IMPACT OF HIGH-VOLUME WOOD-FIRED BOILER ASH AMENDMENT ON SOIL PROPERTIES AND NUTRIENTS

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ABSTRACT

Forest application of boiler ash is fast becoming a popular alternative to landfilling. Boiler ash is a good source of calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), manganese (Mn), and zinc (Zn), but it may potentially increase soil pH and electrical conductivity. A monitoring study was conducted to determine the changes in soil properties and the availability and leachability of nutrients following the application of large quantities of boiler ash in a sandy soil (with a spodic horizon). Two application rates (900 and 1800 Mg ha⁻¹) and two application methods (surface and subsurface) were used in a three-hectare area, which was divided into 15 subplots. Soil samples from different depths were collected over a period of 21 months. Soil pH increased from 5.6 to above 9 and the electrical conductivity increased by up to 2 orders in all plots compared to the controls. The high alkalinity from the ash in the 1800 Mg ha⁻¹ rate depleted the spodic layer, and this was more pronounced in the subsurface treatments. Plant-available water was doubled to

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British soils with application rates ranging from 250 to 1200 Mg ha$^{-1}$ (12,13) increased water holding capacity increases supply of water to plants. However, the results from coal ash application may not be used to accurately predict the changes in soils amended with boiler ash. Hence the effects of boiler ash on both soil physical and chemical properties were investigated in this study.

Forest responses to ash application have been studied most intensively in Scandinavian countries (14,15,16). Increases in pH of forest soils have been shown to be small in many cases (<1), although some studies have shown changes of up to two units (17,18,19) using low ash application rates (<112 Mg ha$^{-1}$). Therefore, when the calcium carbonate equivalent of boiler ash is known, boiler ash can be used as an effective liming agent (3).

There are a few excellent reviews on the nutritional importance of boiler ash (5,20). Boiler ashes are good sources of Ca, K, and Mg as well as other nutrients that are removed when trees are harvested in intensively managed forests (21,22). Boiler ash application has also been recommended as a way of mitigating nutrient imbalances stemming from natural weathering (18,23) and from the effects of acid deposition (24). When an industrial ash, equivalent to 0–1–3 NPK fertilizer, was mixed with two soils at application rates up to 36Mg ha$^{-1}$, the soil extractable P, K, and Ca and pH were linearly related to the ash application rate (25). Greenhouse studies of slash pine (Pinus elliottii L.) response to the application of boiler ash have shown that boiler ash provides micronutrients for plant growth, and when N, P, and K were supplied, that the aboveground biomass production was the same as that of plants supplied with N, P, K, and micronutrients (26).

The purpose of this investigation was to determine the effects of boiler ash on the productivity of forest soils by 1) evaluating changes in soil chemical and physical properties after boiler ash amendment; and 2) investigating the effects of high application rates and methods on the availability and leachability of plant nutrients.

**MATERIALS AND METHODS**

**Site Preparation and Treatments**

The soil used for this study (located in Hawthorne, FL) was an acidic fine sand (Typic Quartzipsamment) with a spodic horizon below 2 m. The site was cleared and de-stumped in September and October 1995. Boiler ash was hauled to the site in November of the same year and the spreading and mixing of the ash was completed in December of 1995. A split-plot design was used with surface and subsurface treatments as main plots, with each plot having an area of ~0.2 ha. In the surface plots, boiler ash was applied at rates of 0, 900, and 1800 Mg ha$^{-1}$.

Increases in soil water holding capacity (WHC) from 12 to 25% in sandy soils amended with 30% of ash (11). Amendment of coarse textured soils with coal ash increased WHC from 20 to 33% in two California soils and from 24 to 94% in...
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Table 1. Chemical and Physical Properties of the Ash and Soil Used in This Study

