# Wood ash effects on nutrient dynamics and soil properties under Mediterranean climate

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# Wood ash effects on nutrient dynamics and soil properties under Mediterranean climate

**María X. Gómez-Rey · Manuel Madeira · João Coutinho**

**Abstract**
• *Aims* This study aims to evaluate the effects of wood ash application on nutrient dynamics and soil properties of an acidic forest soil (Arenosol).
• *Methods* Treatments were loose and pelleted ash application (11 Mg ha$^{-1}$), alone or together with N fertiliser, and control treatment in a lysimeter experiment. Nutrient leaching was followed during a 2-year period and soil chemical and biological properties were evaluated at the end of the experiment.
• *Results* Wood ash increased leaching of total N, $NH_4^+$-N, base cations and P, mainly during the first months, the effect being more pronounced for the loose formulation. At the end of the study period, a positive effect on soil nutrient availability and soil acidity reduction was seen. The application of loose and pelleted ash alone decreased N leaching and increased N microbial biomass at the end of the experiment. The C dynamics was weakly affected.
• *Conclusion* Wood ash can be used to improve nutrient availability and balance nutrient exported by tree harvesting

**Contribution of the co-authors** María X. Gómez-Rey: designing and running the experiment, analysing samples and data and writing the manuscript
Manuel Madeira: designing the experiment and supervising
João Coutinho: analysing samples

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in acid forest soils, the effects at short-term being stronger for loose than for pelleted ash. However, their application should be carried out when vegetation is established to minimise nutrient losses at short-term and reduce the potential risk for water bodies. In N-limited soils, wood ash should be applied with N fertilisers to counteract N immobilisation.

## 1 Introduction

The amount of forest biomass available in Portugal for energy production is estimated to be $2.2 \times 10^6$ Mg year$^{-1}$, including residues from wood industry and paper pulp plants (MADRP 2005). Large amounts of wood ash are expected to be generated in the near future as a result of 15 new biomass power stations, and alternatives to its deposition in landfills are necessary. Wood ash application in acidic soils, mainly in forest systems, has received growing interest given their alkaline properties and capacity to balance nutrient removal by tree harvesting (Eriksson 1998). Ash application may, therefore, improve the nutrient status of most Portuguese forest soils which are acidic and poor in base cations.

Wood ash is characterised by high alkalinity and high Ca, Mg, K and, to a lesser extent, P contents; in contrast, it is generally poor in N (Khanna et al. 1994). Wood ash application to forest soils can lead to an increment in soil pH and base cations saturation (Bramryd and Fransman 1995; Eriksson 1998; Khanna et al. 1994; Ludwig et al. 2002). However, application of unstabilised highly soluble ash can cause a dramatic increase in soil pH and salt concentration (Clapham and Zibilske 1992), which may disturb ground vegetation

(Ferm et al. 1992). Moreover, its application in some soils may increase the solubility of organic C and the $CO_2$ release (Fritze et al. 1994; Weber et al. 1985; Zimmermann and Frey 2002) and may stimulate nitrification and N leaching (Weber et al. 1985). Therefore, to avoid undesirable effects on vegetation and nutrient leaching, stabilisation of wood ash before its application has been encouraged (Steenari et al. 1998). However, the effects of ash application to forest soils may also depend on the respective formulation: loose, crushed hardened, granulated or pelleted ash (Ring et al. 2006; Arvidsson and Lundkvist 2003).

The effects of wood ash on forest ecosystems have mainly been studied in soils of Northern Europe and Northern America (e.g. Ludwig et al. 2002; Park et al. 2005) where environmental conditions favour organic matter accumulation. However, the consequences of ash application in Southern Europe regions, with higher temperature conditions and soils with lower organic C content, have been scarcely studied (Cabral et al. 2008; Perucci et al. 2008; Solla-Gullón et al. 2006) and the effects on C and N dynamics have not been evaluated. Also, the effects of unstabilised and stabilised ashes under Mediterranean conditions have not been compared yet.

Therefore, a study was developed hypothesising that wood ash application in N-limited soils under Mediterranean conditions might lead to changes on soil N and C dynamics. In addition, we hypothesised that the short-term effects on soil properties will be stronger for unstabilised than for stabilised ashes. Thus, our aims were (1) to evaluate the effect of wood ash application on a Mediterranean forest soil before its use on a larger scale and (2) to compare the effects of unstabilised (loose) and stabilised (pelleted) ashes. To evaluate the capability of wood ash to modify the nutrient status of an acidic soil without plant interference and soil spatial variability, a lysimeter experiment was carried out: loose or pelleted wood ash, alone or together with N, was applied to an acidic forest soil and nutrient leaching and soil characteristics were examined over a 2-year period.

## 2 Material and methods

### 2.1 Lysimeter station and materials

The study was carried out in a lysimeter station located at the Instituto Superior de Agronomia, Lisbon. The area has a Mediterranean climate, tempered by an oceanic influence. The 30-year mean (1971–2000) rainfall monitored in the adjacent meteorological station of Lisboa/Ajuda was 675 mm, with a drought period usually extending from late May to September; the mean annual temperature was 16.4°C, ranging from a monthly mean of 11.8°C in January to 21.0°C in August (INMG 2007). During the study period (November

2005–November 2007), rainfall was 209, 857 and 411 mm, respectively, in 2005, 2006 and 2007. The rainiest months were October (182 mm) and November (238 mm) 2006.

The lysimeter station consisted of 20 lysimeters constructed in PVC (29.5 cm inner diameter, 50 cm long, 0.068 $m^2$ soil area). Each lysimeter had, at its bottom, a drainage system 10 cm thick constituted, from the bottom to the top, by a double plastic mesh (2 mm), a gravel layer washed with deionised water, a double layer of filtering material (Terram) and a washed sand layer. At the top of these layers were placed 35 kg (corresponding to 32.8 kg, 105°C dry weight) of sieved (<5 mm) homogenised mineral soil of the A horizon (about 30 cm depth), packed at a bulk density of about 1.4 g $cm^{-3}$. Over this material was placed 0.5 kg (corresponding to 240.0 g, 45°C dry weight) of forest floor litter, which corresponded to the amount of that measured in old Portuguese pine plantations (Madeira et al. 2009). At the lysimeters base, a hole was made and a plastic tube was connected to a sampling bottle (5 L) where leachates were continuously collected. Sampling bottles were kept in the dark to avoid biological growth in the sample.

