

Amelioration Potential of Biomass-Derived Ashes in Agroecosystems

Gabrijel Ondrasek

University of Zagreb, Faculty of Agriculture, Svetosimunska c. 25, R. Croatia

*Corresponding author: gondrasek@agr.hr

Abstract

Bioash (mineral residue left after oxidation of different biomass) is physicochemical complex, ultra-alkaline, and potentially hazardous waste, with a huge potential to become value-added products for; i) chemical amelioration of acid and nutrient-deficient soils in agro-/forest-ecosystems, ii) wastewater purification and iii) civil and bio-tech engineering. It was confirmed that finely-powdered bioash structure is the main operational management obstacles for its use in land amelioration; hence, specifically designed forms (e.g. pellets, microspheres, emulsions, granules) are needed to temporarily stabilized the bioash reactive form(s), making them more applicative. In addition, application and relatively low bioash rates (e.g. several tons per ha) can induce significant perturbations in targeted (cultivated crops/forests, removal of pathogens) and adjunct (bacteria, fungi) biota. Overall, bacteria responded more pronouncedly to ash amendment than fungi. However, amendment effects vary depending on the properties of both the ash and the target soil, so these aspects need to be considered closely.

Key words: Bioash, Acid soils, Chemical amelioration, Soil conditioner, Solid waste

Introduction

The reduction in greenhouse gas emission decarbonisation and promoting bio-renewables, especially forest/agro biomass, has resulted in an increased use of biomass-derived energy sources. However, one of important environmental issue arising from such progressive increase in the amount of biomass used for renewable energy generation is an increase in biomass-derived ash (bioash) waste material (Ondrasek *et al.*, 2021a). However, bioashes as alkaline and mineral-enriched waste co-products have multi-benefit advantages for reusing as soil conditioners in chemical amelioration of agro-/forest-ecosystems and some other sectors (e.g. civil and bio-tech engineering, construction, waste management) (**Figure 1**).

It was confirmed that physicochemical properties of bioash are closely related to their feedstock composition and combustion parameters. For instance, combustion temperatures $>400^{\circ}\text{C}$ increase the levels of bioash carbonisation and promote the aromatic condensation of degraded aliphatic groups, followed by losses of O_2 , H and N atoms during dehydration and decarboxylation processes (Ondrasek *et al.*, 2021a). A pH reaction of wood-derived bioashes is generally strongly alkaline (11.8–13.1), mostly due to a high content of alkaline oxides (e.g. in %; $\text{CaO} >47$, $\text{SiO}_2 >12$, $\text{K}_2\text{O} >11$, $\text{MgO} >4$; Ondrasek *et al.*, 2021a).



Figure 1: Bioashes and their potential for reuse to sustain ecosystem services and underpin circular economy

In comparison with coal ashes, bioashes usually have lower abundance of S-containing minerals (e.g. arcanite – K_2SO_4), making them highly effective in reclamation of soil acidity, nutrient deficiency, and immobilization of potentially toxic metals and/or metalloids.



