Short-term effects of hardened wood ash and nitrogen fertilisation in a Norway spruce forest on soil solution chemistry and humus chemistry studied with different extraction methods

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Abstract

A field trial with wood ash, nitrogen fertiliser, combined wood ash and nitrogen treatment and control was set up in a Norway spruce [*Picea abies* (L.) Karst.] forest, and post-treatment changes and differences in humus chemistry and soil solution chemistry at 40 cm depth were studied from 2013 to 2015. Element concentrations in humus samples were compared using NH_4NO_3 extraction (M1) and nitric acid/perchloric acid digestion (M2). Nitrogen treatment led to significant increases in Mg determined after both M1 and M2. No significant effect of ash or ash+nitrogen treatment on soil C or N in the humus layer was found, while pH and concentrations of many elements after M2 increased in the same samples. Decreases after ash treatment for Al, Co, Fe, Ni, Pb and Zn in humus determined after M1 may be because of decreased mobility due to increased pH. Differences depending on analytical method suggest that methodology should be taken into account when evaluating ecological relevance of differences in element concentrations. In soil solution at 40 cm depth nitrogen treatment led to short-term increases in concentrations of NO_3^-, NH_4^+, Ca, Mg, Co, Ni and Zn and a reduction in pH, while ash treatment led to no clear effects.

Running head: Wood ash and N effects on humus

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Introduction

Ash from biofuel production contains plant macronutrients such as potassium (K), calcium (Ca), phosphorus (P) and magnesium (Mg). The contents of these nutrients make ash suitable for use as a fertilizer, and it has therefore been suggested that use of wood ash in the forest may have beneficial effects on forest tree growth. However, there have been concerns over the ecological effects of relatively high concentrations of heavy metals and arsenic (As) in wood ash (Pitman 2006; Augusto et al. 2008; Huotari et al. 2015).

Any effect – beneficial or unfavourable - will depend not only on the element concentrations in the ash but also on the dose of ash applied (how much and how often) and how the ash is pre-treated. To avoid short-term negative effects to the ecosystem caused by the high reactivity of untreated wood ash, some type of hardening is recommended (Karltun et al. 2008). The ash dose used in experiments with wood ash fertilisation varies widely: doses from one to 44 t ha^{-1} have been applied (Pitman 2006; Augusto et al. 2008). The Swedish

Forest Agency's guidelines (2008) suggest that negative environmental effects will be limited at doses up to three t hardened ash ha^{-1}. However, such effects are likely to differ between sites depending on local geological, edaphological, biological, topographical and climatic conditions.

Wood ash supply can increase soil pH, especially in the upper soil horizons, although the effect is dependent on dose and ash form (Arvidsson & Lundkvist 2003; Jacobson et al. 2004; Saarsalmi et al. 2004; Ozolinčius et al. 2005; Saarsalmi & Levula 2007; Karltun et al. 2008; Ingerslev et al. 2014; Juárez et al. 2015). Other parameters such as base saturation and exchangeable base cations can also be increased (Arvidsson & Lundkvist 2003; Ingerslev et al. 2014; Reid & Watmough 2014; Brais et al. 2015). However, in a meta-analysis Augusto et al. (2008) found no significant effect on pH in soil during the first five years after addition of one to three t ash ha^{-1}. In the longer term, pH increased in both the humus layer and the upper mineral soil, and with large doses of four-eight t ha^{-1} pH increased by up to 2.5 units in the humus layer and 0.7 units in the upper mineral soil.

As ash originates from a large number of trees grown over a larger area than that which is fertilised, elements including heavy metals may become somewhat concentrated locally after ash fertilisation (Huotari et al. 2015). This can increase the total soil reserve of heavy metals such as Cd (Saarsalmi et al. 2004) or Cr (Saarsalmi et al. 2006), but heavy metals such as Cd, Ni and Pb are in very slowly soluble forms in wood ash (Perkiömäki & Fritze 2003; Nieminen et al. 2005), due to the high pH. Soil solution concentrations of Cd have been observed to increase in the short term after wood ash application (Ring et al. 2006); however, another study found no observable increased Cd concentrations in soil solution (Wang et al. 2010). In a field experiment in Germany, concentrations of Pb and Cr in soil solution did not increase significantly, while concentrations of Cd and Zn did increase significantly at some depths but stayed within acceptable limits (Rumpf et al. 2001). In a laboratory experiment, Cd (determined in a water extract) applied together with ash did not appear to show high bioavailability for fungi (Fritze et al. 2001), and Cd in ash did not become more bioavailable to microorganisms due to increased precipitation of acidified rain (Perkiömäki & Fritze 2003). In some studies, elevated concentrations of heavy metals have been found in organisms after ash addition, while in other cases no change or even a decrease has been found (see review by Huotari et al. 2015). Differences in these results might be due to different local geological, edaphological, biological or climatic conditions as well as differences in both field and laboratory methods. Long-term effects are also still unclear: if the soil pH decreases again, heavy metals might start to dissolve into groundwater (Huotari et al. 2015).

In some studies, only total element concentrations in soil have been determined (e.g. Nieminen et al. 2005), while other studies have determined both total and a fraction considered to represent plant-available concentrations, often called “exchangeable” or “extractable” concentrations (e.g. Rumpf et al. 2001; Saarsalmi et al. 2004; Saarsalmi et al. 2006; Saarsalmi et al. 2012; Ingerslev et al. 2014), or only “plant-available” (e.g. Arvidsson & Lundkvist 2003; Saarsalmi et al. 2010; Wang et al. 2010; Norström et al. 2012; Brais et al. 2015), where availability is operationally defined by the method used.

Effects on soil solution are significant mainly in the upper parts of the soil profile (Ozolinčius et al. 2005) and may also be dependent on dose. For example Williams et al. (1996) found only small changes in soil solution chemistry with small doses but large changes after large doses. Shortly after ash application (from a few weeks to a few months), there may be an increase in concentrations of easily soluble ions (e.g. K, Na, SO_4^{2-}) in soil solution (Augusto et al. 2008) as well as Ca and Mg (Ozolinčius et al. 2005). Norström et al. (2012) found temporary increases of K, Ca and SO_4^{2-} in soil solution after wood ash treatment. In some cases (although not always, Ozolinčius et al. 2005; Ozolinčius et al. 2007), increased concentrations of dissolved organic carbon and nitrate have been found (Karltun et al. 2008; Huotari et al. 2015). After some months the concentration of easily soluble ions in soil solution may decrease again (Pitman 2006; Augusto et al. 2008). The amount of K, Ca and Mg in soil solution can, however, remain higher than before fertilization for a longer period. Increased concentrations of Ca, K and Mg have been found in watercourses seven to 26 months after ash treatment (Norström et al. 2011).

On mineral soils in boreal forests it is often nitrogen availability that limits tree growth. As wood ash contains hardly any nitrogen, wood ash spreading without N fertilization may often have little growth effects, especially at less fertile sites (Saarsalmi et al. 2004; Jacobson et al. 2014). A Finnish study showed that ash together with nitrogen led to a longer-lasting growth effect than when nitrogen alone was supplied, suggesting that a combined ash plus nitrogen treatment is optimal for producing tree growth on these soils (Saarsalmi et al. 2012). This might be related to changes in soil nutrient status and microbial processes related to C and N cycling (Saarsalmi et al. 2014). In order to avoid loss of soil nitrogen to the atmosphere by ammonia volatilization, ash should be supplied later than nitrogen (Jacobson 2003).

This paper reports on changes in humus and soil solution chemistry in a stand of Norway spruce (*Picea abies* (L.) Karst.) after application of hardened wood ash and nitrogen fertiliser. Furthermore, we studied the effect of two different analytical methods for determining element concentrations in humus. Although comparisons of soil extraction methods have been carried out previously (e.g. Rautio and Huttunen 2003), we know of no previous paper where this has been done in examining the effects of wood ash and nitrogen fertilisation. Treatment effects on ground vegetation will be analysed in a separate paper.

Focusing on element concentrations in the soil humus layer, our null hypotheses are that element concentrations in the soil humus layer:

(i) do not differ between the pre-treatment plots, and that

(ii) nitrogen fertilisation and wood ash treatment:

(a) do not cause pre- to post-treatment (i.e. between years) changes within treatments,

(b) do not cause differences between the post-treatment plots, and

(c) show the same patterns of treatment effects regardless of analytical method.

Further, we hypothesise:

(iii) that treatments do not affect nutrient concentrations in soil solution at 40 cm depth within the time frame of the experiment.