The mineral soil and the forest floor litter (L and F layers) used in the experiment were collected in a permanent monitoring plot for inventory purposes from a 67-year-old maritime pine (*Pinus pinaster*) plantation, in the Leiria National Forest (39°45′ N; 8°56′ W; 75 m a.s.l.), located in central coastal Portugal, with dry sub-humid climate (30-year mean rainfall of about 800 mm). This plantation is representative of wide areas of Portugal, which are characterised by sandy and acidic soils, with low organic matter content and N availability. Soils are mainly Dystric Arenosols associated with Podzols developed on coastal sand dunes. Soil substrate was collected from the Ah horizon of an Arenosol. The soil was sieved (<2 mm), four subsamples were taken for chemical analysis and the rest of the soil was stored at room temperature until being introduced in the lysimeters, within 4 days after collection. The soil showed a sandy texture (98% of sand) and a low pH (5.1). Exchangeable bases (Ca, Mg, Na and K) and effective cation exchange capacity ($NH_4OAc$ extraction) were 1.09 and 1.49 $cmol_c$ $kg^{-1}$, respectively. Extractable P and K determined by the Egnér–Riehm method (Egnér et al. 1960) were 4.7 and 20.5 mg $kg^{-1}$, respectively. Organic C content was 12.4 g $kg^{-1}$ and C/N ratio was high (45).

Twenty samples (0.25 $m^2$ each) from the forest floor litter layer were randomly collected in the area (Arenosols) where soil substrate was sampled. Four composite samples were obtained for the analysis of C, N, Ca, Mg, K and P contents that were 384, 7.71, 8.21, 1.41, 1.05 and 0.42 mg $g^{-1}$, respectively.

The two forms of wood ash used in this study, obtained from combustion of *Eucalyptus* bark in the CELBI Pulp Company, showed a high pH and low concentrations of

heavy metals (Table 1). Loose ash (diameter <0.2 cm) was collected as fly ash. Fly ash was pelleted (diameter=0.5 cm, length=2 cm) by AB Nordströms Konstruktionsbyra (Sweden).

## 2.2 Treatments

The experimental design consisted of five treatments replicated four times in a completely randomised design: CT, absence of wood ash and fertiliser application (control treatment); LA, loose ash application; LAN, as LA, but with N fertiliser; PA, pelleted ash application; PAN, as PA, but with N fertiliser. Except in the control treatment, 74.8 g of wood ash was applied on the surface of the forest floor litter of each lysimeter (without being incorporated into the soil), which corresponded to 11 Mg ha$^{-1}$ (considering 20 cm of depth). The dose of wood ash applied was assessed considering the lime requirement to achieve a soil pH of 6.5 and the mean CaCO$_3$ equivalents (CCE) of the wood ash. The added amount of wood ash largely exceeded the export of Ca, Mg and K (670, 110 and 251 kg ha$^{-1}$, respectively) due to whole-tree harvesting of maritime pine in the Leiria National Forest (Madeira et al. 2009). As wood ash supply low amounts of N and P, in the treatments LAN and PAN, each lysimeter received 2.27 g (corresponding to 334 kg ha$^{-1}$) of N fertiliser (25%—8% as ammonium, 16% as urea and 1% as dicyandiamide) with low P content (about 2.25%), considering main nutrient limitations of pine plantations in the Leiria National Forest (e.g. N and P; Madeira et al. 2009). The treatment installation was concluded in 7 November 2005, and the study ended 24 months later (November 2007).

## 2.3 Sampling

The volume of lysimeter leachates was recorded and sub-samples were collected for analysis according to the occurrence of rainfall, approximately once a week in the rainy period and once every 2 weeks or once a month in the summer, so that a total of 39 samplings were carried out. Subsamples were filtered (0.45 μm) and stored at −15°C until chemical analyses. At the end of the experiment (December 2007), the lysimeters were destructively sampled to assess soil chemical changes with depth. After removal of the forest floor litter layer remaining on the soil surface, the soil was divided into four depths (0–5, 5–10, 10–20 and 20–30 cm) and samples were dried (45°C) and sieved (<2 mm) for chemical analyses. For the 0–5 and 5–10 cm layers, subsamples of the field-moist soil were stored at 4°C until processing within 3 days after collection to evaluate N mineralisation, soil basal respiration and microbial biomass.

## 2.4 Laboratory procedures

Organic residues were dried at 45°C and ground in a laboratory mill to a particle size of 0.5 mm. The mineral elements (Ca, Mg, K and P) were determined after ashing (6 h at 450°C) and dissolving in HCl. Total N was determined using Kjeldhal digestion. The C content was measured by wet oxidation (De Leenheer and Van Hove 1958). The Ca, Mg and K were measured by atomic absorption spectrometry (AAS; Aanalyst 300, Perkin Elmer) and P by the molybdate-blue method (Murphy and Riley 1962).

Leachates were filtered (0.45 μm) and pH was measured. Dissolved organic C (DOC) and total N were determined by an elemental analyser (Skalar FORMAC Combustion TOC/N), using a near-infrared spectroscope and a chemiluminescence detector, respectively. Concentrations of NO$_3^-$-N and NH$_4^+$-N were determined with a segmented flow autoanalyser, using the α-naphtylamine and sulphanilamide method after reduction with Cd and the modified Berthelot method, respectively (Houba et al. 1994). Calcium, Mg and K were measured by AAS and mineral P by the molybdate-blue method.