Bioash effects on soil pH and nutrients recovery

Numerous studies have been conducted using diverse bioash matrices (e.g. fly ash, bottom ash), revealing positive effects of bioash application on pH and nutrient recovery as well other pedovariables. For instance, controlled experiments confirmed strong basic reaction of wood ash leachates (pH 12-13) (Cabral *et al.*, 2008; Freire *et al.*, 2015) as a result of hydrolysis, dissolution and weathering of dominantly alkaline oxides, hydroxides, carbonates, bicarbonates, silicates, silanols and other metal salts (Doudart de la Grée *et al.*, 2016; Vassilev *et al.*, 2013) capable of displacing exchangeable H^+ , Al^{3+} and/or Mn^{2+} from the soil CEC (Maresca *et al.*, 2018; Shi *et al.*, 2017) or even removing some of them (e.g. Al^{3+}) as precipitates down the soil profile (Li *et al.*, 2010). Consequently, bioashes neutralise strongly and rapidly different acidic soils, and increase availability of most macro/micronutrients in soils. Recently was shown that fly bioash addition can strongly rise soil pH_{KCl} (up to 9.1), and the content of most phytonutrients (up to 5.4-fold); however its addition at >1.25% can restrict the maize root and shoot growth, likely due to alkaline stress as indicated by necrotic and chlorotic symptoms at >5.0% rate (Ondrasek *et al.*, 2021b). In addition, fly bioash increased total concentration of metals in soil (without exceeding the levels recognized as contamination), whereas phytoextraction of Cd, Zn, Mn, Cu and Mo was significantly suppressed (Cd by almost 12-fold), confirming that fly bioash improved soil-plant metal immobilization, shifting rhizosphere biogeochemistry towards chemisorption reactions (Ondrasek *et al.*, 2021b).

Some studies showed that bioashes induce stronger and faster pH recovery as well as higher acid neutralizing capacity (ANC) than other liming materials (e.g. limestone, dolomite) (Cabral *et al.*, 2008; Ondrasek *et al.*, 2020; Ondrasek *et al.*, 2021c). These findings can be explained highly reactive and developed surface and chemically/mineralogically more complex bioash matrix (vs. dolomite/lime) and ii) domination of the more reactive hydroxide fraction (in ash) over relatively slowly reactive carbonate fraction (in dolomite/lime).

Additionally, bioash matrices have a huge potential for further improvements to optimize their use as soil conditioners/fertilizers. For instance, (Zhao *et al.*, 2019) showed that different bioashes can be qualitatively improved if co-incinerated with sewage sludge, resulting in transfer of relatively poorly available P ($AlPO_4$) to its more readily-available mineral forms [e.g. $Ca_2P_2O_7$, $Ca_5(PO_4)_3Cl$,

$Ca_4Mg_5(PO_4)_6$ and $Ca_3(PO_4)_2$] that are highly desirable in fertilizers/soil amendments. The content of other macronutrients such as N (which is lost to the atmosphere in gaseous forms during combustion) can also be boosted in bioash materials. By mixing wood- and peat-derived fly ash with an appropriate proportion of sewage sludge and lime, (Pesonen *et al.*, 2016) created fertilizer aggregates with N content increased by more than an order of magnitude (e.g. from 120 to 2690 mg N/kg).

Bioash effects on soil microbiomes

Given that wood ash has been used as a soil amendment for several decades, many studies have investigated its impact on the soil microbial communities that play a key role in nutrient cycling, plant growth and carbon sequestration (Fierer, 2017). Ash amendments were shown to increase microbial activity as measured by soil CO_2 production (Bååth and Arnebrant, 1994, Khanna *et al.*, 1994), as well as microbial biomass turnover or growth rate (Lupwayi *et al.*, 2009) and nutrient cycling (Perkiömäki and Fritze, 2005; Saarsalmi *et al.*, 2012). In addition, ash addition changed soil bacterial abundance (Bååth and Arnebrant, 1994; Bang-Andreasen *et al.*, 2017; Vestergård *et al.*, 2018). However, some of these effects were recorded only after high application rates or repeated applications of ash (Omil *et al.*, 2013; Pennanen, 2001). In addition to stimulating microbial abundance and activity, the application of ash typically altered soil bacterial community structure (Liiri *et al.*, 2002; Lupwayi *et al.*, 2009; Mahmood *et al.*, 2003; Perkiömäki *et al.*, 2003) or total microbial community structure (Perkiömäki and Fritze, 2005). For instance, by using 16S rRNA gene amplicon sequencing, (Bang-Andreasen *et al.*, 2017) and (Noyce *et al.*, 2016) reported shifts in the soil bacterial community composition after wood ash application, with the enrichment of copiotrophic bacterial groups such as *Bacteroidetes* and a decline in oligotrophic phylum such as *Acidobacteria*. In contrast to (Noyce *et al.*, 2016) who found no difference in the bacterial community with increasing ash addition from 0.7 to 5.7 t ha⁻¹, (Bang-Andreasen *et al.* (2017) found more pronounced effects with increasing ash addition rate from 5 t ha⁻¹ (the current legislation threshold in Scandinavian countries) to 22 t ha⁻¹. However, detrimental effects on soil bacteria were observed only at an extreme, unrealistic rate of 167 t ha⁻¹, with alkaliphilic genus *Alcalibacterium* and spore-forming bacteria dominating.

