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Brigitte A. Knapp
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Preface

Meaningful Use of Biomass Ashes: Closing the Cycle

Biomass ash is the solid residue from the combustion of plant biomass which is increasingly being used for heat and electricity production. Biomass ash contains a wealth of macronutrients and micronutrients. Despite the value of the various elements contained in the ashes, their disposal in landfills is still common practice, generating considerable costs for biomass plant operators and negating the recycling potential of ashes. A prerequisite for sustainable use of ashes in agriculture and forestry, however, is their quality in terms of nutrients, on the one hand, and of heavy metals and organic pollutants, on the other. Appropriate combustion and separation techniques to obtain qualitatively valuable ash fractions are thus highly desirable.

To bring together knowledge and ideas on the reutilization of biomass ashes, the conference "Recycling of Biomass Ashes" was held in Innsbruck in March 2010, focusing on various recycling technologies for biomass ashes. This book comprises 11 chapters that are based on selected conference contributions. An introductory chapter by Insam and Knapp gives an overview of current technologies and future needs for ash recycling. In Chap. 2 (Schiemenz et al.), the virtue of ashes as a phosphorous source is emphasized. In Chaps. 3, 5 and 6, nutrient-related aspects of ashes from wood (Haraldsen et al. and Omil et al.) and olive residues (Nogales et al.) are addressed. Nieminen in Chap. 4 addresses the effect of wood ash on the soil fauna. Bougnom et al. in Chap. 7 and Sarabèr et al. in Chap. 8 discuss the potential of tropical acid soil melioration with ashes (from wood and cocoa residues, respectively). In Chaps. 9 and 10, Mödinger and Berra et al. elaborate on the potential of wood ash use in brick making and in the cement industry, respectively. Ash recycling as a puzzle stone in a sustainable society is addressed by Ribbing and Bjurström in Chap. 11.

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Innsbruck, Austria

Heribert Insam
Brigitte A. Knapp

Contents

Chapter 1
Recycling of Biomass Ashes: Current Technologies and Future Research Needs

Brigitte Amalia Knapp and Heribert Insam

Abstract Biomass ash is a final by-product from biomass incineration and is being produced in increasing amounts. Ash contains a variety of macronutrients and micronutrients and thus requires an appropriate recycling strategy. This chapter addresses various recycling strategies and technologies, with a particular focus on a smart combination of wastes from different sources for optimising recycling efficiency.

1.1 Introduction

Biomass ash is the solid residue accumulating from the thermal combustion of plant biomass for heat and electricity production, containing a variety of macronutrients and micronutrients resistant to incineration. As combustion of biomass is among the dominant bioenergy applications worldwide, increasing numbers of biomass-based power plants are being built and thus vast quantities of ashes are produced. Despite the value of the various elements contained in the ashes, their disposal in landfills is still common practice, generating considerable costs for biomass plant operators and negating the recycling potential of ashes. A prerequisite for sustainable use of ashes in agriculture and forestry, however, is their quality in terms of heavy metal contents and organic pollutants. Appropriate combustion and separation techniques for the different ash fractions are thus highly needed.

To bring together knowledge and ideas on the reutilisation of biomass ashes, a conference entitled "Recycling of Biomass Ashes" was held in Innsbruck in March 2010, focusing on various recycling technologies for biomass ashes. The conference sessions were targeted at the use of ashes as fertiliser or a supplement for organic and inorganic fertilisers as well as their combination with compost and anaerobic sludges. Further, ash amendments to forest soils were a major topic, as was the use of ashes for geotechnical constructions and industrial processes.

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Moreover, national and international policies regulating the application of ash were presented and joint programmes for advancing knowledge in the field of ash recycling were discussed.

In the following chapters an overview of different fields of application for biomass ashes is presented, summarising current knowledge on the reutilisation of biomass ashes and highlighting future research needs. As most investigations on ash recycling are based on wood ash, this chapter will focus on ash produced from wood combustion.