The pH in soil and wood ash was determined in water (soil or ash/solution ratio, 1:2.5). The C content and total N were measured as mentioned above. The mineral elements

**Table 1** Chemical composition of the wood ash (C, N, Ca, Mg, K, P, Al, Fe and Mn in grammes per kilogramme; other elements in milligrammes per kilogramme) and amounts of nutrients applied (in kilogrammes per hectare) to the lysimeters

| Wood ash | Chemical composition | | Amounts applied | |
|---|---|---|---|---|
| | Loose | Pelleted | Loose | Pelleted |
| pH | 12.9 | 12.6 | | |
| CCE (%) | 80 | 83 | | |
| C | 16.5 | 14.2 | | |
| N | 0.08 | 0.20 | | |
| Ca | 103.4 | 117.3 | 1,129 | 1,281 |
| Mg | 23.94 | 26.07 | 261 | 285 |
| K | 32.15 | 35.41 | 351 | 387 |
| P | 4.74 | 2.27 | 51.8 | 24.8 |
| Al | 4.45 | 4.41 | 48.6 | 48.2 |
| Fe | 3.01 | 2.90 | 32.9 | 31.7 |
| Mn | 5.40 | 6.10 | 59.0 | 66.6 |
| B | 193 | 250 | 2.108 | 2.73 |
| Cd | 0.21 | 0.13 | 0.002 | 0.001 |
| Co | 3.26 | 3.75 | 0.04 | 0.04 |
| Cr | 15.4 | 17.0 | 0.17 | 0.19 |
| Cu | 31.0 | 41.6 | 0.34 | 0.45 |
| Ni | 21.9 | 28.1 | 0.24 | 0.31 |
| Pb | 18.9 | 16.6 | 0.21 | 0.18 |
| Zn | 64.7 | 54.0 | 0.71 | 0.59 |

*CCE* calcium carbonate equivalent

in wood ash were taken up in $HNO_3$. The CCE of ash were determined by boiling 1 g of wood ash with 50 ml of 0.5 M HCl, excess acidity being analysed by titrating with 0.25 M NaOH. The soil exchangeable base cations were extracted by the standard method (1 M $NH_4OAc$, adjusted at pH 7.0; Chapman 1965). To assess the effective cation exchange capacity, the extractable acidity (Al and H) was determined after extraction by 1 M KCl (Thomas 1982). Extractable P and K were obtained by shaking 1 g of soil with 20 ml of K $(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ solution at pH 3.7 for 2 h (Egnér et al. 1960). The Ca, Mg, Na, K and Al of the extracts and solutions were quantified by AAS, P was determined as above and other elements by ICP-OES.

N mineralisation, soil basal respiration and microbial biomass in the 0–5 and 5–10 cm soil layers were determined. To measure N mineralisation, about 200 g of moist soil from each lysimeter were incubated under aerobic conditions in polythene bags, at 25°C, 60% of water-holding capacity and darkness, during 60 days. Initial soil moisture content was adjusted after a 7-day period by adding distilled water. Fortnightly, $NO_3^-$-N and $NH_4^+$-N were extracted by shaking 10 g of soil for 1 h with 2 M KCl (soil/solution ratio, 1:5) and $NO_3^-$-N and $NH_4^+$-N in extracts were determined as above. Net nitrification and net ammonification were calculated by the difference between $NO_3^-$-N and $NH_4^+$-N at each incubation time and their respective initial levels.

Soil basal respiration was measured by incubating 50 g of moist soil adjusted to 60% water-holding capacity at 25°C in a 1.5-L sealed glass jar. The $C$-$CO_2$ produced after the 7-, 15-, 30-, 45- and 60-day period was collected in 30 ml of 0.5 M NaOH, which was titrated with 0.5 M HCl to phenolphthalein endpoint, after the addition of 1.5 M $BaCl_2$.

Microbial C ($C_{mic}$) and N ($N_{mic}$) were measured by the chloroform fumigation–extraction method (Vance et al. 1987) and organic C and total soluble N were determined by elemental analysis, as previously described. Contents of $C_{mic}$ and $N_{mic}$ were calculated as the difference between fumigated and non-fumigated samples, using a $K_{EC}$ and $K_{EN}$ factor of 2.64 and 1.85, respectively (Brookes et al. 1985; Vance et al. 1987). Metabolic quotient ($qCO_2$) was calculated as the ratio of hourly basal respiration rate produced after 7 days to the corresponding initial $C_{mic}$ [mg $CO_2$-C (g $C_{mic}$)$^{-1}$ h$^{-1}$].

## 2.5 Statistical analysis

Treatments effects on nutrient leaching and soil chemical and biological properties were tested by one-way ANOVA and differences among means were determined at $p<0.05$ using the Tukey honestly significant difference test. Statistical procedures were performed using Statgraphics plus 5.1 (Manugistics Inc.).

# 3 Results

## 3.1 Nutrient leaching

Lysimeter drainage volume had a similar trend to that of rainfall, with paralleled amounts in both years. Cumulative volume of leachates during the experimental period was similar in all treatments (Table 2). Mean pH of leachates was increased by loose (about 0.25 units) and pelleted (about 0.10 units) ash application relatively to the control treatment, but differences were not significant (Table 2). At the end of the study period, amounts of DOC leached were not significantly affected by treatments (Table 2). Total N leached was significantly lower in treatments with loose and pelleted ash alone (710 and 762 mg/lysimeter in LA and PA treatments, respectively) than in the control. Application of wood ash with N fertiliser promoted significant $NH_4^+$-N losses compared with the control, mainly when applied in loose form (Fig. 1, Table 2). Leaching of $NO_3^-$-N, negligible during the first year of the experiment, was much greater than that of $NH_4^+$-N at the end of the study. Losses of $NO_3^-$-N were mainly affected by the ash form, with a significant reduction only observed for loose ash (treatment LA), and secondarily by N fertiliser application (Fig. 1).

