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Wood ash residue causes a mixture of growth promotion and toxicity in *Lemna minor*

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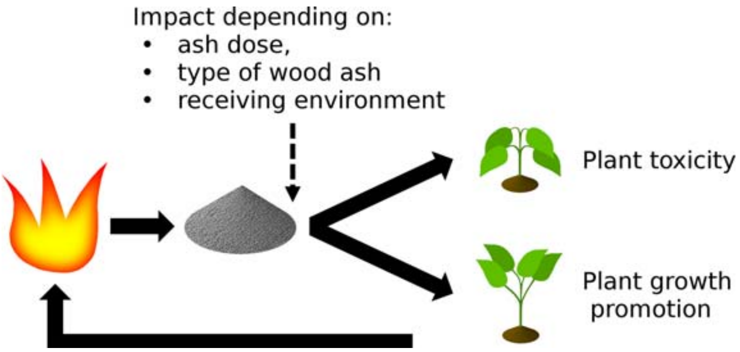
HIGHLIGHTS

- The use of wood as a sustainable biofuel results in generation of wood ash.
- Wood ash solids and leachates contain plant macro-, and micronutrients.
- To inform use of ash, growth enhancing properties were contrasted with toxicity.
- The receiving environment determines the balance of toxicity and growth promotion.
- Ash neutralization increases the margin between growth promotion and toxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of wood as a sustainable biofuel results in the generation of residual wood ash. The ash contains high amounts of plant macronutrients such as phosphorus, potassium, calcium as well as several micronutrients. To explore the potential use of wood ash as a fertiliser, the growth enhancing properties of Sitka spruce (*Picea sitchensis* Bong.) wood ash were contrasted with the potential toxic action, using common duckweed (*Lemna minor* L.) as a model test species. The growth of *L. minor* exposed to wood bottom and fly ash solids and corresponding leachates was assessed in ultra-oligotrophic and eutrophic media. Ash solids and leachates were also tested as neutralized preparations. Suspended ash solids promoted *L. minor* growth up to concentrations of 2.5–5 g/L. Leachates promoted growth up to 10 g ash equivalents per litre, but for bottom ash only. Beneficial effects of wood ash were most pronounced on ultra-oligotrophic medium. However, on such nutrient-deficient medium severe inhibition of *L. minor* biomass and frond growth was observed at relatively low concentrations of fly ash ($EC_{50} = 14$ g/L). On standard, eutrophic medium, higher concentrations of fly ash ($EC_{50} = 21$ g/L), or neutralized fly ash ($EC_{50} = 37$ g/L) were required to impede growth. Bottom ash, or neutralized bottom ash retarded growth at concentrations of 51 g/L and 74 g/L (EC_{50}), respectively, in eutrophic medium. It appears that phytotoxicity is due to the elemental composition of the ash, its alkaline character, and possible interactions between these two properties. Growth promotion was due to the substantial content of plant nutrients. This study underlines the

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importance of the receiving environment (nutrient status and pH) in determining the balance between toxicity and growth promotion, and shows that the margin between growth promoting and toxicity inducing concentrations can be enlarged through ash neutralization.

1. Introduction

The increased use of biofuels as a component of sustainable energy portfolios, results in increased ash production (Demirbas et al., 2009; James et al., 2012; Kuba et al., 2008; Thurdin et al., 2006; Vassilev et al., 2010). This ash consists mostly of inorganic mineral matter, together with smaller amounts of char and organic mineral solids, as well as fluid to gaseous inclusions of both inorganic and organic matter (Vassilev et al., 2013). In order to dispose of large amounts of wood ash, numerous potential after-use options for these complex materials have been proposed and are practised. Inter alia, these include the use of ash for soil fertilization, production of construction materials and sorbents as well as the use of ash for element/mineral recovery (Vassilev et al., 2013). Notwithstanding the valuable plant nutrient content of ash, the bulk of biomass energy ashes is still defined as waste and often disposed of in landfill. Yet, given the increasing scarcity of commercial stocks of some plant nutrients (e.g. phosphate), nutrient recovery needs to be considered.

Minerals contained in ashes originate from bio-accessible sources. Thus, returning such ashes to the original ecosystem is considered by some as re-cycling. Indeed, wood ash applications to, especially, temperate forest ecosystems have been trialled, and impacts on the soil and trees have been assessed (i.e. Mandre et al., 2004; Augusto et al., 2008; Santalla et al., 2011). It has been argued that ash from untreated biofuels (as opposed to timber treated with paint and/or other preservatives) poses a comparatively low contaminant risk to the environment (Demeyer et al., 2001; Emilsson, 2006; Koppejan and van Loo, 2012). However, the chemical composition of biomass ashes can be extremely variable (Pitman, 2006; Vassilev et al., 2010), and some ashes have been shown to contain a considerable contaminant burden (Pöykiö et al., 2009; Vassilev et al., 2010). Therefore, neither the fertilizing-value nor the environmental toxicity of wood ash can be assumed without case assessment.

