Resource recovery from, and beneficial reuse of biomass incinerator ashes

Jihua Zhai

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The candidate confirms that the work submitted is his/her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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Abstract

Use of biomass for energy production is more sustainable than the use of fossil fuels provided the biomass is a waste from another industry or grown sustainably. Solid biomass combustion accounts for ~90% of bioenergy supply, and the resultant combustion ash must be properly managed to promote a circular materials economy. This study aims to address four important issues for a better understanding and management of biomass ash. Firstly, an up-to-date estimate of global biomass ash production is made. It shows an ash generating rate of ~170 megatonnes per year (Mt/yr), which are dominated by municipal solid waste (MSW) ash and wood ash. Future ash production could increase to ~1000 Mt/yr with greater use of agricultural residues and wastes.

Secondly, a phylogenetic analysis is conducted for virgin biomass ash categorisation. The results show plant taxonomy strongly influences the ash chemical composition. Biomass feedstocks that are burnt commercially can usefully be categorised as hardwood, softwood, grass crop residues, and non-grass crop residues. The most abundant elements in hardwood ashes are calcium > potassium > phosphorous, whereas in the softwood ashes they are calcium > silicon > potassium. The most abundant elements in eudicot straw ashes are potassium > calcium > phosphorous > chlorine, and in grass straw ashes they are silicon > potassium > calcium. Differences in major element chemistry between the feedstock categories are visualised using a ternary plot of the normalised CaO, K_2O and SiO_2 contents. Other properties depend principally on whether the feedstock is herbaceous or woody. Herbaceous feedstocks produce significantly more ash (typically 5-9%) than woody feedstocks (typically 1-2%) and their ash has a significantly lower initial deformation (melting) temperature than ash from woody feedstocks, and thus has greater potential to form slag and foul the furnace.

Thirdly, ash properties of five laboratory wood ashes (one softwood ash and four hardwood ashes), three industrial wood ashes, two rice husk ashes and one straw ash are characterised to compare with the established ash categorisation system. The results confirm biomass type and ash generation procedure have significant influence on ash major chemical composition and minerology. Ash from *Alnus* spp., *Crataegus* spp. and *Salix* spp. (three hardwoods) falls within the hardwood ash region in K_2O-SiO_2-CaO ternary diagram and *Cedrus* spp. (softwood) ash situates at the edge of softwood ash region. *Fraxinus* spp. (hardwood) ash falls out of the hardwood ash range, reflecting high K potential in Asterids derived biomass ash. Three industrial wood ashes fall within the softwood ash region and two rice husk ashes of high silica content agree with reports.

Aarhus ash is the straw fly ash and has very high K content (nominal oxide K_2O > 45%) in forms of sylvite, arcanite and kalicinite. All biomass ashes are alkaline in nature (water leachate pH at liquid to solid ratio of 100 ranging from ~9-12). Biomass ash beneficial reuse as a soil improver should consider trace element leaching behaviour as well as concentration limits as some trace elements of potential concern (e.g. Cr and Mo) in ash may exist in easily solubilised forms. Potassium in most ashes is recyclable (>90% extractable) by water leaching. Industrial wood ash contains more problematic trace elements than laboratory wood ash and thus controlling trace elements entrainment during biomass processing and ash production/initial storage may be helpful.

Fourthly, the effect of persistent organic pollutants (POPs) content on potential reuse options for biomass combustion ash is elucidated. Concentrations of three classes of POPs (polycyclic aromatic hydrocarbons, PAHs; polychlorinated biphenyls, PCBs; and polychlorinated dibenzodioxins/furans, PCDD/Fs) in biomass bottom/total ash and fly ash from important biomass fuel sources (agricultural residues, wood, waste wood, paper sludge, sewage sludge and MSW) are collated and compared to proposed limits for reuse as fertiliser, controlled use in soil, or disposal without treatment. Ash POPs content is related to feedstock composition and ash fraction. PAHs, PCBs and PCCD/Fs are significantly more concentrated in fly ash compared to the corresponding bottom/total ash for each biomass type. Data availability for PCBs is lower than other POPs, however a strong correlation between PCBs and PCCD/Fs allows PCBs + PCCD/Fs content to be estimated conservatively as 1.25 x PCCD/Fs content. Typically, bottom/total ash from virgin biomass (e.g. wood and agricultural residues) is compliant with use as fertiliser whereas waste sourced bottom/total ash (e.g. waste wood, municipal solid waste) is more suitable for controlled use in construction. Higher POPs contents in fly ash restrict its use and occasionally ash must be treated to destroy their PCDD/Fs contents before disposal.