1.2 Characterisation of Ash

During incineration of wood and other types of plant biomass, a solid residue is formed, representing about 2% (e.g. willow wood) to 20% (e.g. rice husks) of the input material (Jenkins et al. 1998). Depending on the plant species, the origin of plant, the plant parts used for combustion, the process parameters during incineration and the storage conditions of combustion residues, ashes differ considerably regarding their physical and chemical properties (Demeyer et al. 2001). These characteristics determine the quality of different ash types and their suitability for further applications (Karltun et al. 2008). Moreover, different treatments after combustion (self-hardening, thermal treatment or hardening with the addition of a binding material such as a potassium silicate) affect leaching properties of the ash. Ash pellets with a denser structure and a smaller specific surface area display lower leaching rates (Mahmoudkhani et al. 2007). The application form of biomass ash is of great concern, as untreated ash is difficult to apply evenly to soil and may lead to burning of the plant surfaces. Pretreatment of ash may thus be necessary to prevent such damage by lowering the reactivity of the ash. Pretreated ash products are assumed to be more suitable for application purposes, result in less dust formation during spreading, facilitate even spreading and prolong the fertiliser effect owing to slower decomposition rates (Sarenbo et al. 2009).

1.2.1 Wood Ash Composition

Although carbon (C) is mostly oxidised and nitrogen (N) is emitted in the form of gaseous compounds during combustion, most other elements present in the plant material are retained in the ash (Steenari et al. 1999). Wood ash mainly consists of calcium, potassium, magnesium, silicon, aluminium, phosphorus, sodium, manganese and sulphur, whereas it is N-deficient. Trace elements found in wood ash are iron, zinc, arsenic, nickel, chromium, lead, mercury, copper, boron, molybdenum, vanadium, barium, cadmium and silver, again found in varying concentrations in different types of wood ash (Demeyer et al. 2001; Karltun et al. 2008). The behaviour patterns of these elements differ considerably, as some elements are partially or completely volatilised during combustion, whereas others are retained to a high degree (Miller et al. 2002). Owing to the incomplete combustion of biomass, remaining C can be found in the ash to some extent, usually as charcoal (Karltun et al. 2008). Whereas the amounts of K, S, B, Na and Cu were reported to decrease with furnace temperature, the amounts of Mg, P, Mn, Al, Fe, Si and Ca were not affected by temperature (Misra et al. 1993). However, these effects depend on the tree species incinerated (Pitman 2006). Moreover, a lack of standardisation concerning the methods used for the assessment of major and minor ash-forming elements causes further divergences (Baernthaler et al. 2006).

1.2.2 Heavy Metals and Organic Pollutants in Wood Ash

The heavy metals that may accumulate in wood ash are of special concern when it is used for fertilisation purposes. Compared with coal ashes, ashes derived from wood are lower in heavy metals, but are more alkaline (Campbell 1990). High concentrations of As, Cd, Cr, Pb, Zn and Cu may, however, occur owing to the incineration of surface-treated waste wood and wood treated with industrial preservatives (Krook et al. 2006). Cu concentrations in biomass ashes were frequently shown to exceed critical values according to national regulations in Austria (Neurauter et al. 2004) and Germany (Ministerium für Umwelt und Verkehr Baden-Württemberg 2003). Average Cu contents found in three studies dealing with ash composition are illustrated in Fig. 1.1 (Neurauter et al. 2004; Niederberger 2002; Tóthóva 2005). Whereas the incineration of pure wood led to moderate Cu concentrations in the resulting ash, high Cu contents were found when other biomass, especially roadside greenery and material derived from wood processing, was combusted together with natural wood (samples 9, 10).

Wood ash is better applicable for fertilisation purposes if it is separated into fly and bottom ash during combustion, as heavy metals – except for Zn – accumulate in the fly ash (Pitman 2006; Stockinger et al. 2006). Fly ash is the lightest fraction formed during combustion, being deposited within the boiler or in the filters (Pitman 2006). Ashes may also include organic pollutants such as polychlorinated dibenzodioxin, biphenyls, dibenzofuran and polycyclic aromatic hydrocarbons (PAHs), which are of interest because of their toxic, mutagenic and carcinogenic effects (Lavric et al. 1994; Enell et al. 2008). High amounts of PAHs are ascribed to a poor combustion performance (Sarenbo 2009). Wood ashes may pose a risk not only because of the direct input of organic pollutants, but also because a rise in soil pH following wood ash amendments enhances remobilisation of PAHs and polychlorinated biphenyls (Bundt et al. 2001). An elevated pH also affects metal solubility in soil; however, changes in solubility do not necessarily correlate with incorporation of heavy metals in plants grown on the respective soils (Dimitriou et al. 2006). Another essential issue in regard of ash amendments to soils is leaching of toxic substances to the groundwater (Williams 1997), especially in combination with an elevated pH and high Na content (Morris et al. 2000). Leaching is frequently evaluated in laboratory tests, but