Materials and Methods

We set up a field trial with spreading of wood ash and nitrogen fertiliser in forest at Bærøe farm in Hobøl municipality, south-eastern Norway (latitude 59.56˚N, longitude 10.95˚E, altitude 195-215 m a.s.l.). Mean annual temperature and precipitation at the nearby meteorological station at Ås for the period 1st May 2005 – 30th April 2015 (i.e. before and including the measurement period) were 6.4°C and 899 mm respectively. The soil is variable, podzol/cambisol on thin moraine deposits, which in turn cover Precambrian gneiss. Where there is podzol, there are eluvial and illuvial horizons; however, no iron pan was observed. The topography is slightly undulating with nearby steeper slopes. The vegetation zone is southern boreal and vegetation section slightly oceanic, according to Moen (1999). The experimental site is planted with productive Norway spruce forest with Norwegian site index G17-G20 (Tveite 1977). The forest was planted in the 1950s after logging and thinned in 2006/2007.

Treatment plot size was 25 m x 25 m, including a 5 m buffer zone: all sampling was carried out in the inner 15 m x 15 m area. Before treatment, all trees were measured and stem volume per treatment plot was calculated using the volume functions of Vestjordet (1967). The average standing volume at fertilisation was 302 m^3 ha^{-1}. Four treatments were applied in a block design: 3 t ha^{-1} ash (Ash), 150 kg ha^{-1} ammonium nitrate fertiliser (N), 3 t ha^{-1} ash + 150 kg ha^{-1} ammonium nitrate fertiliser (Ash+N), and an unfertilised control (Ctrl). There were three replicates for each treatment. The forest was fertilised manually with ammonium nitrate at the end of May 2013 and with ash at the end of June 2013. Treatments were applied on the soil surface. The ammonium nitrate fertiliser was Opti-KAS Skog (Yara) and contained 27% N (13.5% as NO_3^- and 13.5% as NH_4^+), 5% Ca, 2.4% Mg and 0.2% B. The wood ash was granulated hardened bottom ash from the sawn timber producer Bergene Holm; the concentrations of various elements in the ash are given in Table 1. High values for Cr and Ti concentrations in the ash might indicate contamination of the wood used to produce the ash (Karltun et al. 2008), although high concentrations of heavy metals have been observed in wood ash without any obvious source (Reimann et al. 2008).

Within each treatment plot, five 1 m^2 vegetation sub-plots were randomly placed and permanently marked. Humus was sampled before treatment (early May 2013) and two years after treatment (May 2015) at four positions beside each vegetation sub-plot (two on each side, none topographically above or below the sub-plot). Mean depth of the humus layer was seven cm. Humus samples were dried and sieved (2 mm), after which they were analysed for pH potentiometrically in a water extract (25 ml water: 10 ml soil) using a glass membrane combination electrode, and for total C and N after grinding the sample, by combustion at 950°C using an Elementar Vario EL with TCD detection. Element concentrations (base cations, P, Al, Fe, trace elements including heavy metals) were determined by ICP-AES (AtomComp 1100, Thermo Jarrell-Ash, MA, USA) in a 1 M NH_4NO_3 extract (M1) according to Ogner et al. (1999). The same elements were also determined by ICP-AES in a mixture of 65 %(v/v) HNO_3/72 %(v/v) $HClO_4$ (5 : 1, v/v) at 220°C in a microwave oven (M2) according to Ogner et al. (1999). Method M1 is assumed to reflect plant-available element concentrations while M2 is closer to providing total element concentrations. Cation exchange capacity (CEC) and base saturation (BS) were calculated from the concentrations determined using M1, and exchangeable acidity (EA) in an M1 extract was determined by endpoint titration to pH 7.00. Cation exchange capacity is the number of exchangeable cations per dry weight that a soil is capable of holding, at a given pH value, and available for exchange with the soil solution. Base saturation is the fraction of exchangeable cations that are base cations (Ca, K, Mg and Na), while exchangeable acidity is the amount of acid cations, aluminium and hydrogen occupying the cation exchange complex; both are thus closely related to CEC.

Soil solution was sampled using two suction lysimeters (Prenart, Denmark) per plot at a depth of 40 cm below the soil surface at monthly intervals during the snow- and frost-free period (roughly, May to October/November). This depth was chosen to represent leaching at the bottom of the main rooting zone. Both sampling points were beside vegetation sub-plots. Samples were analysed for sulphate, nitrate and phosphate by ion chromatography, ammonium by a modified flow injection method, Ca, Mg, K, P and trace elements simultaneously by ICP-AES, and pH potentiometrically using a glass membrane combination electrode, all according to Ogner et al. (1999). The first samplings were done in 2012 before treatment, and the very first sampling was discarded to reduce the risk for the appearance in the data of artefacts due to lysimeter installation. Final sampling took place in the autumn of 2014. Sampling did not take place in 2015 due to lack of funding.

Parts of the forest around the study area were felled in the winter of 2014-2015. We believe that this is unlikely to have influenced the humus sampling that took place in May 2015.

Statistical analysis

For the humus samples, we used statistical analysis to compare treatment plots before and after treatment as well as between years. Comparison prior to treatment gave insight into the naturally occurring variation. Possible treatment effects were identified when comparing observed pre- and post-treatment differences between treatments as well as when comparing changes from pre- to post-treatment (spatial versus temporal differences). Working with the resulting empirical distribution functions and differences between them, which cannot be assumed to be normally distributed, we performed non-parametric tests (Kruskal-Wallis) to determine the statistical significance of the differences and changes. The following data were analysed:

(1) Pre-treatment (2013) differences between the (to-be) treatment plots
(2) Pre- to post-treatment (i.e. between-year) changes within treatments
(3) Post-treatment (2015) differences between treatment plots

Because p values from pairwise comparisons involving multiple comparisons are biased we adjusted the p values according to the Šídák procedure (Salkind 2007). Using the conventional $p \leq 0.05$ for individual comparisons, a test result was considered significant only when $p \leq 0.0127$ for four combinations of data subsets (between-year comparisons within treatments), and $p \leq 0.0085$ for six combinations of data subsets (within-year comparisons between treatments).

Results

Humus chemistry

There were two significant pre-treatment differences found in 2013 after concentrations below the detection limit were excluded: Ni after M1 was significantly lower for the Ash treatment compared to Ash+N, and P after M1 was significantly higher for Ctrl compared to the Ash+N treatment. Hypothesis (i) was thus largely supported.

Soil C concentrations and C/N ratios were not significantly affected by treatment, while the only significant difference in soil N concentrations was for the N treatment compared to the Ash treatment in 2015, where concentrations were higher with the N treatment (Tables 2, 3).

Among the parameters related to soil acidity status (pH, EA, CEC and BS), there were clearly significant between-year changes and between-treatment differences after the Ash and Ash+N treatments. Both Ash and Ash+N treatments led to significant increases in pH, CEC and BS, and significant decreases in EA (Tables 2, 3). There was also a significant increase in EA and reduction in BS in the Ctrl plots from 2013 to 2015 (Tables 2, 3).

The Ash and Ash+N treatments led to many significant between-year changes and between-treatment differences in elements determined by ICP-AES after M1 and M2, while only a few significant changes could be related to the N treatment (Tables 4 and 5). After M2, all significant changes in these elements as a result of the Ash and Ash+N treatments were increases, while after M1 there were both increases and decreases (Table 4). In particular Fe, Ni and Zn decreased after both Ash and Ash+N treatments when determined after M1 (Table 4). For these elements, mean concentrations and standard deviations are given in Supplementary Table S1 and p values in Supplementary Table S2.

There were no significant differences between the Ash and Ash+N treatment plots in 2015 (not shown).

Hypotheses (iia, iib and iic) were rejected.

Soil solution chemistry

There were rapid and obvious, but temporary, effects of the N treatment on soil solution chemistry at 40 cm depth, including increased mean concentrations of NO_3^- and NH_4^+ (not shown as it is to be expected that NH_4NO_3 fertilisation would temporarily raise soil solution NH_4^+ and NO_3^- concentrations), Mg (Fig. 1a) and Ca (Fig. 1b). There was no apparent effect on mean K concentration (Fig. 1c), while mean pH was reduced (Fig. 1d). The pH was reduced more after the N treatment than after the Ash+N treatment (Fig. 1d). Effects of the Ash treatment on soil solution chemistry at 40 cm depth were unclear, although there was a suggestion of slightly higher mean pH in the final sampling in 2014 (Fig. 1d). Hypothesis (iii) was thus supported for the Ash treatment but rejected for the N treatment.