Overall, biomass ash amounts are set to increase with increasing biomass use as biofuels for the global transition of energy production in a more sustainable way. Virgin biomass ash properties are influenced by plant taxonomy and thus biomass evolution-based categorisation can guide ash management usefully. Biomass ash management should consider the leaching behaviour as well as concentration limits of trace toxic elements and meanwhile consider the POPs content in ash (especially for waste biomass fly ash).

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List of Abbreviations

AAS	Atomic absorption spectroscopy
APC	Air pollution control
AR-BA	Agriculture residue bottom/total ash
AR-FA	Agriculture residue fly ash
CO_2	Carbon dioxide
DIW	Deionised water
EJ	Exajoule (=10^{18} J)
est.	estimated
EU	European Union
EU-27	The European Union member countries
FTIR	Fourier transform infrared spectroscopy
GJ	Gigajoule (=10^{9} J)
Gt/yr	Gigatonnes per year (=10^{9} t/yr)
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
IDT	Initial deformation temperature
kg	kilogram
kt	kilotonne (=10^{3} t)
LOD	Limit of Detection
LOI	Loss on ignition
LOQ	Limit of Quantification
mg	milligram
MSW	Municipal solid waste
MSW-BA	MSW bottom/total ash
MSW-FA	MSW fly ash
Mt/yr	Megatonnes per year (=10^{6} t/yr)

Myr	Million years
ng	nanogram
NCV	Net calorific value
p.a.	per annum
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzodioxin/furan
Pg C y^{-1}	Petagrams of carbon per year (=10^{15} g C y^{-1})
POPs	Persistent organic pollutants
PS-BA	Paper sludge bottom/total ash
SI	Supporting information
SOT	Softening temperature
SS-BA	Sewage sludge bottom/total ash
SS-FA	Sewage sludge fly ash
SSIA	Sewage sludge incineration ash
t	tonne (= 10^3 kg)
TDS	Total dissolved solids
TEFs	Toxic equivalency factors
TEQ	Toxic equivalents units
UK	United Kingdom
UN	United Nations
UNEP	United Nations Environment Programme
US EPA	United States Environmental Protection Agency
WAC	Waste acceptance criteria
W-BA	Wood bottom/total ash
W-FA	Wood fly ash
WHO	World Health Organization
wt.%	percentage by weight

WW-BA	Waste wood bottom/total ash
WW-FA	Waste wood fly ash
XRD	X-ray diffraction
℃	Celsius

Chapter 1: Introduction

1.1 Research background

Renewable energy is regarded as the main alternative of traditional fossil fuels to reduce the anthropogenic CO_2 emissions, which is the main cause of climate change. Within recent years, renewable energy contributes to about 18% of the global energy consumption, and the bioenergy derived from sustainable biomass is the largest and most important category contributing ~70% of the total renewable supply (World Bioenergy Association, 2019). Biomass for bioenergy production is considered as carbon neutral provided the biomass is sustainably grown (Demirbas, 2004; Vassilev et al., 2013a) and sometimes even carbon negative (CO_2 capture during combustion and post ash storage (Vassilev and Vassileva, 2020; Vassilev et al., 2021)). However, ash will inevitably be produced when biomass is burnt to generate electricity/heat, and the ash content of varying biomass can differ significantly, for example, ash content for woody biomass is typically 1.5–2% (Vassilev et al., 2010; Zhai et al., 2021), and incineration reduces municipal solid waste (MSW) by ~90 % in volume and ~70%–80% in mass (Ahmed, 1991; Zekkos et al., 2013).

More biomass is anticipated to be used in the coming decades so that different countries can transit their energy production in a more sustainable way to achieve the global goal of carbon emissions reduction. The European Union (EU) has recently set to cut the bloc's carbon emissions by no less than 55% by 2030 in comparison with the 1990 levels, and then gradually reach net zero emissions by 2050 (European Commission, 2021). The United Kingdom (UK) has a similar ambition of reducing its carbon emissions by 78% by 2035 compared to 1990 levels and achieve the net zero goal by 2050 (Dray, 2021). The United States of America (USA) also sets to reduce its carbon emissions by 50-52% from 2005 levels in 2030 and reach net zero emissions by 2050 (The White House, 2021). Therefore, large amounts of biomass ash shall be generated in future, and beneficial or safe ash management options must be explored for the scientific community.

