight rubber stoppers. Samples were incubated in the dark at 15 °C for 40 days. The bottles were added 20 ml extra atmospheric air to secure an overpressure; hence, extraction of headspace gas samples was possible. Headspace gas samples were taken on day 12, 18, 28, and 36 using a syringe. Oxygen (O$_2$) and CO$_2$ levels were measured using a gas chromatograph with a TCD detector (Thermal Conductor) and a Poropak Q column (1.8 cm × 3 cm) with Ar/CH$_4$ as carrier gas and NO$_3$ levels were analysed on a Shimadzu 8ATO-7A5Y tor (Thermal Conductor) and a Poropak Q column (1.8 cm × 3 cm) with Helium (He) as carrier gas. When CO$_2$ levels in the control samples (no ash) reached >5%, all bottles were opened and aerated for 24 h to avoid oxygen depletion. After 40 days of incubation, soil pH, NH$_4^+$ and NO$_3^-$ were determined as follows: 70 ml distilled water was added to each incubation flask and shaken for one hour on a rotary shaker. Subsequently, the flasks were set to sediment for one hour, and 10 ml of the clarified supernatant was extracted for pH measurements, and 20 ml was centrifuged and filtered to determine NH$_4^+$ and NO$_3^-$ content of soil by a 5000 FIASTAR flow injection analyser (Höganäs, Sweden). The N$_2$O measured during the incubation period was calculated as the cumulative N$_2$O production for each incubation flask. Thus, the N$_2$O production will in the following refer to the cumulative N$_2$O production.

2.4. Statistical analysis

The Random Forests (RF) model was used to identify the relative importance and interactions of soil properties on the N$_2$O production following wood ash application. The RF model belongs to a newer assemblage of machine learning models. The advantage of these models is that they can capture complex nonlinear relationships between predictor and response variables more effectively than a linear regression model (Pearson, 2016). We constructed the RF model based on the variable and response variables more effectively than a linear regression model (Pearson, 2016). We constructed the RF model based on the variable and response variables more effectively than a linear regression model (Pearson, 2016). We constructed the RF model based on the variable and response variables more effectively than a linear regression model (Pearson, 2016).

The rfPermute package with the functions rfPermute() and rp.importance() function was used to calculate variable importance (Archer, 2016). Finally, the rfUtilities package holding the rfSignificance() function was used to test for model significance (Jeffrey et al., 2016). The partial dependence plots were produced using the partial dependence plot function in the randomForest package.

One way analysis of variance (P < .05) and Tukey's test were performed for the N$_2$O production for each soil type. Normality of the data was evaluated visually and by using the Shapiro-Wilks test, and Levene's test was performed to confirm the homogeneity of variance before the ANOVA test. All analysis were performed in R software version 3.3.0.

3. Results

3.1. Soil types

As expected, the collected soil types differed greatly in initial soil properties. The three woodland soils (W1, W2, and W3) had initially