<table>
<thead>
<tr>
<th>Element</th>
<th>Papermill Ash (Fresh) (mg kg⁻¹)</th>
<th>Soil (A Horizon) (mg kg⁻¹)</th>
<th>Concentration Ratio of Boiler Ash/Soil Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Available</td>
<td>Total Available</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>100,000 463</td>
<td>130 58.6</td>
<td>190</td>
</tr>
<tr>
<td>Mg</td>
<td>9,000 363</td>
<td>900 4.40</td>
<td>10</td>
</tr>
<tr>
<td>K</td>
<td>8,000 1760</td>
<td>30 5.80</td>
<td>267</td>
</tr>
<tr>
<td>P</td>
<td>3000 14.0</td>
<td>100 0.00</td>
<td>30</td>
</tr>
<tr>
<td>Fe</td>
<td>7000 71.6</td>
<td>800 13.1</td>
<td>9</td>
</tr>
<tr>
<td>Mn</td>
<td>860 26.5</td>
<td>14.0 3.50</td>
<td>60</td>
</tr>
<tr>
<td>Zn</td>
<td>329 27.7</td>
<td>0.70 0.07</td>
<td>470</td>
</tr>
<tr>
<td>Cu</td>
<td>37.0 5.6</td>
<td>1.00 0.10</td>
<td>37</td>
</tr>
</tbody>
</table>

Al 8000 2000 4
Na 26,000 40 650
Ba 177 7.00 26
Pb 60.0 1.30 46
Se 19.0 0.70 27
Ni 10.0 5.00 2
Cr 2.0 4.00 0.5
As 2.0 0.40 5
Cd 3.0 0.50 6
CaCO₃ 250,000 0.00 –

This value represents the EC immediately after incorporating ash into the soil as measured in 5:1 solution to solid extract. The EC decreased to ~10 dS m⁻¹ after 18 months of leaching.

pH 7 (29). Plant extractable micronutrients (Fe, Mn, Zn, and Cu) in the soil were extracted using DTPA solution (30). Concentrations of total arsenic (As), chromium (Cr), and selenium (Se) in the ash and soil were determined using a Perkin-Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer. Concentrations of total chromium (Cr), and selenium (Se) in the ash and soil were determined using a Perkin-Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer.

Analyses of Soil Physical Properties

Moisture characteristics for the control soil and treated soils were determined from soil core samples collected from the field in January of 1997, ~13 months after the ash application. The cores were placed in Tempe cells and subjected to increasing suction from 0 (saturated) to 15,000 cm (dry). Gravimetric moisture content was determined for the cores after 48 hr of equilibration at each suction (27). Saturated hydraulic conductivity was determined by letting water flow freely through a soil column of known length, and collecting and measuring the volume of the leachate per unit time. Bulk densities were determined by measuring the weight of soil in the Tempe cells and dividing it by the cell volumes.

Chemical Analyses

For total elemental concentrations, air-dried soil samples were digested in a CEM MDS-2000 microwave digestion oven using the EPA method 3051 (28). Specifically, 0.5 g of soil were digested in 10 mL concentrated nitric acid and made up to 100 mL with nanopure water. Plant extractable macronutrients (Ca, Mg, and K) in the soil were extracted with 1M ammonium acetate (NH₄OAc) at 1800 Mg ha⁻¹ on the surface and incorporated to a depth of 47 cm. The depth of 41 cm was used because it corresponded to the depth of the disking equipment used. For the subsurface plots! the top 50 cm of soil was removed and ash was applied at 900 and 1800 Mg ha⁻¹ and incorporated to a depth of about 47 cm. The topsoil in the subsurface plots was then put back after 18 months, prior to planting of slash pine seedlings in July of 1997. The total area of the research plot was approximately 3 ha with a total of 15 plots (5 treatments × 3 replicates). The rationale for using these excessively high application rates was to improve moisture retention of this sandy soil with little attention being paid to the potential impacts of ash application on soil chemical properties. This study was therefore carried out to understand the impacts of this worst-case scenario of land application of boiler ash on soil.

A total of five soil samplings were conducted. Soil samples were initially collected quarterly (1/29/96, 4/29/96, and 7/25/96) from six depths (0–20, 20–40, 40–60, 60–80, 80–100 cm) and the spodic horizon) in each research plot. Later, samplings were made after six and nine months (11/12/96 and 09/17/97). Three sub-samples from three locations in each plot were collected using a calibrated augur and mixed to obtain composite samples. Selected chemical and physical properties of the ash and soil used in this study are shown in Table 1.
RESULTS AND DISCUSSION

Most research on the impacts of boiler ash application on properties deals with relatively low application rates, i.e., <50 Mg ha⁻¹ (10, 25, 31). Increased nutrient levels have nonetheless been observed at these low rates (3.5). Therefore, significant increases in elemental concentrations were expected as a result of the high rates of ash application in this study. Although the initial rationale for using very high rates was to increase soil moisture retention, we took this opportunity to understand the potential effects of using such high ash application rates on both fertility and other properties.