The European waste hierarchy sets out 5 steps in consideration of waste management: prevention, reuse, recycling, recovery and disposal (European Commission, 2008). Biomass ash generally contains values that can be directly used or recovered. For example, application of biomass ash that contains Si, K, Ca, P, Mg, etc. as fertiliser materials to agriculture or forestry soils is favourable (Bramryd and Fransman, 1995; da

Costa et al., 2020; Demeyer et al., 2001; Wierzbowska et al., 2020), provided that the contaminants (e.g. trace toxic elements and organic residues) in ash meets the regulatory limits. Meanwhile, value extraction from biomass ash have been widely studied, such as K extraction from agriculture residue ash (Samadhi et al., 2019; Wang et al., 2015), P extraction from sewage sludge ash (Donatello et al., 2010a; Fang et al., 2018; Takahashi et al., 2001), and ferrous and non-ferrous metals recovery from MSW ash (Allegrini et al., 2014; Tang and Steenari, 2016). However, final disposal like landfilling might be required for some biomass ash (Donatello et al., 2010b; Sarenbo, 2009; Zekkos et al., 2013), as from the environmental protection point, these ashes may contain excessive trace toxic elements or organic contaminants that can pose environmental threats if not well managed.

Biomass ash management options based on the waste hierarchy depend primarily on ash characteristics (e.g. bulk chemical composition, contaminants levels, leaching behaviour, etc.), which is typically dependent on the feedstock composition (Cruz et al., 2019; Thy et al., 2006; Vassilev et al., 2013a; Wilén et al., 1996). Unlike the widely studied coal ash, biomass ash has received limited studies and more importantly, numerous biomass feedstocks and their combined incineration can make the ash characteristics more complex. It is therefore imperative to conduct more research on biomass incineration ash to provide guidance on its beneficial and safe management. The overall research background and motivation for this research is depicted in Figure 1.1.

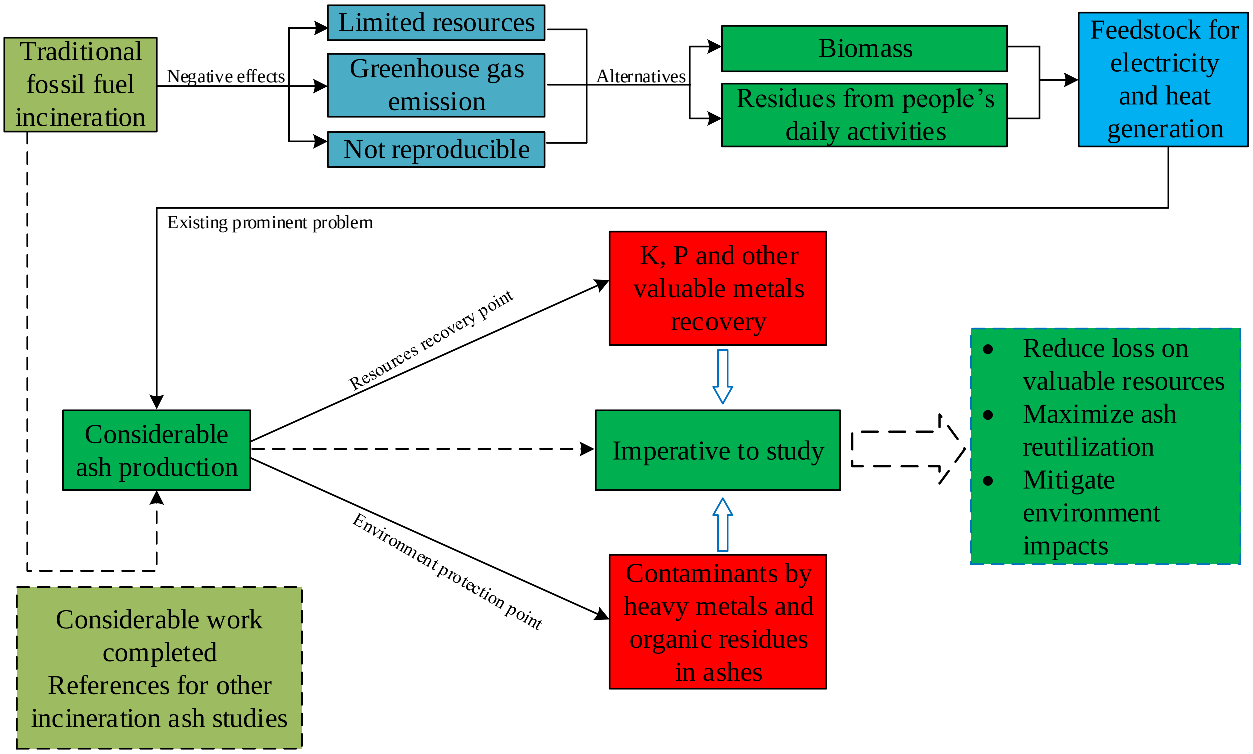

Figure 1.1. Overall research background and motivation for the research.