Mean concentrations of P and the trace elements As, Be, Cd, Cr, Cu, Mo, Pb and Se in soil solution at 40 cm depth were mostly or always under the detection limit, so it was not possible to evaluate differences due to treatment even if these existed. The N and/or Ash+N treatments appear to have led to temporarily increased mean concentrations of Co (Fig. 1e), Ni (Fig. 1f) and Zn (Fig. 1g). Two very high concentrations of Ni in Ctrl plots before treatment may be an effect of lysimeter installation or due to contamination of the soil solution samples.

Discussion

Humus chemistry

Soil shows a high degree of spatial variation due among other things to small-scale variation in geology, temperature, moisture and light availability, and the high standard deviations shown in Tables 2 and S1 reflect this, making it harder to find significant changes and differences. Nevertheless, we observed a number of strongly significant changes from 2013 to 2015 and strongly significant differences between treatments in 2015. The statistically significant pre-treatment differences between plots for 2013 were (as expected) few, and it cannot be ruled out that they were due to chance alone.

There were a few significant changes from 2013 to 2015 in Ctrl, with some evidence of increasing acidity, although pH was not significantly changed. The pH was low in all plots before treatment and in the control plots after treatment. Once the effect of the ash in raising the pH decreases with time and pH in the ash treatment plots thus becomes lower again, immobilised heavy metals might pass into solution again. However, our soil solution results suggest that concentrations will most likely remain low. In this context, it is important to point out that long-term results on the dissolution and bioavailability of heavy metals are lacking (Huotari et al. 2015).

Effects of the ash treatment on humus chemistry were clear and could be seen both in between-year changes for the Ash and Ash+N plots and in between-treatment differences between the Ash and Ash+N plots on the one hand and the Ctrl and N plots on the other. These effects were as expected for pH and base cation concentrations and generally consistent with other findings (Rumpf et al. 2001; Arvidsson & Lundkvist 2003; Saarsalmi et al. 2004; Saarsalmi et al. 2006; Saarsalmi & Levula 2007; Saarsalmi et al. 2010; Wang et al. 2010; Saarsalmi et al. 2012; Ingerslev et al. 2014; Saarsalmi et al. 2014; Brais et al. 2015), with significantly increased pH and concentrations of Ca and Mg with M1, and of Ca, K, Mg and P with M2 for the Ash treatment between 2013 and 2015. However, Norström et al. (2012) found no large differences in Ca, Mg or K in the humus layer between the ash treatment and the control.

There were no statistically significant differences between treatments for soil carbon concentrations. Although at first sight this might be expected as the humus layer consists mostly of organic matter, there was in fact a measurable amount of mineral material in the humus layer at our site so that significant differences in organic matter concentration might have been possible. Only one significant difference between treatments was found for N (which in the humus layer is likely to be largely organic); this was for the N treatment compared with the Ash treatment. The Ash treatment in itself appears not to have affected N concentrations in humus in the first two years after treatment. A number of other studies have found similar results to ours for the effect of ash treatment on C and N concentrations in the organic layer, i.e. no or very few significant differences compared with the control (Arvidsson & Lundkvist 2003; Saarsalmi et al. 2006; Saarsalmi and Levula 2007; Saarsalmi et al. 2010; Ingerslev et al. 2014; Saarsalmi et al. 2014). Exceptions include Saarsalmi et al. (2004), who found that in one experiment wood ash decreased the organic matter content in the humus layer and increased it in the uppermost mineral soil five years after application, while there was no change in the other experiments. Saarsalmi et al. (2012) found increased N concentrations in humus after combined ash and nitrogen treatment. Brais et al. (2015) observed a decrease in organic C in the humus layer two years after ash treatment, while five years after treatment both organic C and Kjeldahl N were higher in the 2 t ha^{-1} treatment compared to both the control and the 8 t ha^{-1} treatment.

The N treatment only led to significantly higher soil N when compared with the Ash treatment. As the N fertiliser was in the form of NH_4^+ and NO_3^- it is likely to have been mostly either taken up by trees and other vegetation or leached from the soil (as was observed). An effect of the N treatment in humus might be observed in several years’ time, as litter from fertilised trees decomposes.

Significance and even direction of changes in concentrations of a number of elements varied with the method used (Tables 4 and 5). In our study, reduced concentrations of Al, Co, Fe, Ni, Pb and Zn determined using M1 (but not M2) were found in the Ash or Ash+N plots in 2015 compared with 2013. This result may be due to these metals becoming more strongly bound in the soil as a result of the pH increase following the ash treatment (from 4.09 to 4.63 for Ash and from 4.09 to 4.77 for Ash+N, Table 2), so that they were no longer extracted by the weak extractant used in M1. Differences in results obtained depending on the analytical method used suggest strongly that the choice of methods should be taken into account when evaluating the ecological relevance of differences in element concentrations, or when comparing the results from different experiments. Methods determining “exchangeable” concentrations of elements are often assumed to give an estimate of what is available for organisms, especially plants. This may be a rough assumption, as confirmatory studies have not generally been made. Also we do not yet know the long-term effects of ash treatment, as pointed out by Huotari et al. (2015), and in any case availability to organisms will vary depending on the organism in question.

Among extractants used to determine “available” plant nutrients in wood ash fertilisation experiments have been NH_4Cl with or without $BaCl_2$ (Brais et al. 2015), 1 M NH_4Cl (Rumpf et al. 2001; Arvidsson & Lundkvist 2003; Wang et al. 2010), 1 M NH_4NO_3 (Ingerslev et al. 2014), 1 M NH_4 acetate (Saarsalmi et al. 2004, 2006, 2010, 2012, 2014), 0.2 M CsCl (Rumpf et al. 2001) and 0.1 M $BaCl_2$ (Saarsalmi & Levula 2007; Norström et al. 2012). It is likely that different extractants will lead to different results. However, it appears that 1 M NH_4 salts have been most often used, and at least these results might be compared with ours with M1. Some of these studies have dealt mainly with carbon, major nutrients, acidity and total trace elements, while exchangeable/extractable trace elements were not considered (Rumpf et al. 2001; Saarsalmi et al. 2006; Saarsalmi & Levula 2007; Saarsalmi et al. 2010; Saarsalmi et al. 2012; Saarsalmi et al. 2014). Decreases in the humus layer after ash treatment have been found for exchangeable Al (Saarsalmi et al. 2004; Brais et al. 2015), probably due to ion exchange; this is comparable to our results for the Ash treatment but not the Ash+N treatment (Tables 4, S1). However no difference was found between ash and control treatments for exchangeable Al in humus by Wang et al. (2010) or Norström et al. (2012), which is comparable with our Ash+N treatment (Table S2). No difference was found for exchangeable Ba in humus by Brais et al. (2015), a result which differs from the large increase found by us (Tables 4, S1). Arvidsson and Lundkvist (2003) obtained mixed results, with exchangeable Cd concentrations in the mineral soil sometimes higher and sometimes lower after ash treatment compared with the control, with higher concentrations possibly due to increased leaching from the humus layer rather than the ash. We found no significant change in Cd after M1 for either Ash or Ash+N treatments (Table S2), so it appears that changes in Cd concentrations are very variable. Norström et al. (2012) found an increase in exchangeable Fe in the E horizon of a podzol after ash treatment, while we found a decrease in Fe after M1 for the humus layer (Tables 4, S1). Brais et al. (2015) found an increase in exchangeable Mn in humus, similar to our results for M1 (Tables 4, S1). Ingerslev et al. (2014) found a decrease in ammonium nitrate extractable Pb (similar to our results after M1 for the Ash treatment but not the Ash+N treatment, Tables 4 and S1) but an increase in extractable Cd in the humus layer after ash treatment (while we found no significant change, Table S2); effects in the mineral soil were minor.