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Bulk density g cm$^{-3}$</th>
<th>pH (H$_2$O)</th>
<th>SOM %</th>
<th>Total C %</th>
<th>Total N %</th>
<th>NH$_4^+$ mg kg$^{-1}$</th>
<th>NO$_3^-$ mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1 Arenosol</td>
<td>0.23 (0.10)</td>
<td>3.9 (0.05)</td>
<td>76 (3.0)</td>
<td>45 (0.000)</td>
<td>1.8 (0.006)</td>
<td>16 (1.0)</td>
<td>63 (1.1)</td>
</tr>
<tr>
<td>W2 Podzol</td>
<td>0.25 (0.13)</td>
<td>4.0 (0.03)</td>
<td>83 (1.6)</td>
<td>41 (0.071)</td>
<td>1.5 (0.002)</td>
<td>13 (1.5)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>W3 Alisol</td>
<td>1.00 (0.11)</td>
<td>4.4 (0.02)</td>
<td>34 (3.1)</td>
<td>19 (0.566)</td>
<td>1.0 (0.026)</td>
<td>40 (1.0)</td>
<td>35 (2.8)</td>
</tr>
<tr>
<td>P1 Histosol low pH</td>
<td>0.18 (0.01)</td>
<td>4.0 (0.03)</td>
<td>96 (0.9)</td>
<td>53 (0.141)</td>
<td>1.0 (0.009)</td>
<td>20 (0.8)</td>
<td>22 (1.3)</td>
</tr>
<tr>
<td>P2 Histic Planosol</td>
<td>0.75 (0.06)</td>
<td>5.8 (0.14)</td>
<td>46 (0.6)</td>
<td>14 (0.071)</td>
<td>1.1 (0.001)</td>
<td>0.2 (0.02)</td>
<td>67 (0.4)</td>
</tr>
<tr>
<td>P3 Histosol high pH</td>
<td>0.24 (0.02)</td>
<td>6.5 (0.05)</td>
<td>77 (0.8)</td>
<td>38 (0.071)</td>
<td>2.9 (0.004)</td>
<td>0.1 (0.02)</td>
<td>42 (1.2)</td>
</tr>
<tr>
<td>A1 Luvisol high pH</td>
<td>1.30$^{a}$</td>
<td>7.2 (0.02)</td>
<td>11 (0.7)</td>
<td>8 (0.170)</td>
<td>0.3 (0.002)</td>
<td>0.2 (0.04)</td>
<td>166 (0.4)</td>
</tr>
<tr>
<td>A2 Luvisol unfertilized</td>
<td>1.40$^{a}$</td>
<td>7.0 (0.07)</td>
<td>5 (0.02)</td>
<td>1 (0.038)</td>
<td>0.1 (0.009)</td>
<td>0.1 (0.03)</td>
<td>31 (1.6)</td>
</tr>
<tr>
<td>A3 Luvisol manure</td>
<td>1.40$^{a}$</td>
<td>6.0 (0.02)</td>
<td>4 (0.03)</td>
<td>1 (0.001)</td>
<td>0.1 (0.000)</td>
<td>0.2 (0.004)</td>
<td>39 (4.4)</td>
</tr>
<tr>
<td>A4 Luvisol NPK</td>
<td>1.40$^{a}$</td>
<td>6.8 (0.03)</td>
<td>4 (0.004)</td>
<td>2 (0.083)</td>
<td>0.2 (0.003)</td>
<td>0.2 (0.003)</td>
<td>32 (5.0)</td>
</tr>
</tbody>
</table>

$^{a}$ Values used based on personal communication with farmers.
low pH ≤ 4.4 and high SOM content 34–83% (Table 2). However, soil W3 had slightly higher pH and lower SOM content compared to soils W1 and W2, due to the difference in vegetation (spruce/fir vs. deciduous forest) and parent material (sand vs. till) (Table 1). The peat soils (P1, P2, and P3) differed in initial pH (Table 2) and the degree of decomposition of the organic material (Table 1). The agricultural soils A2–A4 had similar properties as they were collected from the same location and mainly differed in their management history i.e. unfertilized, manure, or NPK. Soil A1 was a different soil type than soils A2–A4 and had a high initial pH due to a naturally high content of CaCO₃ and a naturally high Fe-content (Tables 1 and 2).

3.2. Random Forests model

The RF regression model was significant at $p < 0.0001$ (Fig. 1). The extracted measure of variable importance indicated that the final resulting pH, wood ash dose, initial NH₄⁺, and final resulting NO₃⁻ content were the most important variables for the prediction of N₂O production from the different soils. Hence these parameters will be the focus of discussion. In contrast, total C, total N, and management added the least explanation to the prediction model (Fig. 1).

3.3. Effect of wood ash amendment on the N₂O production from soil

The effects of wood ash application on the N₂O production differed between soil types. In forest soil W1 and peat soil P1, wood ash application significantly decreased the N₂O production whereas high doses of wood ash (54 t ha⁻¹) significantly increased the N₂O production in the agricultural soils A1, A3, and A4 compared to the control samples (Fig. 2). The results were more variable for the woodland soils W2 and W3, where wood ash application either increased or decreased the N₂O production depending on the ash dose (Fig. 2). Finally, wood ash application did not significantly affect the N₂O production in agricultural soil A2 and peat soils P2 and P3 compared to the control samples. Still, there was a tendency that wood ash caused an increase in N₂O production (Fig. 2). The partial dependence plot showed that the general relationship between wood ash dose and the N₂O production was negative when wood ash was applied at low doses (0–9 t ha⁻¹) and positive at high doses (>20 t ha⁻¹) (Fig. 3).