Leaching of K and Ca was faster and more intense for the loose than the pelleted form. Wood ash application resulted in a fast increment of Ca and K leached amounts, and differences among treatments mostly occurred during the first 4 months of study (Fig. 1). Such differences may be also associated with the rainfall amount, as the leaching of Ca and K was also high in the second winter season of the experiment. A similar trend was observed for Mg and Na leached (data not shown). After the first year of the study, loose ash application significantly increased the amounts of Ca, Mg, Na and K leached in relation to the control; for the ash pelleted formulation, such increase was also significant but less pronounced (Table 2). The effect of wood ash decreased with time and, during the second year, only K leaching showed a significant increment in response to wood ash application. At the end of the study, amounts of Na and K leached were significantly higher in treatments with wood ash than in the control (Table 2). As for base cations, P leached during the first year was significantly higher in treatments with loose ash than in the control. Such differences were still noticeable after 2 years (Table 2, Fig. 1). When pelleted ash was added alone (PA treatment), P leached also increased during the first year, but differences were not observed for the cumulative amount leached after 2 years.

## 3.2 Soil properties

At the end of the experiment, values of pH-$H_2O$ in the 5-cm top soil layer were 0.91 and 0.83 units higher in treatments with loose ash (LA and LAN treatment, respectively) than in

**Table 2** Cumulative volume of leachates (in millimetres), mean pH and cumulative DOC and nutrients (in milligrammes per lysimeter) leached after a 1-year (November 2006) and a 2-year (November 2007) period

| Treatment | Volume | pH | DOC | Total N | $NO_3^-$-N | $NH_4^+$-N | Ca | Mg | Na | K | P |
|---|---|---|---|---|---|---|---|---|---|---|---|
| One-year period | | | | | | | | | | | |
| CT | 344±47 | 4.57 | 2,390±400 | 202±55b | 54±17 | 59±6b | 147±20b | 70±14b | 215±50b | 183±31c | 8±5c |
| LA | 362±42 | 4.48 | 2,799±575 | 217±27ab | 27±9 | 95±18ab | 548±198a | 241±90a | 401±106a | 1,302±366a | 19±3ab |
| LAN | 359±20 | 4.64 | 2,779±267 | 303±44ab | 40±21 | 148±23a | 643±212a | 298±80a | 426±48a | 1,258±215a | 20±6a |
| PA | 322±124 | 4.84 | 2,433±746 | 252±79ab | 42±16 | 84±38b | 577±60a | 233±71a | 367±36a | 784±169b | 19±7abc |
| PAN | 382±21 | 4.66 | 2,494±230 | 341±69a | 65±31 | 155±43a | 508±119a | 229±46a | 323±26a | 645±158b | 9±5cb |
| Two-year period | | | | | | | | | | | |
| CT | 1,080±44 | 4.88 | 4,896±781 | 968±93a | 541±58a | 149±55c | 801±99 | 395±24 | 470±69b | 649±179c | 24±3b |
| LA | 1,081±46 | 5.03 | 6,159±783 | 710±51b | 343±45b | 192±14bc | 818±209 | 385±117 | 692±105a | 2,257±332a | 36±6a |
| LAN | 1,072±24 | 5.15 | 5,766±556 | 892±105ab | 431±91ab | 239±25a | 939±267 | 473±104 | 737±28a | 2,311±114a | 34±5a |
| PA | 1,122±28 | 4.94 | 5,770±545 | 762±34b | 453±46ab | 164±33bc | 1,012±120 | 451±79 | 667±28a | 1,641±131b | 28±5ab |
| PAN | 1,108±47 | 4.89 | 5,301±669 | 969±122a | 499±91a | 229±28ab | 959±186 | 449±38 | 620±48a | 1,460±184b | 25±7ab |

Values are presented as the mean±SD ($n=4$). Treatments are CT, absence of wood ash and fertiliser application; LA, loose ash application; LAN, as LA, but with N fertiliser; PA, pelleted ash application; PAN, as PA, but with N fertiliser. Different letters in the same column and period denote significant differences ($p<0.05$) among treatments by the Tukey multiple range test

the control, while pH differences for pelleted ash were not significant (Fig. 2). Loose ash application also increased exchangeable Ca and Mg (in 0.87 and 0.12 cmol$_c$ kg$^{-1}$, respectively) and extractable P (in 2.5 mg kg$^{-1}$) in the 0–5 cm soil layer, when compared with the control. Treatments with loose or pelleted ash (alone or together with N) showed higher contents of exchangeable K for all soil depths than in the control soil.

In the top soil layer of treatments with loose ash, a significant reduction in extractable acidity was observed (0.10–0.18 cmol$_c$ kg$^{-1}$), while effective cation exchange capacity significantly increased (0.69–1.43 cmol$_c$ kg$^{-1}$) relatively to the other treatments (Fig. 2). Total N (data not shown) and total C (Fig. 2) content in soil showed a similar pattern and both were not significantly affected by treatments.

After 60 days of aerobic incubation, treatments with loose ash (LA and LAN) showed a significant reduction on cumulative net ammonification when compared with the control (Fig. 3). In contrast, the resulting cumulative net nitrification was significantly increased by loose ash application. Such differences were stronger in the 0–5 cm surface soil layer. No significant effects were observed for the pelleted formulation.

Soil basal respiration and respective rate were not significantly affected by treatments (Table 3), while initial metabolic quotient ($q$CO$_2$) values were lower in treatments with wood ash than in the control.

In both 0–5 and 5–10 cm soil layers, soil microbial C and N contents were significantly higher in treatments with loose and pelleted ash alone (LA and PA treatments) than in the control (Table 3). Similarly, the highest C$_{mic}$/C$_{org}$ ratios were generally observed in treatments with wood ash application, but differences were not significant.

## 4 Discussion

The methodology used in this study presents some limitations (e.g. disturbance of soil structure and water transfers, absence of root uptake and exudates). Soil disturbance during lysimeter installation might have induced a higher mineralisation flux, while the absence of plants probably increased the volume of percolating water and modified the nutrient leaching. Although experimental conditions have a limited value in assessing the complexity of field situations, they give insight into the effect of wood ash application on soil properties and C and N dynamics.