Soil solution chemistry

Effects of the N and/or Ash+N treatment on soil solution chemistry included increased concentrations not only of NO_3^- and NH_4^+ (as expected), but also of Mg, Ca, Co, Ni and Zn. These metals are relatively labile in soil solution and can be transported in ionic form

(Brümmer, 1986; McLaren et al., 1986; Likens et al., 1998). This result could have been due to leaching of metal ions from cation exchange sites in the soil followed by leaching downward through the soil profile and/or leaching of Mg and Ca present in the nitrogen fertiliser. The results support the role of NO_3^- as a factor triggering base cation leaching from soil exchangeable sites. However, the effect was pronounced for only a short period after fertilization (Fig. 1a, b, c, e, f, g). In research on the effect of land use on Ca biogeochemistry in a forested catchment, Likens et al. (1998) found that the Ca^{2+} concentration in both soil solution and stream water was positively correlated with NO_3^- leached as a result of facilitated nitrification on deforested area. The reduced pH after the N and Ash+N treatments (Fig. 1d) was likely due to the acidifying effect of nitrogen fertiliser, and the smaller reduction in pH after the Ash+N treatment compared to the N treatment might reflect the tendency of the ash to raise the pH.

Although there were clear effects of the N treatment on soil solution chemistry at 40 cm depth, effects of the Ash treatment on soil solution chemistry were unclear at best and much less pronounced than effects on humus chemistry. This was not unexpected, as effects of wood ash treatment are largest in the uppermost part of the soil (Karltun et al. 2008) and are likely to come later and less clearly at 40 cm depth. The pH elevation as a result of ash addition will reduce leaching of metal ions from soil cation exchange sites. Also, large variation between lysimeters, which is a normal result of soil heterogeneity including differences in soil moisture content, may have hidden differences between treatments.

Leaching of Zn and Ni increased after the N treatment but not the Ash+N treatment (Fig. 1f, g), suggesting that pH decrease is more important for leaching of these elements than their external supply with ash.

Conclusions

In our forest fertilisation trial we found few significant changes following the N treatment but significant increases in many element concentrations and pH after ash treatment. Element concentrations in humus determined after nitric acid/perchloric acid digestion and after ammonium nitrate extraction showed differences when examining the effects of wood ash fertilisation. As far as we know no previous comparison of soil extraction methods has been made in ash treatment studies. Differences in results depending on analytical method suggest strongly that the choice of method should be taken into account when evaluating ecological relevance of differences in element concentrations. Ash treatment led to no clear effects on soil solution chemistry at 40 cm depth, while short-term increases in concentrations of NO_3^-, NH_4^+, Ca, Mg, K, Co, Ni and Zn and a reduction in pH were found after N and/or Ash+N treatment.

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Table 1. Element concentrations and pH in the ash used in the field experiment. Data from Dibdiakova and Horn (2014) and email from J Dibdiakova; unreferenced. All concentrations are on a dry weight basis.

Element	Concentration	Element	Concentration	Element	Concentration	Element	Concentration
C (%)	0.3	Cd (mg/kg)	3.0	Mg (g/kg)	37.3	Sc (mg/kg)	3.9
N (%)	<0.1	Cl (mg/kg)	0.1	Mn (g/kg)	33.1	Se (mg/kg)	12.0
pH	11.6	Co (mg/kg)	18.6	Mo (mg/kg)	6.5	Si (g/kg)	40.7
Al (g/kg)	8.9	Cr (mg/kg)	127.9	Na (g/kg)	0.2	Sr (g/kg)	2.1
As (mg/kg)	0.6	Cu (mg/kg)	20.7	Ni (mg/kg)	50.3	Ti (mg/kg)	367.5
Ba (g/kg)	10.5	Fe (g/kg)	4.6	P (g/kg)	24.2	V (mg/kg)	10.1
Be (mg/kg)	4.6	K (g/kg)	8.2	Pb (mg/kg)	11.9	Y (mg/kg)	3.9
Ca (g/kg)	437.2	Li (mg/kg)	19.9	S (g/kg)	0.9	Zn (g/kg)	0.1

Table 2. Mean concentrations in humus with standard deviations (in parentheses) in 2013 (before treatment) and 2015. EA = exchangeable acidity, CEC = cation exchange capacity, BS = base saturation, all determined in a 1 M NH_4NO_3 extract. All concentrations are on a dry weight basis.

	Ctrl		N		Ash		Ash+N	
Parameter	2013	2015	2013	2015	2013	2015	2013	2015
C (%)	42.1 (6.6)	42.7 (7.9)	39.2 (9.2)	44.0 (3.0)	38.5 (10.5)	39.5 (5.7)	41.2 (7.5)	43.2 (6.4)
N (%)	1.57 (0.25)	1.58 (0.37)	1.50 (0.35)	1.62 (0.13)	1.44 (0.32)	1.42 (0.23)	1.59 (0.26)	1.62 (0.28)
C/N (g/g)	26.9 (2.6)	27.0 (2.8)	26.1 (3.2)	27.1 (2.3)	26.8 (2.5)	27.8 (2.0)	26.0 (2.6)	26.7 (3.1)
pH	4.07	3.92	3.99	3.94	4.09	4.63	4.09	4.77
EA (mmol/kg)	112 (31)	143 (33)	107 (33)	140 (34)	100 (43)	45 (41)	123 (50)	43 (31)
CEC (mmol(+)/kg	337 (57)	340 (61)	312 (69)	351 (41)	309 (87)	520 (136)	329 (61)	537 (140)
BS (%)	63.5 (6.1)	55.3 (5.4)	62.7 (7.9)	57.7 (9.9)	64.8 (6.2)	86.5 (10.2)	59.3 (10.6)	87.5 (6.6)

Table 3. Results of Kruskal-Wallis tests (p values) of between-year and between-treatment differences in mean concentrations in humus for 2015. Only parameters included in Table 2 and for which one or more p values were significant are included. EA = exchangeable acidity, CEC = cation exchange capacity, BS = base saturation, all determined in a 1 M NH_4NO_3 extract. Significant results after Šídák corrections in bold face (critical value $p < 0.0127$ for between-year differences and $p < 0.0085$ for between-treatment differences in 2015).

	Ctrl	N	Ash	Ash+N	Ctrl vs. N	Ctrl vs. Ash	Ctrl vs. Ash+N	N vs. Ash	N vs. Ash+N
Parameter	2013-2015	2013-2015	2013-2015	2013-2015	2015	2015	2015	2015	2015
N	0.868	0.407	0.819	0.820	0.950	0.158	0.663	**0.008**	0.885
pH	0.028	0.395	**0.000**	**0.000**	0.967	**0.000**	**0.000**	**0.000**	**0.000**
EA	**0.012**	0.017	**0.001**	**0.000**	0.534	**0.000**	**0.000**	**0.000**	**0.000**
CEC	0.788	0.206	**0.000**	**0.000**	0.917	**0.000**	**0.000**	**0.000**	**0.000**
BS	**0.001**	0.040	**0.000**	**0.000**	0.056	**0.000**	**0.000**	**0.000**	**0.000**

Table 4. Significant between-year changes in element concentrations in humus 2013-2015 determined in a 1 M NH_4NO_3 extract (M1) or after $HNO_3/HClO_4$ digestion (M2).

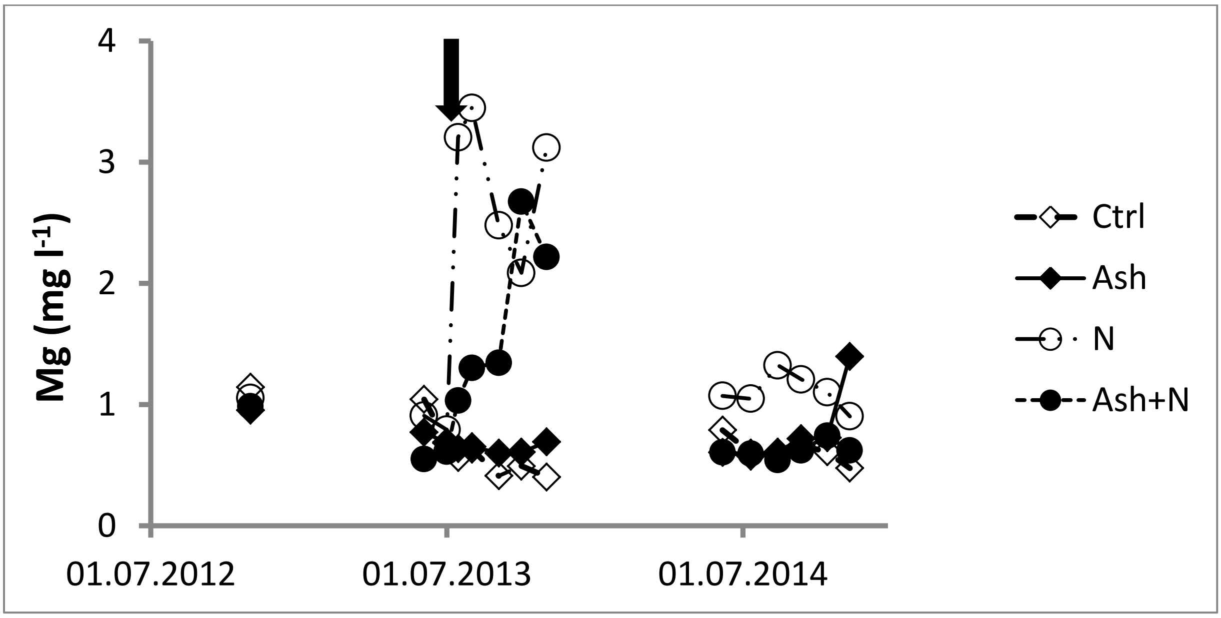
	M1				M2			
	Ctrl	N	Ash	Ash+N	Ctrl	N	Ash	Ash+N
Increase	-	Mg	Ba, Ca, Mg, Mn, Si, Sr	Ba, Ca, Mg, Mn, Si, Sr	-	Mg, S	B, Ba, Ca, Cr, Cu, Mg, Mn, P, Se, Sr	B, Ba, Ca, Cr, Cu, K, Mg, Mn, P, Se, Sr
Decrease	P	-	Al, Co, Fe, Ni, Pb, Zn	Fe, Ni, Zn	B	-	-	-