1.2 Research question statement

Outcomes of many previous studies can be primarily divided into two main aspects: ash characterisation (Dahl et al., 2009, 2010; Demeyer et al., 2001; Olanders and Steenari, 1995; Vassilev et al., 2013a) and ash beneficial management (Demeyer et al., 2001; Fukasawa et al., 2017; Silva et al., 2019; Vassilev et al., 2013b) (see more information in literature section). In brief, the ash characteristics are mostly studied via bulk chemical composition analysis, mineral phase identification and surface morphology characterisation; the ash beneficial management mostly include the specific value recovery from biomass ash (e.g. K and P extraction and valuable metals recovery from municipal solid waste ash) and ash beneficial reuse (e.g. ash direct use as fertiliser or soil amendment, ash reuse as partial feedstock for construction materials production and ash reuse after proper treatment as adsorbent material).

However, regarding biomass ash management, some issues remain unclear:

- **Question 1: How much biomass ash is produced globally, and what is the distribution pattern of biomass ash across the globe as affected by biomass**

types? About 480 million tonnes of ash were estimated in 2013 (Vassilev et al., 2013a), however, such value seems to be out of date and lack the significance on guiding ash management as this estimation was based on even much earlier data and references.

- **Question 2: How should biomass ash be scientifically categorised?** This is needed so that we can know ash characteristics and guide ash management with the changing biomass availability, but has received limited study (Vassilev et al., 2012).
- **Question 3: How will the biomass feedstock influence the ash characteristics and what are the resulting implications for biomass ash management?** This will require detailed experimental data of several different biomass ashes, and a systematic discussion with the established ash categorisation method in Question 2 is needed.
- **Question 4: What is the level of persistent organic pollutants (POPs) in biomass ash and to what extent will POPs affect ash management?** This has received less attention, with more focus to date on toxic trace metals, the other barriers to beneficial reuse of biomass ash (Dahl et al., 2009, 2010; Demeyer et al., 2001; Someshwar, 1996).

1.3 Research aims and objectives

This project aims to address some key variables (research questions above) that can promote biomass ash management. Specially, the following objectives are proposed for this research:

- **Objective 1:** To assess the global biomass ash amounts, ash distribution and developing trend.
- **Objective 2:** To explore viable biomass ash categorisation method for guiding ash management.
- **Objective 3:** To compare the ash characteristics of laboratory and industrial biomass ash and discuss their implications for ash management based on the established ash classification method.
- **Objective 4:** To investigate the distribution differences of POPs with ash categories and ash size fractions, and evaluate the effects of POPs on biomass ash beneficial reuse or safe disposal.

1.4 Thesis structure

This thesis contains 7 chapters (see Figure 1.2). The starting chapter 1 makes the rationale of this research and chapter 2 conducts the extensive literature review on ash characteristics and current ash management practices as a function of biomass feedstocks. Chapter 3 estimates the biomass ash amounts that can be produced globally and a prediction is also made for future ash production (delivering objective 1). Chapter 4 explores the viable biomass ash categorisation method that can support ash management (delivering objective 2). Chapter 5 presents the experimental results of some lab-obtained ashes and industrial ashes. Discussions on ash characteristics and their implications for ash management are also provided in this chapter (delivering objective 3). Chapter 6 focuses on the effects of persistent organic pollutants on biomass ash management considering ash categories and ash size fractions (delivering objective 4). Finally, the summary and overall discussion of this project are provided in Chapter 7, and some recommendations for future work are also included in this chapter.