An important consideration in this study was the size of the experiment plots. The plot size of 0.2 ha was large enough to cause significant variation within each plot. Although soil subsampling was done within each plot, application of large quantities of ash using heavy equipment resulted in heterogeneity within the same treatments (data not shown). This heterogeneity was reflected in large standard deviations observed in our data.

In this study, soil samples were taken from six depths (up to spodic horizon), but only data from the surface soils (0–20 cm) is discussed. The boiler ash was mixed with the surface soil, thus the surface soil was most impacted by the ash. The impacts of boiler ash application on groundwater pollution are discussed in another publication.

Changes in Soil Properties

The most significant changes in soil properties were in pH, electrical conductivity and water holding capacity. The magnitude of change in these properties was particularly high in our case because of the very high application rates used.

Soil pHs ranged from 5.6 in the control plots to above 9.5 for all treatment plots, representing an increase of at least four units (Fig. 1a). This is expected since large amounts of boiler ash of extremely high pH (11.4) were applied to the soil (Table 1). Such drastic changes in pH in soils are not unprecedented.

Changes in (a) pH, (b) electrical conductivity, and (c) moisture characteristics in surface soils (0–20 cm) with time after application of papermill ash.
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leaching samples amended with lower amounts of ash with significant amounts of simulated rainfall prior to greenhouse studies (36) or by leaching with pore volumes equivalent to 18 months of rainfall in Mariott columns (11). The high leaching rate of salts lowers soil salinity and hence improves plants' ability to take up nutrients and water.

In terms of physical properties, boiler ash increased the soil's water holding capacity significantly at all suctions evaluated (Fig. 1c) for both application methods. For the control soil, the moisture contents at field capacity and permanent wilting point (100 to 300 cm suction) were 8 and 14% respectively (6% plant available water). The corresponding values for the ash-amended soils were 10 to 16% (6% plant available water) and 30 to 42% (12% plant available water) in the 900 and 1800 Mg ha⁻¹ treatments respectively (Fig. 1c). Under typically dry soil conditions (above 300 cm suction), the ash-amended soil contained 10 to 30% moisture compared to <8% for the control. Application of high rates of ash therefore increases the chances of plant survival under conditions of extended water stress in soils. The finer texture of the ash increased total soil porosity and changed the pore size distribution of this predominantly sandy soil (Table 1). On the other hand, the saturated hydraulic conductivity of soil decreased from 28.2 cm hr⁻¹ in the controls to 18.8 and 8.6 cm hr⁻¹ in the 900 and 1800 Mg ha⁻¹ surface treatments respectively (Table 2). This decrease is a direct result of the reduction in pore sizes induced by ash addition, causing water to stay longer in the root zones where it is most needed. The reduction in saturated hydraulic conductivity was linear within the range of boiler ash application rates used ($r = 0.99$).

The soil bulk density before boiler ash application was around 1500 kg m⁻³. It decreased to 1360 and 1230 kg m⁻³ after incorporating boiler ash (particle density <500 kg m⁻³) at rates of 900 and 1800 Mg ha⁻¹, respectively (Table 2). The decrease in soil bulk density improves root penetration, soil aeration for both plant roots and microbial communities, and improves soil trafficability (37).

Macronutrients

Calcium, Mg, and K are all essential macronutrients for plant growth and their increase is desirable for managed forest systems, which like our site, are continuously losing Ca, Mg, and K through harvesting and leaching. Increased base saturation has been shown to have both long-term and short-term nutritional benefits for forest soils (2.7). A direct relationship was shown between increased Ca, Mg, and K and plant growth and yield (25). However, other researchers have also shown that macronutrients like Ca, K, and Mg exhibit differential solubility in ash-amended soils (36).

months for the Bh horizon (located at >2 m below surface) to reach pH levels close to those of the surface soil in our study (data not shown). The Bh horizon contains much more colloidal materials, making it more resistant to changes in pH than other horizons. Surface soil pH decreased from above 9.5 to around 8.6 after seven months for all treatments mainly due to leaching of the easily leachable K and Na carbonates that buffer pH at very high values (Fig. 1a).