The influence of wood ash on nutrient dynamics and soil properties depended on the form of ash applied. Wood ash did not exhibit a significant effect on the pH of leachates, while loose ash application increased pH and reduced extractable acidity on the top soil layer at the end of the study period. This finding supports the efficiency of unstabilised
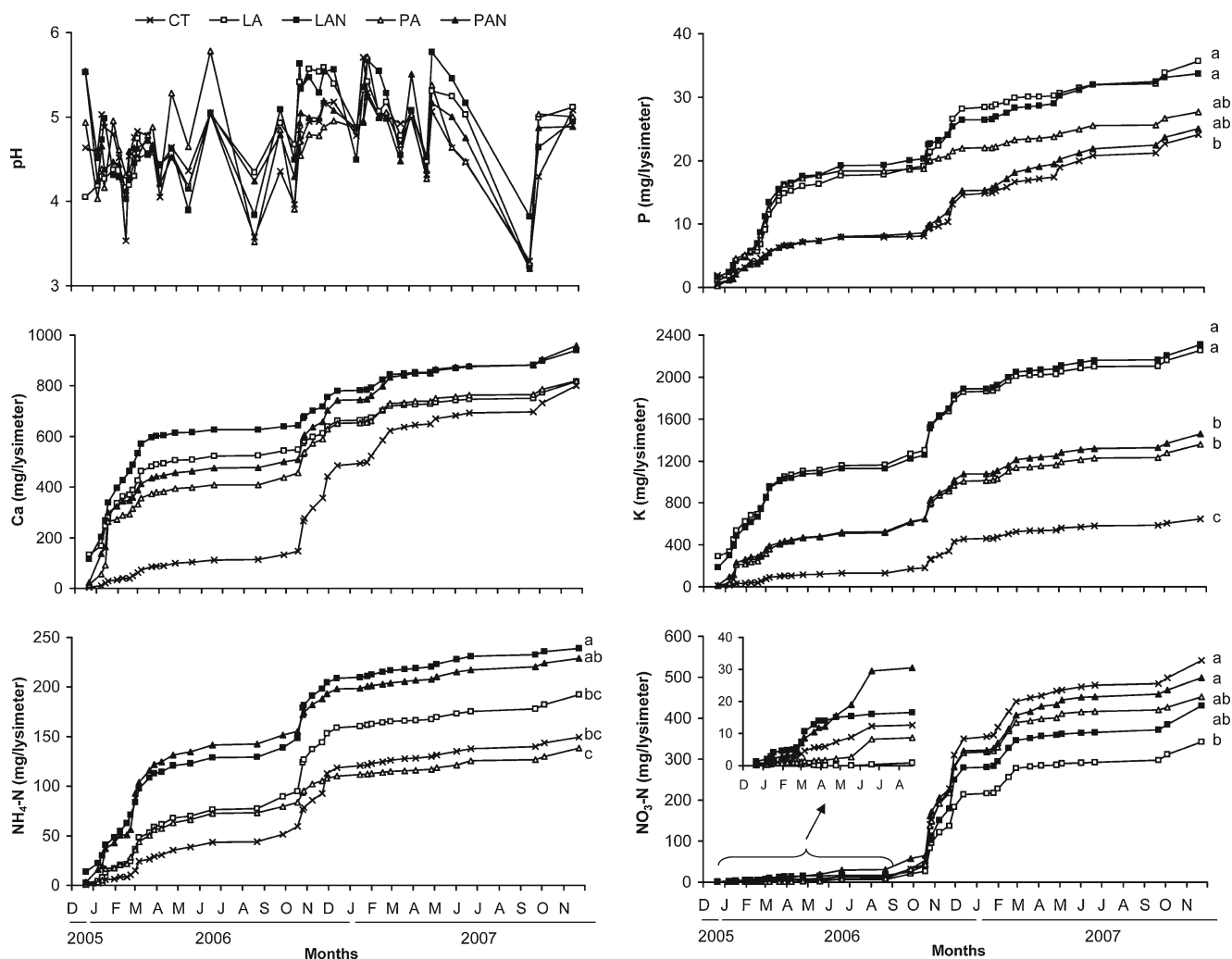
Fig. 1 Mean pH of the leachates and cumulative losses (in milligrammes per lysimeter) of Ca, K, NH₄⁺-N, NO₃⁻-N and P from the lysimeters over the experimental period ($n=4$). Different letters for data at the end of the study denote significant differences ($p<0.05$) among treatments. Treatments are *CT* absence of wood ash and fertiliser application, *LA* loose ash application, *LAN* as LA, but with N fertiliser, *PA* pelleted ash application, *PAN* as PA, but with N fertiliser

wood ash to correct acidity of forest mineral soils at the short-term, as reported in several studies (Ludwig et al. 2002; Park et al. 2005). Stabilisation of wood ash by pelleting, granulation or hardening reduces the reactivity of the ash (Eriksson 1998) and explains the absence of appreciable changes after pelleted ash application during the studied period, although a positive effect on soil pH could be expected in the long-term. Also, in a previous laboratory incubation (Gómez-Rey et al. 2006), a significant and fast soil pH increment was initially observed using loose ash at doses similar to that used in this study, but no significant effect was detected even 20 weeks after pelleted ash addition. Although our data do not allow to predict how long this increase would last, loose ash effect on soil acidity reduction might persist or be increased for several years (6–16 years) after its application, as reported by Augusto et al. (2008) in a recent meta-analysis study.

Leaching of base cations and phosphorus following wood ash application mostly occurred during the first year of the study, when loose ash application enhanced Ca, Mg, Na, K and P amounts in leachates. Given the slower dissolution of pelleted ash (Ring et al. 2006), its effect on nutrient leaching during the study period was of less magnitude when compared with the loose formulation, a trend also observed in a laboratory simulation for long-term leaching of untreated and stabilised wood ash (Steenari et al. 1998). However, the effect of pelleted ash on nutrient leaching might be increased during the following years.