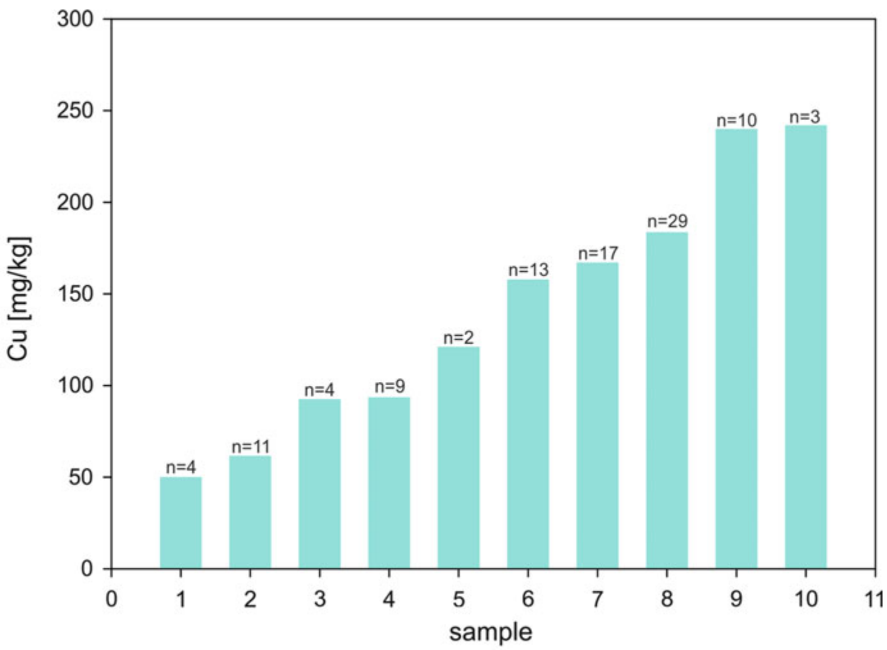

Fig. 1.1 Cu concentration (mg/kg) detected in a variety of ash samples derived from plain wood incineration, or combined incineration of wood with other biomass. (Data compiled from Neurauter et al. 2004, sample 4; Niederberger 2002, samples 5–10; Tóthóva 2005, samples 1–3)

these tend to overestimate or underestimate *on-site* leaching processes and thus it is difficult to assess the real situation in the field (Reijnders 2005).

1.3 Areas of Application for Wood Ashes

As versatile as wood ash is, its potential areas of application are:

- Ash application in forest ecosystems

  Wood ash is commonly applied to forest ecosystems to return nutrients extracted through whole-tree harvesting and to counteract soil acidification (Sect. 1.3.1).

- Wood ash as fertiliser or fertiliser supplement in agroecosystems

  Wood ash rich in nutrients but displaying a low concentration of heavy metals or organic pollutants is also suitable as fertiliser or fertiliser supplement for agricultural and horticultural purposes (Sect. 1.3.2).

- Wood ash for geotechnical constructions and industrial processes

Typical applications in this field are the construction of roads and parking areas, the use of ash as a surface layer in landfills and admixture of ash for concrete, brick or cement production (Sect. 1.3.3).

1.3.1 Ash Application in Forest Ecosystems

The effect of wood ash application on forest ecosystems has been intensively studied in northern European countries where ash is used as fertiliser in boreal forests (Aronsson and Ekelund 2004). Owing to extensive forest harvesting (especially whole-tree harvesting), reuse of ashes was established to avoid base element depletion of forest soils, leading to increasing acidity as well as decreasing amounts of nutrients and organic matter in the soil, thus threatening forest productivity (Stupak et al. 2008).