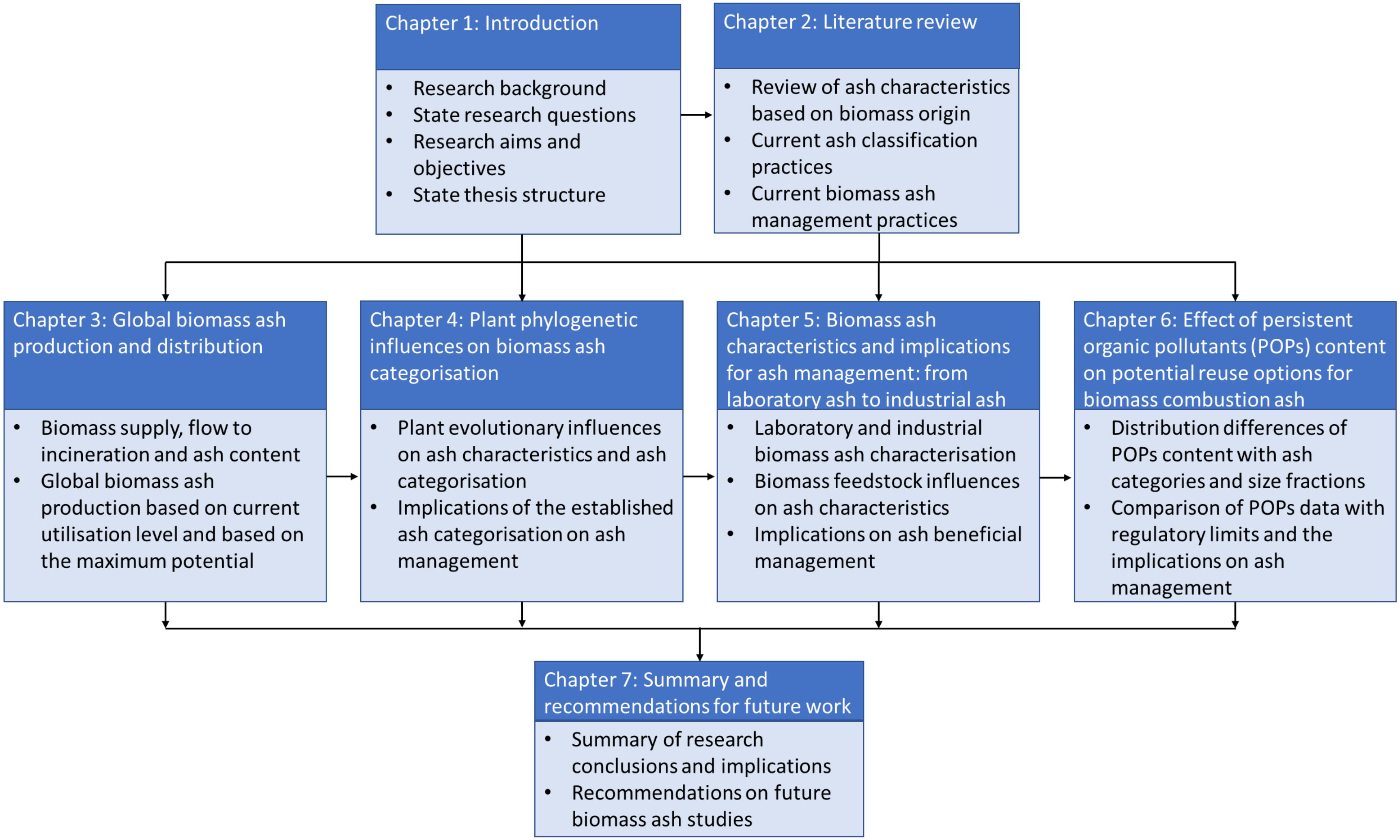

Figure 1.2. Thesis structure.

1.5 References

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Chapter 2: Literature review

2.1 Introduction of biomass and biomass ash

Traditional fossil fuels are non-renewable resources and major sources of greenhouse gases; it is therefore imperative that energy production transitions to more sustainable fuels in the coming decades. The proportion of global energy consumption supplied from fossil fuels has dropped from ~95% in 1970 to ~80% of the worldwide energy consumption in 2016 because of advances in other energy technologies and increasing public awareness of the need for change (Dawson, 2019; Trading Economics, 2020). The balance in global energy consumption has been supplied by nuclear energy (~2%) and renewable energy sources (~18%) (World Bioenergy Association, 2019). Renewable energy sources in current global energy supply include bioenergy, hydro, solar, wind, geothermal and tidal. Bioenergy derived from sustainable biomass is the largest and most important category contributing ~70% of the total renewable supply (World Bioenergy Association, 2019). Combustion of solid biomass accounted for 91% of biomass energy supply in 2017, with liquid biofuel and biogas contributing 7% and 2% to biomass supply, respectively (World Bioenergy Association, 2019).

There are different definitions of biomass (Demirbas, 2005; Demirbaş, 2001; McKendry, 2002; Vassilev et al., 2010; World Bioenergy Association, 2019). The word is widely used to describe “all organic material that stems from plants (including algae, trees and crops)” (McKendry, 2002). Thus, biomass includes all plant-derived wastes, and is divided into four main types: woody plants, herbaceous plants/grasses, aquatic plants and manure. Subsequently, the definition has been refined to “contemporaneous (non-fossil) and complex biogenic organic–inorganic solid products generated by natural and anthropogenic (technogenic) processes” (Vassilev et al., 2010), and the list of categories has been extended to wood and woody biomass, herbaceous and agricultural biomass, aquatic biomass, animal and human biomass wastes (including bones, meat-bone meal, chicken litter, various manures, etc.), contaminated and industrial biomass wastes (including municipal solid waste (MSW), sewage sludge, demolition wood, paper sludge, etc.), and biomass mixtures.