At the end of the study period, the amount of K leached increased by wood ash application; this increase accounted for 34% and 68% of the amount of K supplied to lysimeters by ash (pelleted and loose ash, respectively). In contrast, enhancement of Ca, Mg and P amounts in leachates was only 1.6%, 3.3% and 2.0%, respectively, of the quantity supplied
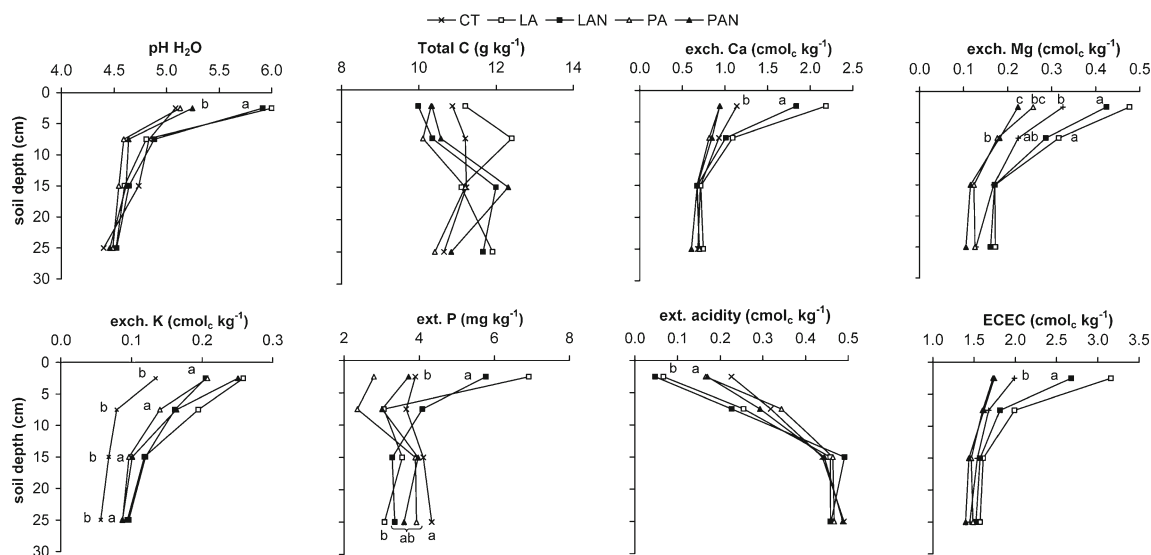
**Fig. 2** Values of pH and contents of total C, exchangeable Ca, Mg and K, extractable P, extractable acidity and effective cationic exchange capacity (*ECEC*), calculated as the sum of extractable acidity (Al and H) and exchangeable cations (Ca, Mg, Na and K) in the mineral substrate of lysimeters at the end of the study period, according to depth (*n*=4). Significant differences (*p*<0.05) among treatments in the same depth were marked with different letters. Treatments as in Fig. 1

by both ashes. These differences are explained by the mineralogical speciation of wood ash in which K occurs in salt forms easily dissolved (Steenari et al. 1999), while Ca and Mg are mainly in carbonate forms and P is bound in compounds with low solubility (Steenari and Lindqvist 1997).

Our results show that loose ash recycling as soil amendment may have a great potential to balance base cations and phosphorus losses due to the harvest of Portuguese eucalypt and pine plantations (Cortez 1996; Madeira et al. 2009). In fact, an enhancement of exchangeable Ca, Mg and K and extractable P was observed, at the end of the study, in the top soil layer (0–5 cm) due to loose ash application,

accounting for low proportions of Ca, Mg, K and P (11%, 4%, 8% and 3%, respectively) initially applied as mineral soil, forest floor, wood ash and fertiliser. This was associated with the displacement of Al³⁺ and H⁺ from the exchangeable complex, which is in conformity with the rise of pH values, especially in the LA and LAN treatments (Fig. 2). However, the increment of base cations in the exchangeable complex was much greater than the reduction of extractable acidity. Given the similar organic C content in all treatments (Fig. 2), such difference may be mostly associated with the enhancement of exchange sites (variable negative charges) in soil colloids (mostly organic matter) as a result of the pH

**Fig. 3** Cumulative soil net ammonification and net nitrification during 60 days of aerobic incubation. Significant differences (*p*<0.05) among means (*n*=4) in the same period were marked with different letters. Treatments as in Fig. 1
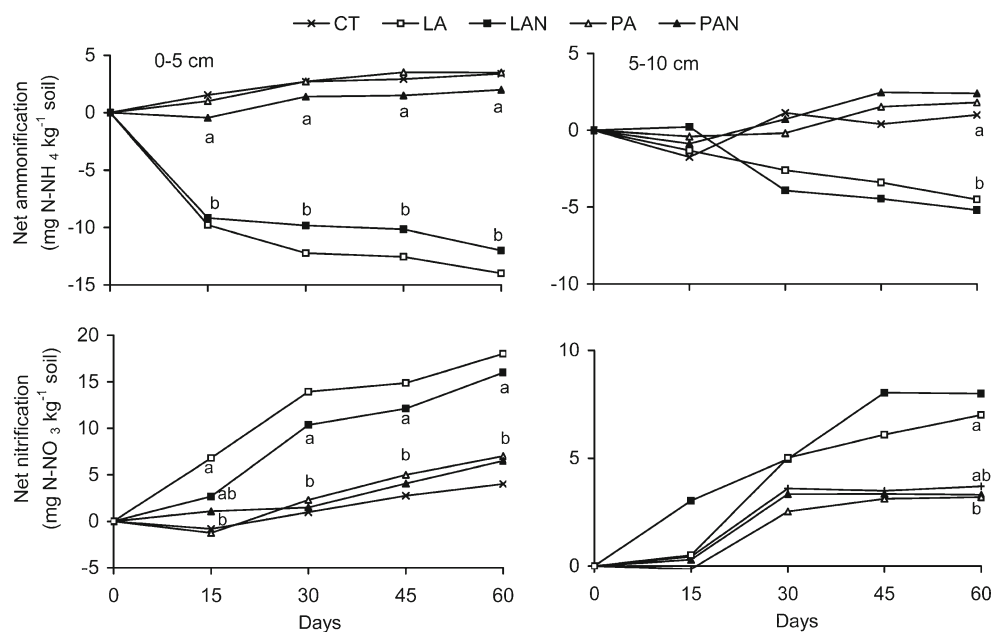
**Table 3** Cumulative soil basal respiration (in milligrammes of C-CO$_2$ per kilogramme of soil) during 60 days of incubation, soil basal respiration rate (SBR, in milligrammes of C-CO$_2$ per gramme of C), metabolic quotient ($q$CO$_2$, in milligrammes of C-CO$_2$ per gramme of C$_{mic}$ per hour) and contents of microbial C and N (C$_{mic}$ and N$_{mic}$, in milligrammes per kilogramme) for mineral substrate at 0–5 and 5–10 cm depth