1.3.1.1 Effects of Wood Ash Application on Soil Properties

Wood ash is applied to forest soils to alleviate nutrient depletion and soil acidification, either alone or in combination with N fertiliser. Wood ash is also applied as lime replacement, providing base cations to increase soil pH (Steenari et al. 1999; Meiwes 1995; Brunner et al. 2004). This liming effect can be attributed to Ca and Mg carbonates in the ash as well as to its fine structure (Pitman 2006). Arvidsson and Lundkvist (2003) observed an increased soil pH after 3 Mg ha^{-1} wood ash application in young Norway spruce (*Picea abies*) stands. Moreover, concentrations of exchangeable Ca and Mg as well as the effective cation-exchange capacity were elevated compared with the control. As salts contained in the ash started to dissolve after application, high K, Na and SO_4 concentrations were also found in the soil (Augusto et al. 2008). Jacobson et al. (2004) reported an increased soil pH and base-cation content 5 years after amendment with self-hardened and crushed ash (3, 6 or 9 t ha^{-1}) or pelleted ash (3 t ha^{-1}) on two different coniferous sites in Sweden, whereby the ash formulation did not have an effect on soil chemistry despite differences in solubility. Basic substances used to amend soil may, however, foster nitrification and nitrate leaching in soil ecosystems and hence enhance soil acidity, counteracting the positive effects of wood ash application (Meiwes 1995). Since ash components bind to organic substances in the humus layer of forest soils, fertilisation effects of wood ash amendments on soil acidity and extractable Ca and Mg were found to last for many years (Bramryd and Fransman 1995; Saarsalmi et al. 2001, 2004, 2005; Mandre et al. 2006). The impact of wood ash applications (9 and 18 Mg ha^{-1}) on soil properties in different tree stands (European larch, aspen and poplar) was evaluated in a 7-year experiment in Michigan, revealing that wood ash was able to foster long-term productivity and repeated applications may even have the potential to make up for biomass-C losses due to plantation management operations (Sartori et al. 2007).

1.3.1.2 Effects of Ash Amendments on Trees and Ground Vegetation in Forest Ecosystems

When looking at the effect of wood ash amendments on tree growth in Nordic countries, Augusto et al. (2008) revealed a considerable site dependency using a meta-analysis approach. Whereas wood ash was not able to improve tree growth on mineral soils, it had a significant effect on trees planted on organic soils. Reviewing different studies from Finland, Sweden and Switzerland with regard to the impact of wood ash applications on tree growth and vitality, Lundström et al. (2003) reported neutral or even negative effects of ash fertilisation. Investigating the effect of hardened wood ash application (up to 3 Mg ha^{-1}) on ground vegetation in young Norway spruce stands on mineral soils, Arvidsson et al. (2002) found that biodiversity and plant biomass were not affected. In a Swiss forest, fine roots of spruce were influenced by ash application (4 t ha^{-1}) on mineral soil, whereby ash fertilisation enhanced the number of root tips, forks and the root length, but resulted in decreased root diameters (Genenger et al. 2003). In a set of field experiments applying wood ash (1–9 Mg ha^{-1}) on 30–60-year-old Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) Karst.) stands on mineral soil in Sweden, stem growth was only promoted when N (150 kg ha^{-1}) was added, whereas wood ash amendments without N did not lead to significant responses (Jacobson 2003). The same was true for combined wood ash and N applications on a Scots pine (*Pinus sylvestris*) stand on a low-productivity mineral soil, where wood ash plus N positively influenced tree growth even 20 years after application. Nitrogen fertilisation alone only led to a short-term effect (Saarsalmi et al. 2006). Whereas wood ash or sludge application alone did not have any influence on the structure of a commercial willow plantation in central Sweden in a 3-year experiment, harvestable shoot biomass was increased by a combined sludge (2.6 t ha^{-1}) and ash (5.5 t ha^{-1}) treatment and thus gave results comparable to fertilisation with mineral fertiliser corresponding to 14.5 kg P ha^{-1} $year^{-1}$, 48 kg K ha^{-1} $year^{-1}$ and 100 kg N ha^{-1} $year^{-1}$ (Adler et al. 2008). However, this treatment showed negative effects on wood fuel quality concerning P, K and heavy metal concentrations in the bark and wood. Plant growth or biomass production was also not influenced by wood ash fertilisation (10 and 20 Mg ha^{-1} for 3 years) in a willow plantation on a silt loam soil in the state of New York (Park et al. 2005). In this experiment, wood ash did not have an impact on nutrient concentrations of foliar, litter and stem tissue, whereas the concentrations of soil-extractable P, K, Ca and Mg were significantly higher than in control plots. In contrast, Moilanen et al. (2002) observed a positive effect of ash fertilisation (8 and 16 t ha^{-1}) on tree volume growth even 50 years after amendment on a drained peat mire, being accompanied by elevated nutrient concentrations in the peat.