Table 5. Significant between-treatment differences in element concentrations in humus 2015 determined in a 1 M NH_4NO_3 extract (M1) or after $HNO_3/HClO_4$ digestion (M2).

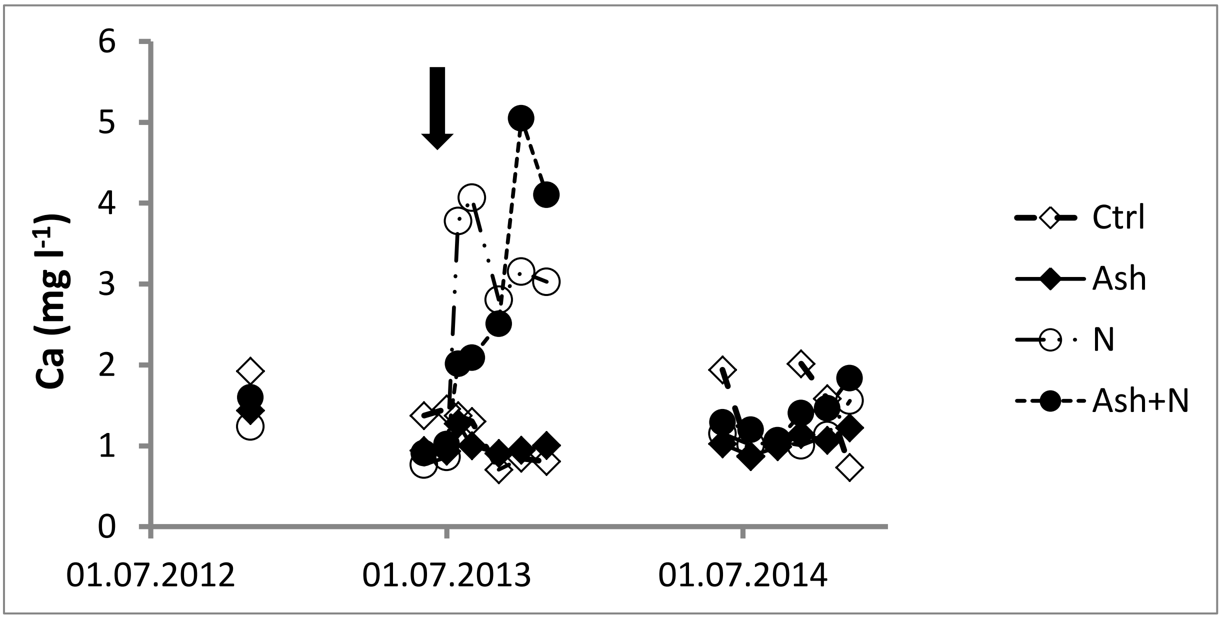
	Ctrl vs. N		Ctrl vs. Ash		Ctrl vs. Ash+N		N vs. Ash		N vs. Ash+N	
	Crtl>N	Ctrl<N	Ctrl>Ash	Ctrl<Ash	Ctrl>Ash+N	Ctrl<Ash+N	N>Ash	N<Ash	N>Ash+N	N<Ash+N
M1	-	Mg	Al, Fe, Ni, Pb, Zn	Ba, Ca, Mg, Mn, Si, Sr	Pb, Zn	Ba, Ca, Mg, Mn, Si, Sr	Al, Cd, Fe, Ni, Pb, Zn	Ba, Ca, Mg, Mn, P, Si, Sr	Cd, Pb, Zn	Ba, Ca, K, Mg, Mn, Si, Sr
M2	-	B, Mg	-	B, Ba, Ca, Cr, Cu, K, Mg, Mn, P, Se, Sr	-	B, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, P, Se, Sr	-	B, Ba, Ca, Cr, Cu, K, Mg, Mn, P, Se, Sr	-	B, Ba, Ca, Cr, Cu, K, Mg, Mn, P, Se, Sr

Figure legends

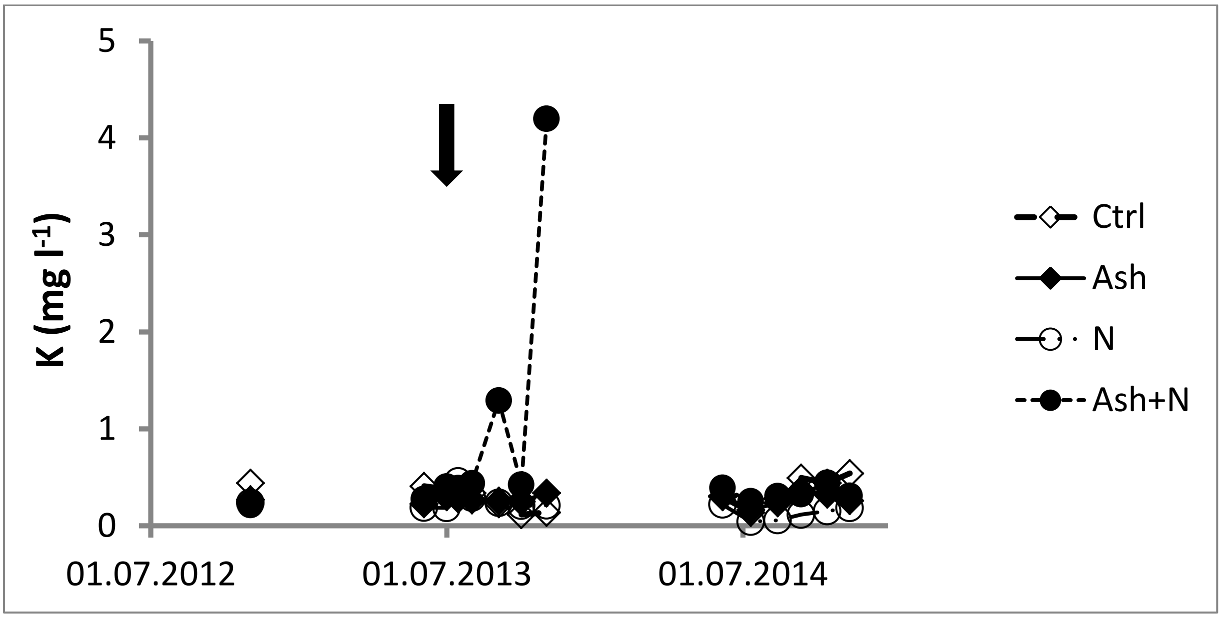
Figure 1. Variation with time of mean (a) Mg concentration, (b) Ca concentration, (c) K concentration, (d) pH, (e) Co concentration, (f) Ni concentration and (g) Zn concentration in soil solution at 40 cm depth. Ctrl = control, Ash = 3 t wood ash ha^{-1}, N = 150 kg N fertiliser ha^{-1}, Ash+N = 3 t wood ash ha^{-1} + 150 kg N fertiliser ha^{-1}. A downward-pointing arrow marks the time point for wood ash spreading.