3.4. Relationship between key predictor variables, wood ash application, and N₂O production

In all soil types, wood ash amendment resulted in a pH increase (Fig. 2). The highest wood ash dose (54 t ha⁻¹) increased pH between 1.6 and 3.6 pH units, depending on soil type, compared to control samples. The partial dependence plot revealed that the relationship between the N₂O production and final soil pH was negative in the pH range from 4.0–5.3 and positive in the pH range from 8.0–9.0. Whereas, pH did not influence the N₂O production in the pH range from 5.3–8.0 (Fig. 3).

The initial NH₄⁺ content was highest in the natural soils with initially low pH (W1, W2, W3, and P1), whereas the agricultural soils and natural soils with pH close to neutral had approximately 100 times less initial content of NH₄⁺ (Table 1). The partial dependence plot revealed that the relationship between initial NH₄⁺ content and N₂O production was overall positive (Fig. 3).

There was a general trend towards an increase in the final soil NO₃⁻ content following wood ash application. However, in soils W1, P1, and A2, the NO₃⁻ content did not increase at the highest wood ash dose (54 t ha⁻¹). Furthermore, the NO₃⁻ content was not notably affected by wood ash application in soils A1 and W2 (Fig. 4). According to the...
partial dependence plot, the relationship between N2O production and final soil NO3− content was positive from 0 mg kg−1 to approximately 50 mg kg−1, whereas there was no clear relationship between the two parameters at higher concentrations (Fig. 3).

4. Discussion

4.1. pH effects on the N2O production from soil

As expected wood ash amendment increased the pH in all soils. Correspondingly, the RF model suggested that the final resulting soil pH was the strongest predictor for the N2O production from the different soil types (Fig. 1). In addition, the RF model specified that the relationship between N2O production and the final resulting pH was not straightforward, as the relationship was U-shaped (Fig. 3). This picture was somewhat, but not completely reflected in the relationship between wood ash application and N2O production (Fig. 3). Hence, the effect of the ash amendment depends to some extent on the initial soil properties, as the final resulting pH is a combined effect of basic soil properties (affecting the buffer capacity) and wood ash dose. Therefore, the final resulting pH rather than wood ash application rate was the better predictor for the N2O production. In essence, the RF model results indicate that wood ash applied at low doses (3–9 t ha−1), with less effect on soil pH (pH < 8), reduced or had no significant effect on the N2O production from a wide range of different soil environments. In contrast, there was a tendency towards increased N2O production when the soils became alkaline (pH > 8) which was achieved at the highest wood ash amendment rates for some soils (Figs. 2, 3 and 5).

In general, increasing pH in acidic soils stimulates the microbial activity and modulates the composition of the soil microbial community (Fierer and Jackson, 2006), which in turn can affect the rate and end products of the N2O producing processes (Šimek et al., 2002). Accordingly, the microbial activity, continuously measured as the O2 consumption, increased in all soils amended with wood ash, except for the initially alkaline soil A1 (S1, Fig. A). We attribute this phenomenon to the combined effect of nutrient addition and pH increase by the wood ash.