The results presented are attributed to the fact that ash is low in N, which is the main limiting element for plant growth on mineral soils in boreal forests. In contrast, ash fertilisation was considered to be more suitable for peatland forests displaying higher N contents (Hånell and Magnusson 2005) and was found to promote tree growth (height, diameter and biomass) of a young *Pseudotsuga menziesii* plantation and a *Pinus radiata* plantation on N-rich mineral soil in

Spain (Solla-Gullón et al. 2006, 2008). Besides enhanced stem-wood growth of Norway spruce, Rosenberg et al. (2010) also observed increased CO_2 evolution rates even 12 years after wood ash applications (6 Mg ha^{-1}) on a N-rich soil, indicating that ash amendments of N-rich sites have to be evaluated carefully regarding their effect on C and N cycling.

1.3.1.3 Effects of Ash Amendments on Soil Microorganisms

Fertilisation of coniferous forest soil with wood ash (5 t ha^{-1}) was demonstrated to affect microbial biomass (on the basis of phospholipid fatty acid analysis). Fungi reacted more sensitively to wood ash treatment than bacteria, which was reflected by decreasing fungal-to-bacterial phospholipid fatty acid ratios (Baath et al. 1995). Because ectomycorrhizal fungi are known to play an important role in the nutrient supply of trees, Hagerberg and Wallander (2002) investigated the effect of wood ash amendment on a Norway spruce forest floor and revealed an increase in ectomycorrhizal biomass. The ectomycorrhizal fungus *Piloderma* sp. was found to frequently colonise granulated wood ash in a wood-ash-fertilised spruce forest, suggesting a direct impact on nutrient mobilisation (Mahmood et al. 2001, 2002). *Piloderma* sp. was moreover assumed to affect short-term storage of Ca derived from wood ash granules, whereas no effect on P storage or release was discovered (Hagerberg et al. 2005). Gaitnieks et al. (2005) reported a positive effect of wood ash (6 t ha^{-1}) on *Suillus* sp. when it was applied prior to planting of Scots pine seedlings; this was accompanied by increased root and needle biomass of the seedlings.

In a long-term study on different forest sites, wood ash fertilisation (5–8 t ha^{-1}) led to increased CO_2 production caused by enhanced microbial activity but did not influence N_2O emissions, although nitrification and denitrification may have been affected by wood ash application (Maljanen et al. 2006a, b). This effect was shown by Ozolincius et al. (2006) in a *Pinus sylvestris* stand in Lithuania, revealing an increase of ammonifying, nitrifying and denitrifying microorganisms after wood ash application (1.25–5 t ha^{-1}). In contrast, Saarsalmi et al. (2010) did not find changes in net nitrification when investigating the effect of wood ash (3 t ha^{-1}) combined with N (0.15 t ha^{-1}) on soil microbial processes in two coniferous stands in Finland 15 years after application.

1.3.1.4 Effects of Ash Amendments on Soil Fauna

Wood ash application at rates of 1 and 5 t ha^{-1} in a Scots pine stand in central Finland decreased numbers of the enchytraeid worm *Cognettia sphagnetorum*, and slightly changed the soil microarthropod community. Soil chemical parameters were also influenced by these treatments, whereas microbial communities were only affected by the higher ash concentration (Haimi et al. 2000). Enchytraeid size and abundance were found to be reduced in microcosms containing 30 g humus from a Norway spruce forest and amended with 480 mg wood ash, but the negative effect could be offset by sucrose, indicating that the impact of wood ash on soil animals in forest ecosystems is mainly linked to C input rates. Negative effects may thus be avoided by minimising C limitations for decomposers (Nieminen 2008; see Chap. 4, Nieminen 2011).