Mg (mg l-1)
0
1
2
3
4
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

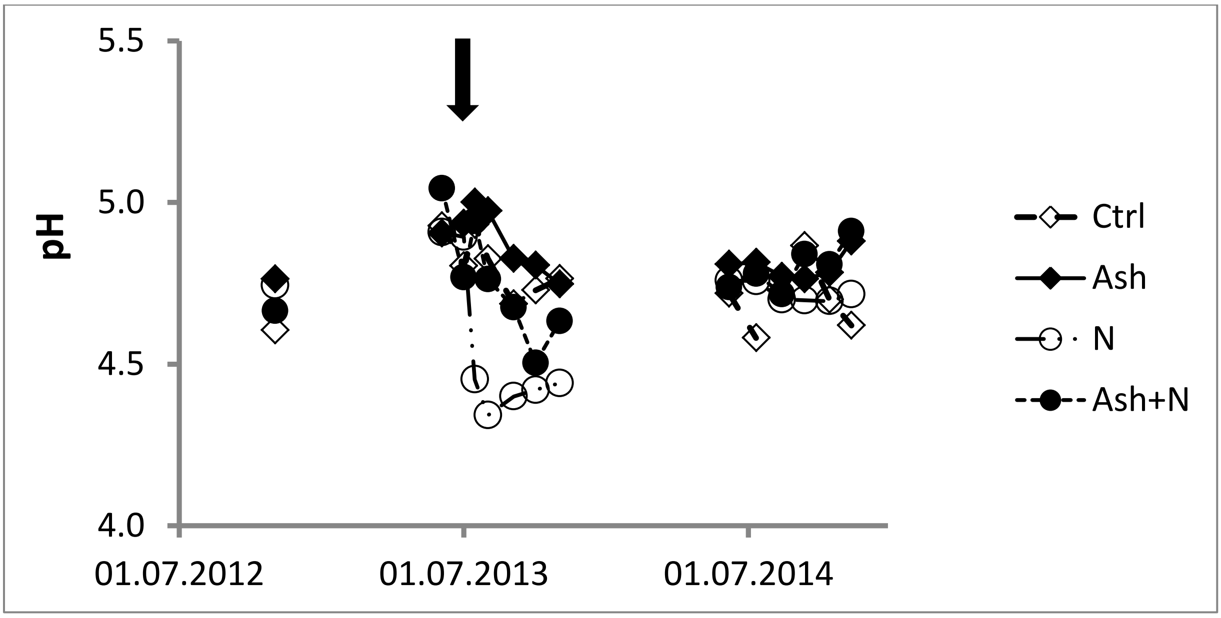
(a)


Ca (mg l-1)
0
1
2
3
4
5
6
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

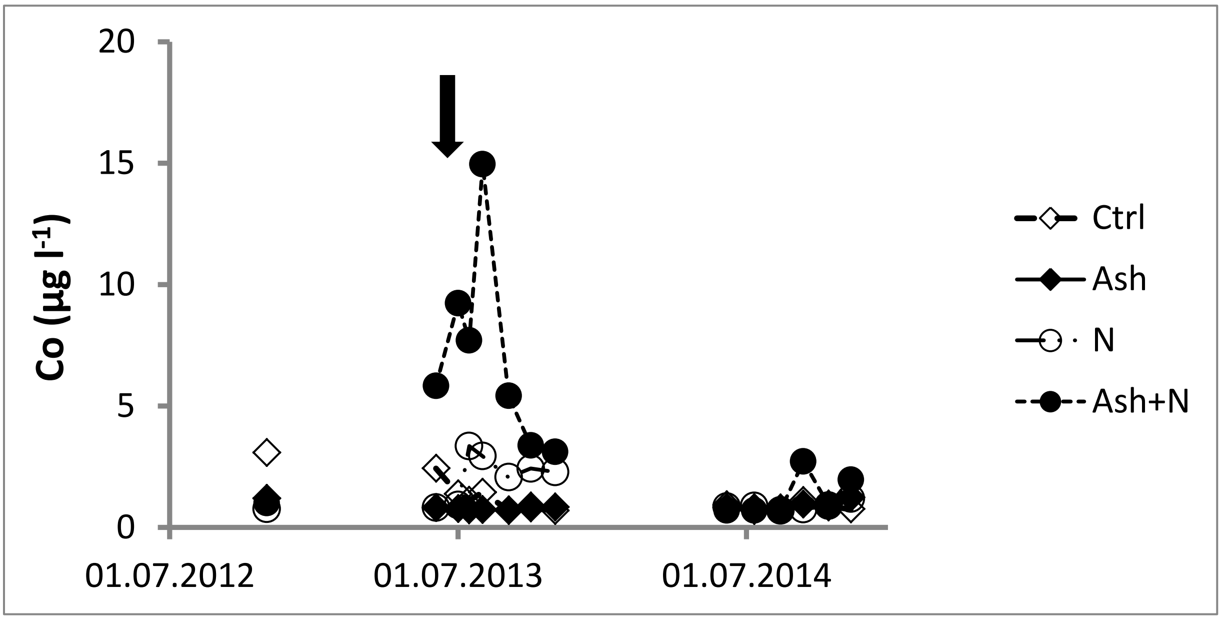
(b)


5
4
3
2
1
0
K (mg l^{-1})
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

(c)

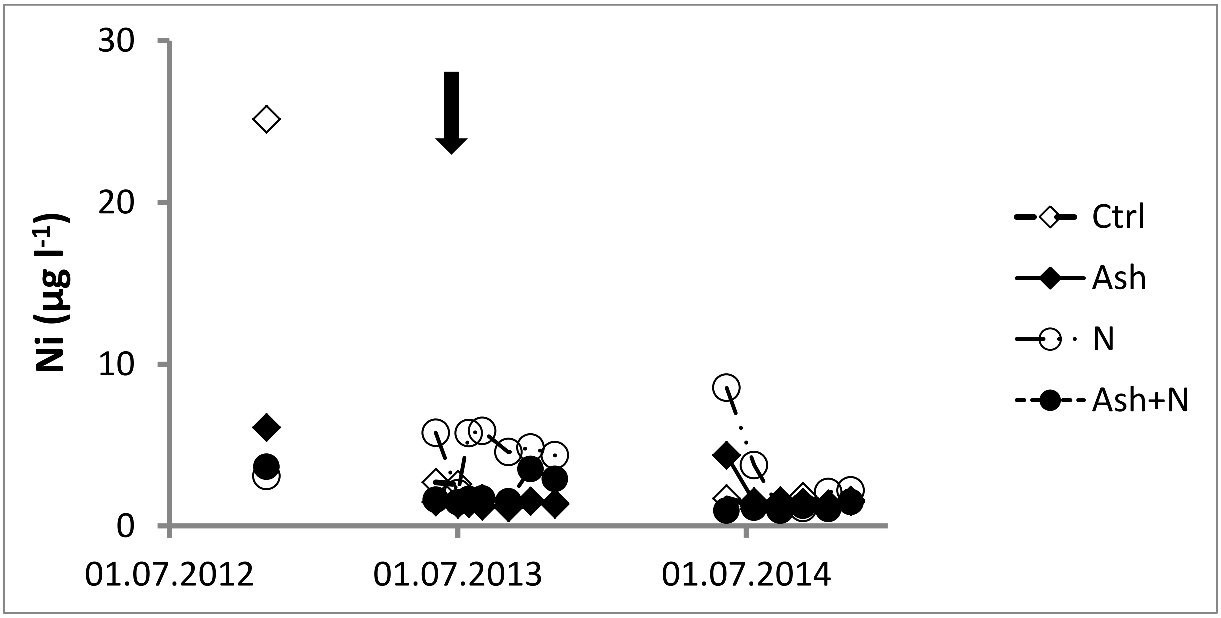

5.5
5.0
4.5
4.0
pH
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

(d)