| Treatment | Basal respiration | SBR | $q$CO$_2$ | C$_{mic}$ | C$_{mic}$/C$_{org}$ | N$_{mic}$ |
|---|---|---|---|---|---|---|
| 0–5 cm | | | | | | |
| CT | 150.8±21.5 | 14.2±3.2 | 5.8±1.2[a] | 52.6±4.7c | 0.18±0.05b | 3.7±0.6b |
| LA | 163.8±28.1 | 18.2±3.7 | 2.3±0.3bc | 93.5±3.6ab | 0.25±0.02ab | 8.2±2.4a |
| LAN | 171.2±35.0 | 21.4±3.9 | 3.2±1.2b | 61.6±2.6bc | 0.16±0.04b | 5.7±0.9bc |
| PA | 122.2±19.9 | 14.8±2.4 | 1.1±0.3c | 118.2±14.9a | 0.35±0.09a | 7.6±0.1ac |
| PAN | 138.4±35.1 | 19.5±4.6 | 3.4±0.8b | 89.7±23.8b | 0.24±0.07ab | 4.4±1.1b |
| 5–10 cm | | | | | | |
| CT | 114.3±19.6 | 11.3±3.9 | 3.4±0.7[a] | 69.2±17.1bc | 0.25±0.05a | 5.6±0.9b |
| LA | 91.7±18.0 | 9.1±2.5 | 1.3±0.5b | 152.7±49.9a | 0.33±0.09a | 11.1±1.8a |
| LAN | 64.5±9.1 | 7.9±1.9 | 3.0±0.8a | 36.7±11.6c | 0.10±0.04b | 9.3±0.3ab |
| PA | 107.4±29.5 | 13.9±5.2 | 1.2±0.4b | 127.4±41.6a | 0.33±0.10a | 9.9±2.5a |
| PAN | 77.4±19.0 | 9.7±3.9 | 2.6±0.6a | 76.3±47.6b | 0.23±0.08ab | 9.2±2.2ab |

Values are presented as the mean±SD ($n$=4). Treatments as in the Table 2. Different letters in the same column and soil layer denote significant differences ($p$<0.05) among treatments by the Tukey multiple range test

increment, as reported by Khanna et al. (1994) for effects of ash derived from *Eucalyptus* litter on forest soils. The absence of significant differences between the pelleted ash treatments (PA and PAN) and the control for extractable base cations, extractable acidity and pH may be a result of the smaller amount of base cations released by the pelleted ash. Similar limited effect on soil nutrient and base cation status was reported by Wang et al. (2010) for granulated wood ash in the short-term (5 years). However, as concluded by these authors, pelleted ashes will likely have positive effects with time and can be used for long-term nutrient compensation, following the findings of Arvidsson and Lundkvist (2003) for hardened crushed ash and those of Callesen et al. (2007) for granulated wood ash.

As observed in other studies (Park et al. 2005), soil enrichment in Ca and Mg was only observed at the upper soil layer while increments in exchangeable K were detected in deeper layers, possibly due to its higher mobility. When pelleted ash was applied, only exchangeable K increments were detected. In contrast, exchangeable Ca and Mg tended to decrease in treatments with pelleted ash relatively to the control. This trend may be ascribed to the lower solubility of Ca and Mg than K in pelleted ash, which may favour their displacement from the exchange sites. We also emphasise that the restriction of Ca and Mg changes mostly to the 0–5 cm soil layer may be associated with the fact that ashes were applied directly on the surface of the forest floor litter (not incorporated), which may reduce effects on the soil exchangeable complex, as reported by Khanna et al. (1994).

As for base cations and phosphorus, an initial increase of total N and NH$_4^+$-N leaching was observed during the first year after wood ash application, mainly when added together with N fertiliser. This suggests that wood ash application to forest plantations growing on sandy soils may affect the quality of water bodies due to the increase in N and P leaching. However, root uptake (trees and understory) was not taken into account in the present study and, therefore, losses may be lower under field conditions. In addition, the dose of N applied in the present study was quite high (83.5 kg ha$^{-1}$) and, therefore, a reduced risk is expected for lower doses.

At the end of the study period, total N leaching was reduced by the application of loose and pelleted ash alone likely due to the low soil N availability of the studied soil. In contrast to some sites of the Northern European forests, the studied site is N limited due to the low N input from the atmosphere (4.0 kg ha$^{-1}$ year$^{-1}$; Cortez 1996), low soil organic matter and high C/N ratio of the forest floor layer (50) and of the mineral soil (41), which is above the critical condition for N release (Harmsen and Van Shreven 1955). This pattern suggests that N may have been immobilised in the microbial biomass, which agrees with the higher N microbial contents observed at the end of the study in treatments with wood ash alone (Table 3). In fact, the mean increment on microbial N content observed for the LA or PA treatments (5.0 and 4.1 mg kg$^{-1}$, respectively), estimated for the whole lysimeter (175 and 143 mg/lysimeter), is relatively close to the reduction on total N leached obtained (258 and 206 mg/lysimeter, respectively). Thus, our results suggest that ash addition may not enhance tree growth of stands established in the studied soils, as also reported by Augusto et al. (2008) for N-limited mineral soils. In fact,

soil N immobilisation following wood ash application may reduce N availability for trees, decreasing tree growth, as suggested by Bramryd and Fransman (1995) for Scots pine growing in poor Scandinavian soils (C/N >30) after liming. Also, Jacobson (2003) reported a stem growth decrease in response to wood ash application at poor Scandinavian coniferous stands, while stem growth increased in more fertile sites. The negligible effect on N leaching observed in treatments where wood ash was applied with N fertiliser suggests that, in N-limited soils as those of the present study, N fertiliser supply is required to promote soil N availability.