1.3.1.5 Contamination Risks Through Wood Ash Application in Forest Ecosystems

Heavy metal concentrations have to be considered when wood ash is recycled to forests; thus, the quality of the applied ash is of great concern to avoid accumulation of heavy metals in the environment (Stupak et al. 2008). In a microcosm experiment performed by Fritze et al. (2000), Cd derived from wood ash application on forest soils did not show any harmful effects on the microbial activity or fungal and bacterial community structure. In the same experiment, ash treatments were found to induce a shift in archaeal community patterns, whereas Cd alone or with ash did not have an influence (Yrjälä et al. 2004). When looking at the heavy metal contents of forest berries (*Rubus chamaemorus*, *Vaccinium vitis-idaea*, *Vaccinium uliginosum*) or mushrooms (*Russula paludosa*, *Lactarius rufus*, *Lactarius trivialis*, *Suillus variegates*, *Paxillus involutus*) on different Finish forest sites after wood ash fertilisation (4–14 t ha^{-1}), Moilanen et al. (2006) observed no accumulation of heavy metals or even a decrease in the long term. Similar results were found in six *Pinus radiata* plantations repeatedly fertilised with 4.5 t wood ash per hectare in northwestern Spain, leading to a decrease of Zn, Cu and Cd levels in some mushroom species, which was attributed to an increase in soil pH. Only Mn concentrations were elevated in all mushroom species investigated (*Amanita muscaria*, *Russula sardonia*, *Tricholoma pessundatum, Laccaria laccata*, *Micena pura*, *Suillus bovinus*, *Xerocomus badius*). Heavy metals did not accumulate in tree needles or ground vegetation (Omil et al. 2007). Another aspect of recycling ashes back to the soil is the accumulation of ^{137}Cs (Hedvall et al. 1996). However, application of wood ash at a level of 3.0 and 4.2 kg ha^{-1} contaminated with 30–4,800 Bq ^{137}Cs per kilogram on different coniferous forest sites in Sweden did not significantly increase radioactivity in the biological system (soil, field vegetation, tree parts) when measured 5–8 years after ash amendment, which was partly attributed to the antagonistic effects of wood ash K on ^{137}Cs (Högbom and Nohrstedt 2001). This finding was confirmed in a 100-year-old Scots pine (*Pinus sylvestris* L.) stand on Fe podsol in central Finland, on which ash fertilisation (1, 2.5 and 5 t ha^{-1}) led to a reduction of ^{137}Cs concentrations in lingonberries (*Vaccinium vitis-idaea* L.) analysed 2 and 7 years after application of ash (Levula et al. 2000).

1.3.2 Ash as Fertiliser or Fertiliser Supplement in Agroecosystems

Wood ash is not only a valuable fertiliser in forest ecosystems, it can also benefit agricultural soils, especially acid soil types.

Analysing the impact of wood ash (5 and 20 t ha^{-1}) on an Italian agricultural soil regarding its physicochemical, microbiological and biochemical properties, Perucci et al. (2008) observed increasing pH values and electrical conductivity as well as decreasing microbial biomass C in the first months after application, but no long-term effects of ash amendments were found. Enhanced crop production for barley (*Hordeum vulgare* L.) and canola oil seed (*Brassica rapa* L.) was monitored when Boralf soils in central Alberta were supplemented with wood ash (12.5 or 25 t ha^{-1}) in combination with N fertiliser (Patterson et al. 2004a). Although wood ash was, moreover, found to positively influence canola seed oil content, it may impair oil quality owing to an increase in the concentration of glucosinolate (Patterson et al. 2004b).

Combining wood ash with N sources is an interesting option for designer composts or fertilisers. Admixture of 8 and 16% wood ash and organic wastes prior to composting did have positive effects on the composting process (temperature, microbial activity) and the quality of the final product (no increase in heavy metal concentrations, improved nutrient balance) (Kuba et al. 2008). In comparison with mineral and organic fertilisers, wood-ash-amended compost was superior for the recultivation of a Tyrolean ski run, increasing plant cover and soil microbial biomass and respiration (Kuba et al. 2008) (Fig. 1.2). Composts produced with 8% wood ash admixture fostered utilisation of C sources (polymers, carboxylic and amino acids, alcohol, and carbohydrates) in a MicroResp™ assay and led to a change in microbial community structure, whereas compost with 16% ash altered bacterial and fungal community composition, but did not enhance C utilisation (Bougnom and Insam 2009). Bougnom et al. (2009, 2010) demonstrated that compost produced with wood ash supplement (8 and 16%) may be a cheap alternative to liming in tropical areas, where many soils are characterised by a low pH. Wood ash alone also significantly increased pH and electrical conductivity in a tropical soil in Cameroon and was found to supply nutrients to the soil (Voundi Nkana et al. 2002). Besides raising soil pH, wood ash amendments (4 and 6 t ha^{-1})

Fig. 1.2 Application of wood-ash-amended composts (8 and 16% w/w) in a reclamation trial on a ski slope in the Austrian Alps (Mutterer Alm, Tyrol, 1,700 m above sea level). The trial was set up in a randomised block with four replicates, including the two ash-amended composts as well as control plots and plots fertilised with organic or mineral fertilisers. (Photo: BioTreaT)