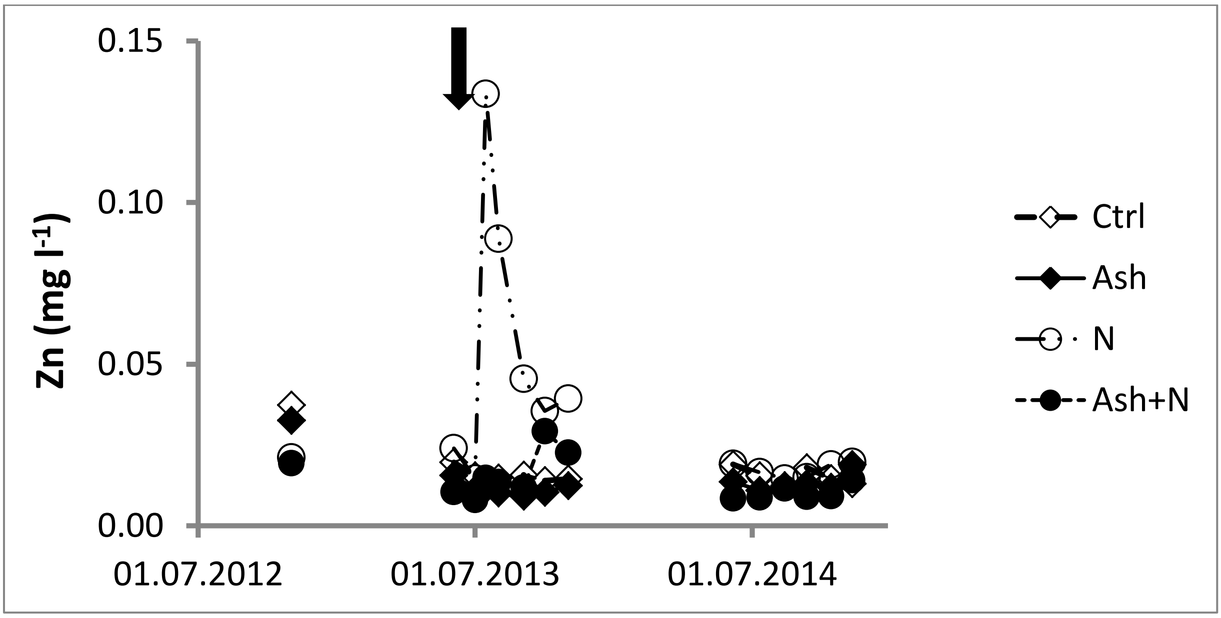
20
15
10
5
0
Co (µg l-1)
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

(e)



30
20
10
0
Ni (µg l-1)
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

(f)


0.15
0.10
0.05
0.00
Zn (mg l-1)
01.07.2012
01.07.2013
01.07.2014
Ctrl
Ash
N
Ash+N

(g)

Table S1. Mean concentrations in humus with standard deviations (in parentheses) in 2013 (before treatment) and 2015. Only chemical parameters for which all the data were above the detection limit are included. All concentrations are on a dry weight basis. Determinations were made in a 1 M NH_4NO_3 extract (M1) and after $HNO_3/HClO_4$ digestion (M2).

		Ctrl		N		Ash		Ash+N	
Parameter	Method	2013	2015	2013	2015	2013	2015	2013	2015
Al (mg/kg)	M1	0.15 (0.09)	0.22 (0.20)	0.20 (0.20)	0.32 (0.42)	0.18 (0.15)	0.11 (0.16)	0.37 (0.31)	0.14 (0.15)
Al (mg/kg)	M2	2.78 (0.78)	3.22 (1.09)	3.36 (1.36)	3.97 (2.22)	3.83 (1.54)	4.45 (1.65)	3.86 (1.88)	4.31 (2.22)
As (µg/kg)	M2	1.76 (0.82)	1.88 (0.97)	1.98 (0.71)	2.27 (0.78)	1.98 (0.68)	1.92 (0.89)	2.00 (0.82)	1.95 (0.89)
B (µg/kg)	M2	5.34 (0.97)	4.16 (0.62)	4.47 (0.96)	5.13 (0.97)	5.16 (1.70)	8.48 (3.75)	4.93 (1.59)	9.73 (4.40)
Ba (µg/kg)	M1	73.0 (17.1)	69.9 (21.7)	73.3 (29.4)	75.6 (25.0)	61.3 (19.2)	164.8 (59.2)	63.6 (13.8)	177.0 (38.5)
Ba (µg/kg)	M2	83.9 (17.9)	86.6 (21.0)	85.2 (34.5)	91.3 (26.5)	73.2 (18.9)	245.5 (111.5)	74.2 (11.9)	245.7 (89.0)
Ca (mg/kg)	M1	3.08 (0.70)	2.64 (0.64)	2.77 (0.83)	2.78 (0.85)	2.74 (0.88)	7.28 (2.80)	2.66 (0.91)	7.50 (2.80)
Ca (mg/kg)	M2	4.24 (0.80)	3.95 (0.67)	4.04 (0.95)	4.09 (0.91)	4.39 (0.91)	11.36 (5.22)	3.95 (1.42)	10.60 (5.00)
Cd (µg/kg)	M1	0.38 (0.16)	0.35 (0.12)	0.40 (0.13)	0.43 (0.13)	0.39 (0.19)	0.26 (0.20)	0.38 (0.16)	0.26 (0.14)
Cd (µg/kg)	M2	0.59 (0.16)	0.65 (0.17)	0.66 (0.20)	0.88 (0.33)	0.65 (0.20)	0.77 (0.22)	0.69 (0.19)	0.79 (0.22)
Co (µg/kg)	M1	0.42 (0.43)	0.47 (0.53)	0.45 (0.31)	0.50 (0.37)	0.45 (0.23)	0.28 (0.25)	1.26 (1.89)	0.62 (0.79)

Co (µg/kg)	M2	1.46 (0.53)	1.50 (0.70)	1.73 (0.80)	1.95 (1.16)	1.82 (0.66)	1.92 (0.54)	2.69 (2.76)	3.07 (2.84)
Cr (µg/kg)	M2	4.77 (0.98)	5.37 (1.05)	5.46 (2.07)	5.79 (1.45)	5.95 (2.12)	10.91 (3.31)	5.10 (1.16)	8.65 (2.41)
Cu (µg/kg)	M2	7.69 (1.72)	7.95 (1.86)	7.98 (1.76)	9.11 (1.78)	7.23 (1.93)	14.79 (7.79)	8.62 (2.11)	20.80 (19.96)
Fe (mg/kg)	M1	0.034 (0.019)	0.028 (0.012)	0.038 (0.029)	0.036 (0.037)	0.035 (0.019)	0.015 (0.014)	0.070 (0.078)	0.017 (0.013)
Fe (mg/kg)	M2	2.54 (0.86)	2.72 (0.90)	2.87 (1.71)	3.28 (1.72)	3.48 (1.85)	4.09 (2.42)	3.46 (1.88)	3.93 (2.16)
K (mg/kg)	M1	0.72 (0.12)	0.60 (0.13)	0.64 (0.15)	0.54 (0.08)	0.69 (0.20)	0.68 (0.17)	0.65 (0.17)	0.71 (0.16)
K (mg/kg)	M2	1.07 (0.15)	1.08 (0.21)	1.01 (0.23)	1.00 (0.13)	1.18 (0.28)	1.37 (0.26)	1.02 (0.12)	1.28 (0.27)
Mg (mg/kg)	M1	0.44 (0.10)	0.43 (0.10)	0.41 (0.10)	0.55 (0.10)	0.46 (0.11)	0.86 (0.23)	0.46 (0.10)	0.94 (0.20)
Mg (mg/kg)	M2	0.69 (0.11)	0.73 (0.11)	0.76 (0.36)	0.98 (0.43)	0.84 (0.20)	1.47 (0.45)	0.74 (0.15)	1.43 (0.30)
Mn (mg/kg)	M1	0.30 (0.14)	0.24 (0.14)	0.24 (0.10)	0.21 (0.10)	0.29 (0.17)	0.45 (0.20)	0.32 (0.29)	0.50 (0.24)
Mn (mg/kg)	M2	0.39 (0.20)	0.31 (0.18)	0.30 (0.11)	0.27 (0.13)	0.38 (0.21)	1.04 (0.68)	0.43 (0.43)	1.14 (0.89)
Mo (µg/kg)	M2	0.56 (0.15)	0.51 (0.17)	0.54 (0.17)	0.49 (0.17)	0.57 (0.17)	0.39 (0.19)	0.61 (0.20)	0.54 (0.22)
Na (mg/kg)	M1	0.16 (0.03)	0.14 (0.04)	0.18 (0.09)	0.14 (0.03)	0.16 (0.05)	0.16 (0.04)	0.17 (0.04)	0.15 (0.03)
Na (mg/kg)	M2	0.21 (0.03)	0.25 (0.04)	0.24 (0.07)	0.25 (0.04)	0.23 (0.05)	0.29 (0.06)	0.22 (0.03)	0.25 (0.05)
Ni (µg/kg)	M1	1.70 (0.51)	1.57 (0.61)	1.74 (0.69)	1.77 (0.63)	1.54 (0.47)	0.77 (0.59)	2.00 (0.67)	1.18 (0.92)
Ni (µg/kg)	M2	4.91 (1.15)	5.09 (1.36)	5.48 (1.73)	6.07 (1.66)	4.73 (1.11)	5.87 (1.27)	5.40 (1.20)	6.98 (2.08)