Modern biomass and solid fuel fired power plants produce two major residue fractions; bottom ash (BA) and fly ash (FA). Additional precipitation techniques (i.e. cyclone or bag filters) allow for further partitioning of the FA. Although different ash types accrue in separate parts of the furnace, the waste streams are commonly combined and both ashes are collected in a single waste bay. As a result few studies distinguish the two prime ash types (Park et al., 2012; Poykio et al., 2011; Steenari et al., 1999). Rather, the literature on wood ash composition and recycling describes either the composite material (Augusto et al., 2008; Demeyer et al., 2001; Etitgni and Campbell, 1991; Pitman, 2006; Someshwar, 1996), or just one ash fraction (Aronsson and Ekelund, 2006; Pöykiö et al., 2009; Steenari and Karlfeldt Fedje, 2010). Data on both the toxicity and growth promoting potential of these distinct types of ashes from clean (i.e. un-treated) wood fuel are scarce. Such data are important to inform policies for the recycling of clean wood ash (i.e. see Emilsson, 2006; Haglund, 2008).

Standardised ecotoxicological testing of the impacts of ash on terrestrial organisms is common practice, and typically involves testing the mobile fraction, for example water based ash leachates (Barbosa et al., 2013; CEN, 2002; Jenner and Janssen-Mommen, 1993; Lapa et al., 2002; Tsiridis and Samaras, 2006; Wadge and Hutton, 1987). Wood ash leachates may naturally occur following heavy rain and flooding and in a "worst case" scenario can be leached into downstream waterbodies. Similarly, suspended, solid wood ash can end up in the aquatic environment. Given the complexity of ash, leached compounds may not be the only ones determining environmental effects. Mineral, as well as organic matter from ash, have also been shown to adsorb and precipitate dissolved elements and compounds, thus potentially altering the native nutrient balance in the soil (Chirenje et al., 2006; Chojnacka and Michalak, 2009).

Standard aquatic toxicological testing has been used to quantify wood ash impacts on a range of species (Barbosa et al., 2013; Stiernström et al., 2011). However, standardised testing with photoautotrophic models (i.e. plants and algae) is based on supplying non-limiting nutrient levels to a media, which will therefore mask any growth stimulating effect of ash. The additional use of a nutrient-poor medium allows the assessment of such growth stimulating (i.e. fertilizing) properties. The alkaline pH of wood ash creates a further dilemma for ecotoxicological assessments. The validity of standardised toxicological test results is typically conditional upon the pH being within the defined range of the test organism tolerance. Therefore, the pH of non-neutral waste extracts is commonly adjusted to pH 6–8 (Lapa et al., 2002; OECD, 2006; Römbke et al., 2009). This practice is inadequate when assessing the toxicity of highly alkaline ash to be reintroduced to the natural environment, as any pH dependent risk will be underestimated, while pH dependent changes in solubilisation and speciation may be promoted (Barbosa et al., 2013).

This study set out to assess growth stimulating and toxic effects of clean wood ash on the primary producer *Lemna minor* (L.). It is hypothesised that (i) growth stimulating and toxic effects of wood ash can be separated based on their concentration dependence, and (ii) that both types of effects are moderated by the specific receiving environment. The study assesses these effects under different trophic conditions, using both native and pH neutralized solid ash and ash leachate (Fig. 1), to generate a comprehensive overview of the potential impacts of ash recycling on this plant species. Results will be discussed in the context of recent wood ash recycling recommendations.

2. Material and methods

2.1. Characteristics of wood ash and corresponding leachates

Origin and sampling

The wood ash was collected from the conveyors of a 3.8 thermal MW rotating grate wood boiler, located at a commercial sawmill in Co. Cork, Ireland. The wood-fuel comprised a mixture of Sitka spruce sawdust, wood chips and bark shavings (sawmill wood processing residues) which was burned at 700–800 °C. The wood burned in the boiler was sourced locally in south-west Ireland. Bottom ash (BA) accrues below the firing grates at the base of the boiler. This type of ash contains heavy, large constituents such as clinker agglomerates and chunks of char in addition to small, powderous particles. Fly ash (FA) was collected from the post-furnace filter system where it had been transported with the flue gas. In contrast to bottom ash, fly ash consists of powderous, light weight ash and small char particles. Ash samples were stored in opaque 50 L barrels (HDPE, with clamp top lid) in a sheltered area at ambient temperature.

Physico-chemical analyses

Particle size distribution of bottom and fly ash was analysed in the range between 63 μm and 6.3 mm by dry sieving according to Deutsche Industrie Norm 18123 (DIN, 1996). Analysis of loss on ignition (LOI) at 500 °C was performed for bulk ash samples following DIN 18128 (DIN, 2002). Ash sub-samples for each replication and leachate were dried at 30 °C for 3–4 days until the weight remained constant, and the particle fraction >4 mm was removed. Leachates were prepared according to the European Norm (EN) 12457-2 one stage leaching test for granular