N2O production under acidic soil conditions is usually caused by denitrification and heterotrophic nitrification (Šimek and Cooper, 2002; Markved et al., 2007; Zhang et al., 2015a). In contrast, autotrophic nitrification performed by bacteria is sensitive to low pH and will mainly contribute to N2O production at neutral and high pH (S1, Table A) (Baggs et al., 2010). Thus, changing the soil pH may affect which processes are mainly responsible for the N2O production. In line with our findings, several studies have suggested that raising pH by e.g. liming may reduce N2O emissions from acidic soil environments (Yamulki et al., 1997; Barton et al., 2013; Wang et al., 2018). On the other hand, elevated pH may lead to an increase in the rate of nitrification and thus a higher production of N2O (Baggs et al., 2010). However, the exact relationship between pH and N2O emissions from soil is complex,
Conversely, ash application reduced the N\textsubscript{2}O production in soils W1, W2, W3, and P1 (Figs. 2 and 5). These were all natural soils with similar properties such as initially low pH and high SOM content (Tables 1, 2). In general, when soil pH increases, the rate of denitrification and nitrification also increase, due to higher microbial activity and thus substrate availability (i.e., N\textsubscript{2}O, and NH\textsubscript{4}\textsuperscript{+} (Šimek and Cooper, 2002; Baggs et al., 2010). However, for denitrification, the emitted N\textsubscript{2}O relative to N\textsubscript{2} decreases with increasing pH. Thus, the emitted N\textsubscript{2}O from denitrification is generally higher at acidic conditions (Šimek and Cooper, 2002; Mcmillan et al., 2016; Shaaban et al., 2018). Therefore, an increase in soil pH induced by wood ash amendment may have resulted in reduced N\textsubscript{2}O emissions from denitrification in the acidic soils. The particular mechanisms controlling the product ratio (N\textsubscript{2}O:N\textsubscript{2}) from denitrification at shifting pH is still up for debate. Especially the relationship between soil pH and the relative abundance of bacteria possessing the nosZ gene encoding the reductase of N\textsubscript{2}O to N\textsubscript{2} has drawn much attention (Philippot et al., 2009; Liu et al., 2010; Zhang et al., 2015b). Accordingly, it has been suggested that the N\textsubscript{2}O reductase enzyme is sensitive to low pH (Šimek and Cooper, 2002; Liu et al., 2010). However, based on experiments with denitrifying bacteria Shawanella lothica, Kim et al. (2017) suggested that enhancement of NO\textsubscript{2}\textsuperscript{-} reduction to N\textsubscript{2}O rather than a decrease in N\textsubscript{2}O reduction to N\textsubscript{2} was the actual cause of high N\textsubscript{2}O accumulation in acidic environments. However, N\textsubscript{2}O production from denitrification is not solely controlled by pH. Hence, other environmental factors such as the NO\textsubscript{3}\textsuperscript{-} content, the NO\textsubscript{3}\textsuperscript{-}:NO\textsubscript{2}\textsuperscript{-} ratio, and the C:N ratio have been reported to overlap the effect of pH (Blackmer and Brenner, 1978; Yoon et al., 2015; Kim et al., 2017). Recently, Senbayram et al. (2019) found that the addition of NO\textsubscript{3}\textsuperscript{-} to soil inhibited the reduction of N\textsubscript{2}O to N\textsubscript{2} resulting in an increase in N\textsubscript{2}O emissions regardless of soil pH. Accordingly, the authors proposed that the NO\textsubscript{3}\textsuperscript{-} content and not soil pH was the major factor controlling the product ratio (N\textsubscript{2}O:N\textsubscript{2}) from denitrification. In this study, ash application increased the NO\textsubscript{3}\textsuperscript{-} content in most soils (Fig. 5) (except in soil A1 and W2), possibly due to increased nitrification at elevated soil pH. Similar increases in soil NO\textsubscript{3}\textsuperscript{-} content have previously been reported for wood ash amended soils (Kahl and Fernandez, 1996; Arshad et al., 2012; Vestergård et al., 2018). However, a tendency towards a positive relationship between N\textsubscript{2}O production and the final resulting NO\textsubscript{3}\textsuperscript{-} content was only observed in the low range of approximately 0–50 mg NO\textsubscript{3}\textsuperscript{-} kg soil\textsuperscript{-1} (Fig. 3). Thus, there was no indication to soil ash dose.

Ash-induced increases in N\textsubscript{2}O production was mainly observed in the cultivated mineral soils with near-neutral pH and low SOM content (A1, A3, and A4) (Figs. 2, 5 and Table 2). Specifically, the highest doses of wood ash application (54 t ha\textsuperscript{-1}) significantly increased the N\textsubscript{2}O production from cultivated soils that had received NPK or manure (A1, A3, and A4), yet not from the unfertilized agricultural soil A2 (Figs. 2 and 5). Higher N\textsubscript{2}O production, due to higher substrate availability, from soils amended with conventional NPK fertilizers or manure, has previously been reported (Meng et al., 2005; Ding et al., 2013). The ash induced increase in pH may have resulted in a higher nitrification rate and thus increased the N\textsubscript{2}O production from this process. However, a significant increase in the N\textsubscript{2}O production from NPK or manure treated soils was only observed at very high ash applications that raised the soil pH to 8.8–9.6 pH. Such high soil pH is not considered beneficial from an agricultural perspective due to restricted nutrient availability of nutrients such as phosphorus (P) (Brady and Weil, 2008). Thus, our results suggest that moderate ash applications (3 t ha\textsuperscript{-1}) do not pose a great risk for short-term enhancement of N\textsubscript{2}O emissions even from the cultivated mineral soils.