The pH of the boiler ash used in this study was significantly higher than that of the soil (Table 1). The ratios of Na, K, Ca, and Mg in the ash to that of soil were 650, 267, 190, and 10, respectively (Table 1). Therefore, for the pH and salinity of the soil to go down, a considerable amount of leaching of alkaline-earth and alkaline metal salts in the ash had to take place. The solubilities of the predominant carbonates in the ash are 0.014 g CaCO₃, 0.106 g MgCO₃, 71 g Na₂CO₃, and 1120 g K₂CO₃ per liter of cold water (34). Taking 1300 mm as the average annual rainfall for the site, it would take at least two and half years to leach all the CaCO₃ from the soil assuming no protection of carbonate by soil particles.

The pH of the surface soil decreased and stabilized at approximately 8.6 after the initial seven months (Fig. 1a) due to the presence of CaCO₃. This is consistent with our expectations because K and Na carbonates are much more soluble than Ca and Mg carbonates. There was very little change in pH in the subsequent 14 months showing that the CaCO₃ was still present in the soil in large quantities (~10%). Soil clay and organic matter generally protect carbonate from dissolution. From these soils, the time it takes for the carbonates to leach out completely tends to be much longer than theoretical values indicate (9.35). Most micronutrients precipitate out of solution at this high pH of 8.6. Boiler ash should therefore be applied based on liming equivalent (20% in this case) to avoid this problem.

In addition to pH concerns, the change in electrical conductivity (EC) value must also be considered since high EC reduces plants' ability to take up water and nutrients. In this study, the EC in the surface soil increased by up to two orders of magnitude in all treatments (8.6 to 9 dS m⁻¹) compared to the control of 0.02 dS m⁻¹, indicating significant accumulation of soluble salts in the soil (Fig. 1b). However, up to 50 times reduction in EC in the surface soil was observed after only four months of leaching. Sodium and potassium salts are very soluble and thus leached out quickly, resulting in significant reduction in EC (K decreased from 700 to <200 mg kg⁻¹ in the 1800 Mg ha⁻¹ treatments).

At the end of the monitoring period, the surface treatments still had up to 18 times the EC of the control (0.37 dS m⁻¹ in the 1800 Mg ha⁻¹ surface treatment compared to 0.02 dS m⁻¹ in the control). The EC values of the lower parts of the profile were up to three times higher than those of the surface at the end of the study, indicating that the salts were still migrating through the soil (data not shown). Other researchers have also noted reduction in EC and pH after pre-
lie in the different compositions of the ash used in the two studies. The mobilization of elements from ash into soil leachate was in the order of \( K > Mg > Ca > P \), which is consistent with this study \((40, 41)\).

Although the total amount of \( Ca \) increased significantly \((from 130 \text{ mg kg}^{-1} to about 6190 \text{ and } 14,200 \text{ mg kg}^{-1} \) in the 900 and 1800 \( \text{ Mg ha}^{-1} \) surface treatments, respectively; Table 2), the proportion of available \( Ca \) went down significantly \((from 45\% to less than 5\%)\). Potassium and Mg did not show decreases in relative percentage of plant extractable elements. Plant extractable Mg actually increased with time \((from 1\% to about 30\%; Table 2)\) and this may have been due to its slow release in soil. Calcium and Mg decreased linearly with total rainfall \((Fig. 2a, b)\). Approximately the same amount of \( Ca \) and Mg were lost prior to the first \textit{sampling} \((taken a few weeks after the ash incorporation with
increase (Tables 1 and 2). Manganese also had the second highest availability among the micronutrients (after Zn), ranging from 1 to 7%. The high solubility of Mn in this experiment may be linked to its adsorption on Ca and Mg carbonate surfaces (45) and the dissolution and leaching of MnCO₃ at high pH (31). The high concentrations of plant extractable Zn, ranging from about 4 to 7%, was in agreement with our expectations from the high percentage of available Zn in the ash. This was also in agreement with other published results that show that Zn is easily soluble in soil (46,47). Care must be taken in future applications to reduce the amount of Zn and Mn applied as these may become toxic at high concentrations.

Iron concentrations in the ash amended soils increased from a background concentration of 800 mg kg⁻¹ to 1100 and ~1700 mg kg⁻¹ in the 900 and 1800 Mg ha⁻¹ treatments, respectively (Tables 1 and 2). Both Mn and Fe are essential micronutrients for plant growth but they may become toxic to plants at high concentrations. The ash used in this study had very high concentrations of Mn and Fe (Table 1). However, Fe precipitates under conditions of high pH such as those used in this study. This is manifested in the very low concentrations of plant available Fe (Table 2) and it also explains the low Fe leachability with time. This reduces the toxicity concerns that may arise from the presence of high total concentrations of these elements. However, there may be concerns about Fe toxicity as pH drops with time. Lowering the application rate is a possible solution.