Biomass ash is the unavoidable by-product of solid biomass combustion, and Figure 2.1 illustrates the formation process of biomass ash within a grate furnace (Yin et al., 2008).

Typically, fixed bed combustion (usually on a grate), fluidized bed combustion, pulverized fuel combustion and dust combustion are four major technologies that are used in industry for energy conversion from biomass. Bioenergy generation is normally undertaken in electricity only, heat only and combined heat and power plants (The International Renewable Energy Agency, 2021; Wiser, 2013). Biomass ash is mainly composed of inorganic constituents of the feedstock and differs in its physical and chemical properties from ash produced by more traditional fuels such as coal (Dunnu et al., 2010; Masiá et al., 2007; Wigley et al., 2007). Thus, alternative reuse or, if necessary, disposal strategies are required (Ahmaruzzaman, 2010). Better understanding of biomass ash characteristics is needed if that ash is to be put to productive use (to deliver a circular energy economy or promote a circular materials economy), or disposed of safely with the minimum investment of further energy in that disposal (Vassilev et al., 2013a, b).

In general, two ash size fractions are generated: bottom ash and fly ash (Agrela et al., 2019; Obernberger et al., 1997; Vassilev et al., 2013a; Yin et al., 2008). Bottom ash is coarse ash fraction discharged from furnace combustion chamber, whereas fly ash is fine ash fraction recovered from the flue gases outside the combustion chamber. There are many factors that can determine biomass ash properties, and thus dictate the appropriate measures for subsequent ash management. The primary factor that determines the chemical composition of the ash is the biomass feedstock composition (Cruz et al., 2019; Thy et al., 2006; Vassilev et al., 2013a; Wilén et al., 1996), but factors such as the physical nature of the feedstock, and the type, size and operating status of the incinerator can determine the efficiency of combustion and the partitioning of volatile elements (Burvall, 1997; Demirbas, 2005; Obernberger et al., 2006; Rajamma et al., 2009; Yin et al., 2008). Biomass ashes are usually rich in elements such as Si, K, Ca, P, Mg, etc. (Antonkiewicz et al., 2020; da Costa et al., 2020; Obernberger et al., 1997; Tan and Lagerkvist, 2011), so it may be possible to recover essential plant nutrients like potassium and phosphorus or apply the ash directly to agricultural or forestry soils (many biomass ashes are relatively benign (Bramryd and Fransman, 1995; Demeyer et al., 2001; Wierzbowska et al., 2020)). Management of ash from the combustion of waste biomass (such as MSW and sewage sludge) may be more challenging as it can contain elevated concentrations of contaminant trace metals (Donatello et al., 2010c; Fang et al., 2018; Fedje et al., 2010). However, even these ashes may contain values that can be extracted to off-set management costs (sewage sludge incineration ash, SSIA, typically contains ~15% P_2O_5 which is comparable to natural phosphate rock (Cyr et al., 2007; Donatello and Cheeseman, 2013; Donatello et al., 2010b; Smol et al., 2016)), and MSW incineration ashes contain a variety of ferrous and non-ferrous metal that can be recovered (Allegrini et al., 2014; Johannessen, 1996; Tang and Steenari, 2016).