In contrast with total N and $NO_3^-$-N, loose ash application enhanced P leaching. No data on microbial P ($P_{mic}$) contents were obtained. As the $C_{mic}/N_{mic}$ ratio in our study (8–15) is close to that reported by Achat et al. (2010) for comparable systems, the $N_{mic}/P_{mic}$ ratio reported by those authors (0.6) may be used for the present study. Then, P immobilisation might have increased to about 290 mg/lysimeter. Despite this possible increase of P in microbial biomass, leaching of P was not prevented, suggesting that the soil used in the present study did not avoid P leaching, agreeing with Achat et al. (2009) who measured negligible P buffer capacity in similar soils. As organic P in leachates was not measured, the amount associated with organic matter is unknown. Therefore, further research should be developed to assess deeper understanding on the effects of ash application on P leaching.

At the end of the study, soil incubation under laboratory conditions showed that loose ash application increased net nitrification, agreeing with the trend previously reported for laboratory incubations carried out with soil taken in the same site and with similar ash dose (Gómez-Rey et al. 2006). These results suggest that high doses of untreated ash may favour $NO_3^-$-N losses such as reported for other forest soils (with soil C/N ratio lower than 35) from regions with cold climate (Ludwig et al. 2002). However, such treatment differences were not observed under the studied lysimetric conditions, as $NO_3^-$-N amounts in leachates were significantly reduced by loose ash and were not significantly affected by pelleted ash. Discrepancy between both studies may be partially associated with more intense denitrification in the lysimeter system. The increased soil pH may also favour losses of soil N by denitrification as a result of nitrifying microbial populations and nitrification process stimulation (Khanna et al. 1994). The application of N fertiliser combined with wood ash might induce additional N losses by denitrification, following the trend reported by Ozolincius et al. (2006) for an Arenosol amended with wood ash.

Carbon dynamics was weakly affected as DOC in leachates, and soil basal respiration was not significantly different between treatments. This trend does not support the findings of other studies carried out in peat and mineral forest soils in cold climate conditions where wood ash application promoted increases in DOC (Weber et al. 1985) and soil respiration (Fritze et al. 1994; Khanna et al. 1994; Nohrstedt 2001; Zimmermann and Frey 2002). Also, soil respiration stimulation was observed in ash-amended soils of humid areas of the Iberian Peninsula (Solla-Gullón et al. 2006). The lack of significant effects observed in our study may be related to the low soil organic C content. In fact, by incubating a range of Australian forest soils, Khanna et al. (1994) reported that effects of wood ash addition on organic C dynamics decreased in soils with low organic matter content.

Values of microbial metabolic quotient ($qCO_2$) were comparable to those reported for Mediterranean soils with similar C content (Garcia et al. 1994). Microbial C increment by wood ash application led to a lower $qCO_2$, indicating that use efficiency of substrate C by microorganisms may be higher in amended soils, as reported by Insam and Haselwandter (1989). This pattern does not agree with the higher (Fritze et al. 1994) or similar (Zimmermann and Frey 2002) levels in $qCO_2$ found in cold regions, as well as with the lack of changes reported for wetter areas of the Iberian Peninsula (Solla-Gullón et al. 2006). Our results suggest that wood ash application could create favourable conditions (e.g. better nutrient availability and soil pH) for soil microbial community in acidic soils of dry sub-humid Mediterranean regions.

At the end of the study, low proportions of Ca, Mg and P (11.9%, 6.0% and 5.8%, respectively) initially applied with the loose ash were measured in leachates and mineral soil layers; these proportions were lower when wood ash was applied in pelleted form. This result suggests that nutrients supplied by ash were mostly retained in the organic layer covering the mineral soil, minimising ash effects on mineral soil layers. This is supported by the fact that dissolution of ash components is expected to be slower when ash is applied to the soil surface than when it is mixed with acidic soils (Khanna et al. 1994). Therefore, greater doses of wood ash, mainly in pelleted form, could be applied in forest systems of sub-humid Mediterranean regions without dramatic changes on soil properties, suggesting that the studied soils may be used for ash disposal. Nevertheless, our results indicate that such application should be carried out some years after tree planting or when understory vegetation is established, mainly in forest plantations growing in sandy soils with low effective cation exchange capacity. Under these circumstances, roots demand would minimise nutrient losses at the short-term, reducing water quality risks and contributing to enhance soil nutrients availability in the long-term. Also, the possible negative impacts of wood ash on seedlings are avoided. However, further studies are needed to evaluate wood ash effects on C and N dynamics in organic soil layers as well as the interactions between these

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layers and nutrients released from the ash. Likewise, the interactions with plants will be also evaluated through appropriate field trials to assess how the improvement of soil nutrient availability promoted by wood ash application could affect the nutrient status and growth of the tree stands.

## 5 Conclusions

Our results showed that, applied at a dose to achieve a soil pH of 6.5, loose ash improved nutrient availability and reduced soil acidity, resulting in an alternative to lime and commercial fertilisers for counteracting nutrient removal by tree harvesting in acidic forest soils of sub-humid Mediterranean regions. Such improvement of base cations availability is mostly associated with the enhancement of the soil effective cation exchange capacity. However, C dynamics was not significantly affected by wood ash application. On the contrary, wood ash should be applied together with N fertiliser to balance soil N immobilisation in N-limited soils as those of the present study. At the short-term, pelleted ash application showed negligible effects, suggesting that it may be used in higher doses, but its effect on Ca and Mg losses from the soil mineral layers should be taken into account. In fact, the increment on nutrient leaching at the short-term suggests that both forms of wood ash show potential risks for water contamination. Our results are consistent with the conclusions of former Nordic experiments, suggesting that guidelines proposed for Northern Europe could be used for Mediterranean regions. However, field studies are necessary to evaluate the long-term effects on soil and plants and to determine the highest dose that can be applied without deleterious effects on soil pH and C and N losses.

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