Copper concentrations in surface soil did not change except in the 1800 Mg ha⁻¹ surface treatment (Table 2). Twenty to 30% of this copper was available for plant uptake but this was not enough to warrant any concerns about its toxicity to plants. Pot studies have shown that slash pine plants amended with boiler ash using high application rates may not require additional micronutrients for optimum growth (2,5,26). This is important because the Zn, Fe, Cu, and Mn that is added by ash is used up by plants and an ash application cycle can be developed whereby ash is applied after the added nutrients have been depleted. This allows multiple application of ash to the same land over time. Caution, however, must be taken as the damage of application of these extremely high rates of boiler ash to soil may outweigh its minimal benefits.

CONCLUSIONS

This study showed that addition of boiler ash improved soil physical properties by increasing plant available water, reducing saturated hydraulic conductivity and bulk density in this sandy soil. In addition, boiler ash significantly increased total and available soil micronutrients (Ca, Mg, K, and P) and micronutrients (Fe, Mn, Cu, and Zn) and this was supported by increased plant growth in a separate greenhouse study (26). However, significant increases

88 mm of rain) as were lost during the following three months (372 mm of rainfall). A similar linear pattern was observed in Ca and Mg leaching using eucalyptus ash (40). In our study, the curve gradients in the Ca and Mg graphs were much lower than that of K, which had an exponential decrease due to the higher initial leaching of K salts. Other studies have also shown very high K leachability (38). It is difficult to predict how much rainfall would be needed to leach out all the added elements because other factors relating to soil–metal interactions also come into play.

In general, the base concentrations in the 1800 Mg ha⁻¹ treatments were about double those of the 900 Mg ha⁻¹ treatments (Table 2). There were significant differences between the surface and subsurface treatments at the beginning of the study but the subsurface treatments had lost more metals than the surface at the end of 21 months. This was possibly due to the presence of higher concentrations of fine particles and organic matter in the surface soils than the subsurface soils.

Although there was a five-fold increase in P concentrations in the ash-amended soils, <25% of this P had been lost by the end of the first year (Fig. 2d). This may be attributed to the lower solubility of P under conditions of high soil pH. When P levels were increased (3), there was no increase in plant uptake or improvement in plant growth because phosphate will easily undergo ligand exchange with hydroxylated mineral surfaces and thus become unavailable (42). The low concentrations of plant available P in all treatments (<0.1%; Table 2) is a testimony of this. The high concentrations of Ca in our study may have fixed P as calcium phosphates. A significant increase in P dissolution was observed when ash was mixed with an acid soil (43). Phosphate leaching also occurs when all the hydroxylated surfaces have been saturated by P (due to oversupply) and this may explain the steeper curve in our 1800 Mg ha⁻¹ treatment (Fig. 2d).

Micronutrients

As previously noted, most studies dealing with boiler ash applications do not consider micronutrients due to the low amounts of boiler ash applied (10,44). For example, no changes were observed in trace metal concentrations after application of boiler ash to a Maine forest soil (3). Their application rates were, however, considerably lower than the rates used in this study (~20 Mg ha⁻¹ compared to 900 and 1800 Mg ha⁻¹).

In this study, total concentrations of Zn, Fe, and Mn (Table 2) were significantly elevated following ash application. Manganese concentrations were more than doubled in the 900 Mg ha⁻¹ treatments and quadrupled in the 1800 Mg ha⁻¹ treatments. Among the micronutrients, Mn had the highest concentration in the ash (Table 1) and it had the highest relative concentration
in soil pH and electric conductivity in the soil were undesirable and may adversely impact plant growth. Application of such large quantities of boiler ash also adds significant amounts of trace metals and other elements that may be harmful to plants and/or the environment in general. A separate study on the impact of high-volume ash application on groundwater quality is under review. We strongly discourage the use of high rates in land application of boiler ash in forest soils. Instead agronomic rates based on the calcium carbonate equivalence should be used to reduce the impact on both groundwater and plants.

REFERENCES