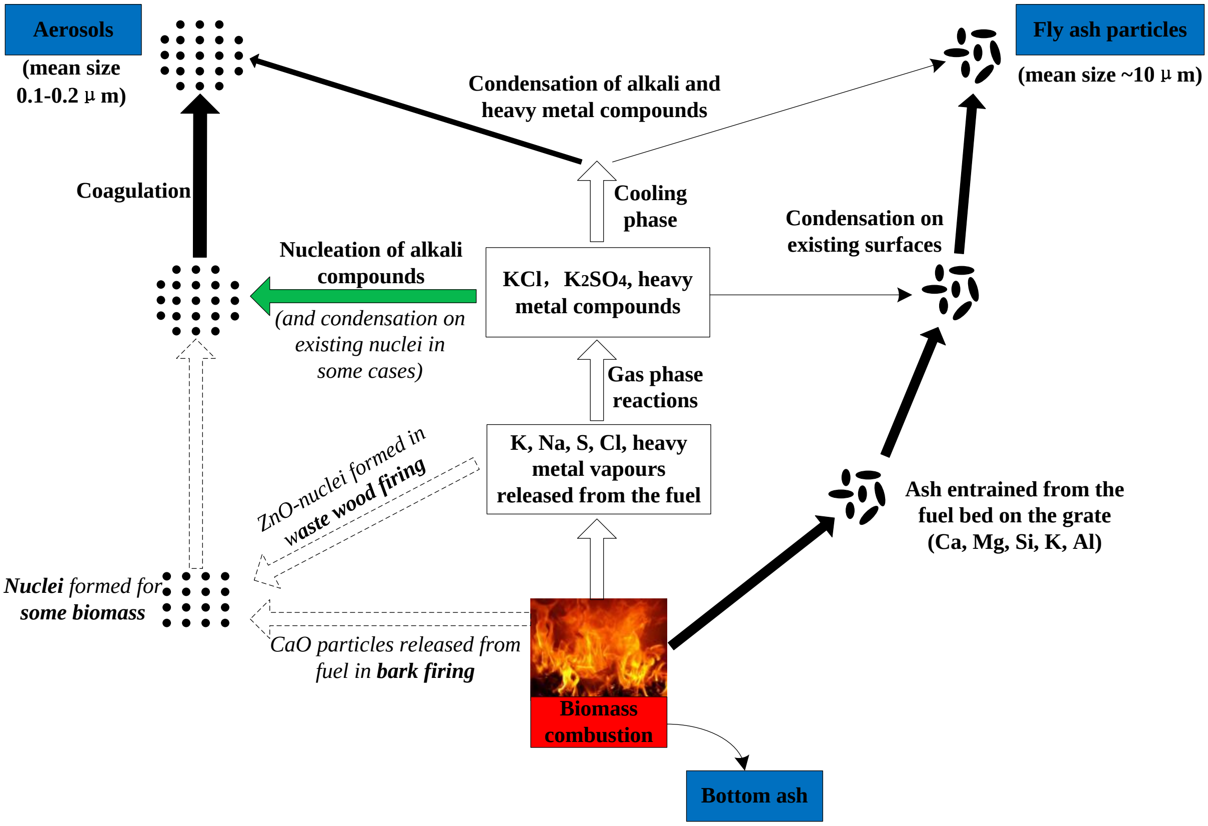


Figure 2.1. Schematic diagram of biomass ash formation pathways (modified from Yin et al., 2008).

Considering different definitions of biomass and the primary influence of biomass type on biomass ash property, biomass scope must be given for this review. In the following subsections, ash from combustion of agricultural residues, energy crops, woody biomass, forest residues, recovered wood, paper sludge, sewage sludge, and municipal solid waste are specially considered (Zhai et al., 2021b).

2.2 Biomass ash characteristics

2.2.1 Ash from agriculture residues

There are many crops globally grown for human's demand and their abundant residues after harvesting support the agriculture residues as the promising bioenergy source. Table 2.1 lists the major agriculture residues that can be used as biofuels. Based on the low estimates, agriculture residues are dominated by the residues from maize (36%), rice (18%), wheat (14%), sugarcane (9%) and soybean (8%). The first three are cereals crops and produce 68% of total agriculture residues (World Bioenergy Association, 2019). Therefore 13 separate reports of maize ash (Aksoğan et al., 2016; Arvelakis et al., 2004; Bryers, 1996; ECN.TNO, 2020; Masiá et al., 2007; Vassilev et al., 2014), 10 reports of rice ash (Bakker et al., 2002; Jenkins et al., 1996; Liu et al., 2009; Llorente and García, 2005; Miles et al., 1995; Okasha, 2007; Skrifvars et al., 2005; Thy et al., 2006; Wu et al., 2009; Xiao et al., 2011) and 12 reports of wheat ash (Arvelakis et al., 2001; Demirbas, 2004; Jenkins et al., 1996; Llorente and García, 2005; Miles et al., 1995; Niu et al., 2010; Thy et al., 2006; Wilén et al., 1996; Wu et al., 2009), were identified in the literature for relevant ash compositional analysis (see Appendix A for further details).

Table 2.1. Theoretical global agriculture residues potential (modified from World Bioenergy Association, 2019).