Fig. 3. Partial dependence plot obtained from the random forests model for the four most important variables (see Fig. 1) for the prediction of N\textsubscript{2}O production, based on incubation experiments including ten different soils (Tables 1 and S1 (Table C)). The y-axes represent the mean of the predicted values of the response variable in log (µg N\textsubscript{2}O m\textsuperscript{-2}) corresponding to the particular independent variables on the X-axis. Red dotted lines indicate a negative relationship between the response variable and the independent variable, green dotted lines indicate that there is no clear relationship between the response and independent variable, and blue dotted lines indicate a positive relationship between the response and independent variable.
parallel in different microsites and both processes may be affected by ash-induced changes to pH and nutrient addition. Thus, pH cannot solely explain the development of N\textsubscript{2}O emissions from soil, however, in this study, the final resulting pH was a good overall indicator of the effect of wood ash application on N\textsubscript{2}O emissions from contrasting soil environments.

4.2. Wood ash amendment as an N\textsubscript{2}O mitigation strategy?

Wood ash amendment was mainly beneficial with a reduction in N\textsubscript{2}O emissions or unaltered N\textsubscript{2}O emission rates depending on soil type. The greatest mitigating effect on the N\textsubscript{2}O outlet of wood ash was observed at an application rate of 9 t ha\textsuperscript{-1}, whereas higher applications did not further reduce the emitted N\textsubscript{2}O from most soils (Fig. 2). To date, the legislative regulations of ash applications are limited to applications of only 2–7.5 t ha\textsuperscript{-1} 100 y\textsuperscript{-1} in Europe (Silva et al., 2019). Based on our observations, such relatively low applications of wood ash will reduce the emitted N\textsubscript{2}O from most soil environments in the short-term or cause no changes in the emitted N\textsubscript{2}O; albeit this positive effect should be considered in relation to the effects on other greenhouse gasses (CO\textsubscript{2} and CH\textsubscript{4}). Furthermore, Maljanen et al. (2006b) found no significant effects of wood ash application (5–8 t ha\textsuperscript{-1}) on N\textsubscript{2}O emissions from five boreal forests soils 14–50 years after application, indicating that the long-term effects of relatively low wood ash applications on N\textsubscript{2}O emissions are negligible. Finally, wood ash contains all macro- and micronutrients except for N. Therefore, wood ash application combined with N application is considered as a management strategy on N poor sites (Saarsalmi et al., 2006). As soils with a history of N fertilizers resulted in an increase in N\textsubscript{2}O emissions, more research is needed to identify potential negative interactions between wood ash and N fertilizers and the effect on N\textsubscript{2}O emissions from different soil environments.

Fig. 4. Final water-extractable NO\textsubscript{3}\textsuperscript{-} content in the soil incubations ±S.D. (n = 3).

Fig. 5. The ten soils included in the incubation experiment (Tables 1 and S1 (Table C)) grouped according to their response to wood ash application with regard to the cumulative N\textsubscript{2}O production. Important soil properties are linked to the different groups. Red group: wood ash significantly (p < 0.05) decreased the N\textsubscript{2}O production, blue group: wood ash significantly (p < 0.05) increased the N\textsubscript{2}O production, and yellow group: wood ash had no significant effect (p > 0.05) on the N\textsubscript{2}O production at any wood ash application rate. Two soils overlap in the groups (W2 and W3) as wood ash either increased or decreased the N\textsubscript{2}O depending on application dose in these soils.
5. Conclusion

Wood ash application at different rates had various effects on the emitted N$_2$O from contrasting soil environments. The final resulting soil pH rather than the wood ash amendment rate was the key predictor for N$_2$O production from different soils. The relationship between the final resulting pH and the N$_2$O production was U-shaped. Thus, the soil pH and N$_2$O production was highest at low pH (~5.3 pH) and high pH (~8.0 pH). Therefore, wood ash application at low rates <9 t ha$^{-1}$ may mitigate N$_2$O production from acidic soils with high SOM in the short-term. Still, the underlying mechanisms controlling the effects of elevated soil pH induced by wood ash amendment on N$_2$O production needs to be further investigated. Likewise, interactions between wood ash amendment and N application should be considered when using wood ash as a soil management tool.

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Appendix A. Supplementary data

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References