P (mg/kg)	M1	0.14 (0.03)	0.11 (0.03)	0.12 (0.04)	0.09 (0.03)	0.12 (0.03)	0.18 (0.09)	0.10 (0.04)	0.16 (0.10)
P (mg/kg)	M2	0.72 (0.13)	0.80 (0.18)	0.70 (0.17)	0.81 (0.13)	0.71 (0.15)	1.09 (0.20)	0.75 (0.17)	1.17 (0.22)
Pb (µg/kg)	M1	4.54 (2.19)	5.05 (2.17)	5.11 (2.74)	6.20 (2.97)	4.68 (2.43)	2.56 (2.07)	5.07 (3.06)	2.52 (1.33)
Pb (µg/kg)	M2	46.3 (15.4)	45.5 (15.4)	51.9 (18.4)	59.3 (21.5)	48.0 (18.4)	46.8 (18.5)	49.7 (17.8)	52.5 (16.5)
S (mg/kg)	M1	0.105 (0.018)	0.104 (0.021)	0.103 (0.024)	0.099 (0.010)	0.097 (0.027)	0.105 (0.025)	0.110 (0.027)	0.117 (0.028)
S (mg/kg)	M2	1.59 (0.30)	1.84 (0.45)	1.54 (0.37)	1.88 (0.19)	1.47 (0.37)	1.72 (0.34)	1.66 (0.32)	2.01 (0.50)
Sc (µg/kg)	M2	0.90 (0.32)	1.22 (0.58)	1.15 (0.59)	1.33 (0.61)	1.26 (0.64)	1.49 (0.57)	1.17 (0.66)	1.45 (0.82)
Se (µg/kg)	M2	0.79 (0.21)	0.89 (0.32)	0.79 (0.21)	0.91 (0.40)	0.83 (0.28)	1.35 (0.43)	0.83 (0.33)	1.55 (0.70)
Si (µg/kg)	M1	34.4 (6.6)	31.7 (8.6)	27.7 (6.2)	26.6 (5.6)	30.4 (7.2)	141.9 (142.8)	32.4 (7.1)	133.2 (129.3)
Sr (µg/kg)	M1	23.9 (7.4)	22.6 (7.5)	20.5 (7.3)	21.3 (6.8)	20.7 (7.2)	39.2 (11.3)	21.2 (4.5)	40.6 (7.6)
Sr (µg/kg)	M2	33.1 (6.1)	33.5 (5.6)	30.2 (10.7)	30.9 (7.8)	34.3 (7.8)	63.1 (19.5)	30.9 (4.2)	58.6 (15.6)
Ti (µg/kg)	M2	233 (101)	185 (57)	290 (147)	215 (80)	321 (157)	203 (77)	254 (111)	186 (54)
V (µg/kg)	M2	10.4 (3.0)	9.9 (2.9)	11.0 (5.1)	10.5 (2.8)	13.9 (6.2)	13.4 (6.1)	10.9 (3.3)	10.0 (2.8)
Y (µg/kg)	M2	2.6 (1.7)	3.8 (3.8)	3.1 (2.0)	3.7 (2.8)	3.0 (1.7)	3.3 (1.3)	4.7 (4.8)	5.9 (6.7)
Zn (µg/kg)	M1	52.4 (17.2)	47.6 (14.8)	52.4 (16.1)	51.6 (17.2)	44.4 (22.9)	23.4 (18.7)	43.6 (18.9)	24.4 (12.0)
Zn (µg/kg)	M2	66.7 (20.9)	63.1 (17.8)	66.2 (19.5)	68.5 (20.3)	57.1 (27.9)	54.3 (19.7)	56.5 (20.6)	58.6 (13.3)

Table S2. Results of Kruskal-Wallis tests (p values) of between-year and between-treatment differences in mean concentrations in humus for 2015. Only parameters included in Table S1 and for which one or more p values were significant are included. Determinations were made in a 1 M NH_4NO_3 extract (M1) and after $HNO_3/HClO_4$ digestion (M2). Significant results after Šídák corrections in bold face (critical value $p < 0.0127$ for between-year differences and $p < 0.0085$ for between-treatment differences in 2015).

		Ctrl	N	Ash	Ash+N	Ctrl vs. N	Ctrl vs. Ash	Ctrl vs. Ash+N	N vs. Ash	N vs. Ash+N
Parameter	Method	2013-2015	2013-2015	2013-2015	2013-2015	2015	2015	2015	2015	2015
Al	M1	0.199	0.272	**0.010**	0.017	0.633	**0.006**	0.065	**0.003**	0.027
B	M2	**0.003**	0.135	**0.005**	**0.000**	**0.005**	**0.000**	**0.000**	**0.005**	**0.000**
Ba	M1	0.724	0.724	**0.000**	**0.000**	0.724	**0.000**	**0.000**	**0.000**	**0.000**
Ba	M2	0.740	0.455	**0.000**	**0.000**	0.663	**0.000**	**0.000**	**0.000**	**0.000**
Ca	M1	0.085	0.852	**0.000**	**0.000**	0.633	**0.000**	**0.000**	**0.000**	**0.000**
Ca	M2	0.229	0.772	**0.000**	**0.000**	0.351	**0.000**	**0.000**	**0.000**	**0.000**
Cd	M1	0.803	0.575	0.068	0.089	0.152	0.059	0.085	**0.004**	**0.005**
Co	M1	0.917	0.724	**0.004**	0.059	0.520	0.115	0.468	0.034	0.520

Co	M2	0.677	0.868	0.520	0.372	0.349	0.026	**0.007**	0.319	0.206
Cr	M2	0.171	0.350	**0.000**	**0.000**	0.395	**0.000**	**0.000**	**0.000**	**0.001**
Cu	M2	0.663	0.106	**0.000**	**0.000**	0.085	**0.000**	**0.000**	**0.000**	**0.000**
Fe	M1	0.548	0.272	**0.001**	**0.001**	0.548	**0.002**	0.028	**0.003**	0.042
K	M1	0.044	0.044	0.984	0.604	0.206	0.165	0.065	0.036	**0.004**
K	M2	0.724	0.708	0.054	**0.005**	0.205	**0.004**	0.071	**0.000**	**0.003**
Mg	M1	0.788	**0.001**	**0.000**	**0.000**	**0.002**	**0.000**	**0.000**	**0.000**	**0.000**
Mg	M2	0.419	**0.008**	**0.000**	**0.000**	**0.007**	**0.000**	**0.000**	**0.001**	**0.000**
Mn	M1	0.141	0.351	**0.005**	**0.010**	0.663	**0.003**	**0.001**	**0.001**	**0.000**
Mn	M2	0.254	0.494	**0.001**	**0.002**	0.709	**0.000**	**0.000**	**0.000**	**0.000**
Ni	M1	0.221	0.756	**0.000**	**0.005**	0.272	**0.001**	0.040	**0.000**	0.010
Ni	M2	0.852	0.237	0.021	0.014	0.054	0.046	**0.002**	0.868	0.171
P	M1	**0.004**	0.062	0.078	0.044	0.245	0.021	0.120	**0.006**	0.040
P	M2	0.106	0.071	**0.000**	**0.000**	0.868	**0.000**	**0.000**	**0.000**	**0.000**
Pb	M1	0.468	0.290	**0.011**	0.036	0.229	**0.002**	**0.003**	**0.001**	**0.001**
S	M2	0.120	**0.010**	0.093	0.017	0.788	0.548	0.254	0.141	0.178

Se	M2	0.557	0.767	**0.001**	**0.004**	0.752	**0.004**	**0.007**	**0.009**	**0.006**
Si	M1	0.263	0.604	**0.000**	**0.000**	0.056	**0.000**	**0.000**	**0.000**	**0.000**
Sr	M1	0.576	0.648	**0.000**	**0.000**	0.633	**0.000**	**0.000**	**0.000**	**0.000**
Sr	M2	0.852	0.663	**0.000**	**0.000**	0.300	**0.000**	**0.000**	**0.000**	**0.000**
Zn	M1	0.431	0.984	**0.008**	**0.004**	0.300	**0.000**	**0.000**	**0.001**	**0.000**