In addition, some studies revealed that the fungal communities showed only minimal responses to ash

addition compared to bacterial communities (Bang-Andreasen *et al.*, 2020; Mahmood *et al.*, 2003; Noyce *et al.*, 2016). Other studies found that addition of high rates of ash to soil increased fungal abundance (Bååth *et al.*, 1995; Bang-Andreasen *et al.*, 2020), especially the abundance of fast-growing saprotrophic fungi such as the genera *Mortierella* and *Peziza* as well the order Hypocreales (Bang-Andreasen *et al.*, 2020). Compared to free-living fungi, the impact of ash on ectomycorrhizal (EM) and arbuscular mycorrhizal (AM) fungi, which make symbiotic associations with plant roots improving plant nutrient uptake, remains less clear. Several studies reported changes in EM fungal species composition after wood ash applications. Typical acidophilic species such as *Tylospora fibrillosa*, *Piloderma croceum* and *Russula ochroleuca* decreased in relative abundance, whereas that of species from genera *Amphinema* and *Tuber* increased (Kjøller *et al.*, 2017; Klavina *et al.*, 2016; Mahmood *et al.*, 2002; Taylor and Finlay, 2003). In contrast, (Cruz-Paredes *et al.*, 2019) did not observe a change in the EM fungal community composition after adding up to 6 t ha⁻¹ of wood ash, possibly because the applied doses, which were within the recommended dosage range, were much lower than high doses in other studies, e.g. 50 t ha⁻¹ in (Klavina *et al.*, 2016). Despite above-mentioned changes in microbial activity and community composition, some studies showed no, or only minor, microbial response to wood ash addition (Aronsson and Ekelund, 2004; Huotari *et al.*, 2015). However, given a prolonged impact of ash (e.g. nearly 14 years after application of silico-aluminous/sulfo-calcic fly ash (Leclercq-Dransart *et al.*, 2019); or 30-52 years after application of wood bioash (Moilanen *et al.*, 2006; Saarsalmi *et al.*, 2012), long-term field studies in different pedo-conditions are highly desirable to underpin elucidation of ash-induced changes to soil microbiomes.

Bioash effects on other pedovariables

Bioashes contain a relatively high proportion of Si and its pozzolanic forms and thus can have beneficial effects on physico-mechanical variables in texture-heavy clayey soils. For instance, addition of fly ash (up to 15% w/w) in clay soil significantly reduced the bulk density and improved the soil structure, i.e., porosity, workability, root penetration and water retention (Sahu *et al.*, 2017), and modestly improved soil hydraulic conductivity (Chang *et al.*, 1977). Application of the S-Ca and Si-Al fly ashes was shown to be effective in lowering soil bulk density in the long term, i.e., even around 14 years after amending the soil (Leclercq-Dransart *et al.*, 2019). In highly expansive

and plastic or soft soils (e.g. sensitive to variations in water content, showing strong volumetric changes as cracking/shrinkage), use of different ashes stabilized the soil and improved consistency, reduced plasticity index (i.e. free swelling and compressibility), and decreased soil dry density, making it coarser than original soil (Jafer *et al.*, 2018; Mir and Sridharan, 2013). For wider practical application and amelioration of hydraulic and mechanical soil properties, the durability and long-term impacts of bioashes under different field-relevant conditions should be validated further.

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