Crops	Residues (million tonnes)		Ratio of each crop residue	
	Low	High	Low	High
Maize	1532	4540	35.53%	37.78%
Rice	770	2041	17.86%	16.99%
Wheat	618	1235	14.33%	10.28%
Barley	118	192	2.74%	1.60%
Millet	31.3	56.9	0.73%	0.47%
Oats	23.4	36.3	0.54%	0.30%
Rye	12.4	22	0.29%	0.18%
Sorghum	51.8	426	1.20%	3.55%
Olives	4.7	4.7	0.11%	0.04%
Rapeseed	107	152	2.48%	1.26%
Soybeans	353	1389	8.19%	11.56%
Sunflower	105	153	2.44%	1.27%
Oil palm	110	140	2.55%	1.17%
Cassava	46.7	292	1.08%	2.43%
Sugarbeet	60.2	120	1.40%	1.00%
Sugarcane	368	1216	8.54%	10.12%

The mean composition and compositional range of cereal crops residue ash are shown in Table 2.2. Cereal crop residue ash compositions are dominated by SiO_2 (51%) and K_2O (17%), with moderate amounts of CaO and Cl_2O (6% each) and with minor amounts (<3%) of other elements. 12 separate reports of sugarcane residue ash composition have been found (Bahurudeen and Santhanam, 2015; Dayton et al., 1999; ECN.TNO, 2020; Faria et al., 2012; Gabra et al., 2001; Jenkins et al., 1996; Turn et al., 2006; Turn et al., 1997; Wilén et al., 1996). Sugarcane residue ashes have similar SiO_2 content (54%) to cereal crop residue ashes but somewhat lower K_2O (8%) and CaO (5%) but correspondingly higher Al_2O_3 (11%) and Fe_2O_3 (8%). 5 separate reports of soybean residue ash composition have been analysed (Bryers, 1996; ECN.TNO, 2020; Werther et al., 2000; Zhou et al., 2017). Soybean residue ash contains considerably less SiO_2 (21%) than cereals and sugarcane (which are all types of grass), but higher K_2O (21%), CaO (17%), MgO (6%) and P_2O_5 (5%), with minor amounts (<3%) of other elements (evolution of eudicot plants, such as soybean diverged from monocot plants, such as grasses ~150 Myr ago (Chaw et al., 2004; Magallón, 2009)).

The agricultural residues reported in Table 2.2 are predominantly food crops grown on uncontaminated land, so the trace element compositions of their residue ashes are not routinely reported in the literature. However, previous work on agricultural residues reviewing 66 grass (monocot) straw and 48 non-grass (eudicot) straw ashes (Zhai et al., 2021a) showed that the Cu, Pb, Cd and Hg contents of all these ashes were below the Swedish limits, and most were below the Finnish limits, for use as a forest fertiliser (just one grass straw ash exceeded the Finnish limit for Pb) (Dahl et al., 2010; Swedish National Board of Forestry, 2002).

Table 2.2. Mean chemical compositions on biomass ash from different feedstocks (wt.%). Number of valid samples are indicated in superscript and minimum and maximum of reported values are given in parenthesis (n.d. – no data).

Item	CaO	SiO_2	K_2O	Cl_2O	P_2O_5	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	TiO_2
Agriculture residues											
Cereal crops	6.1 ^{35} (0.46-17)	51 ^{35} (28-75)	19 ^{35} (2.0-48)	5.8 ^{14} (0.69-16)	3.2 ^{29} (0.61-10)	1.9 ^{28} (0.070-8.0)	1.6 ^{32} (0.10-7.1)	2.8 ^{35} (0.59-7.4)	3.3 ^{29} (0.84-11)	2.2 ^{35} (0.080-15)	0.11 ^{18} (0.010-0.43)
Sugarcane	5.3 ^{12} (3.0-13)	54 ^{12} (42-73)	8.4 ^{12} (1.7-24)	0.40 ^{3} (0-1.1)	2.4 ^{10} (0.89-6.0)	11 ^{11} (0.98-23)	8.0 ^{12} (0.43-21)	3.1 ^{11} (1.2-5.8)	3.3 ^{10} (0.40-8.2)	1.1 ^{10} (0.26-2.8)	2.1 ^{8} (0.070-3.9)
Soybean	17 ^{5} (4.7-33)	21 ^{5} (1.7-33)	21 ^{5} (6.7-31)	n.d.	4.8 ^{5} (2.3-7.3)	3.4 ^{3} (0.50-7.4)	2.1 ^{5} (0.32-3.9)	5.6 ^{5} (0.90-9.8)	3.0 ^{4} (1.2-4.7)	1.7 ^{5} (0.52-5.3)	0.090 ^{3} (0.030-0.20)
Energy crops											
Woody crops	42 ^{25} (31-54)	4.3 ^{24} (0.40-17)	20 ^{25} (9.6-33)	0.62 ^{2} (0.37-0.88)	9.3 ^{25} (0.15-17)	1.4 ^{25} (0.090-6.7)	0.86 ^{25} (0.20-3.8)	6.4 ^{25} (0.24-18)	2.6 ^{15} (1.2-4.0)	1.2 ^{25} (0.10-3.1)	0.10 ^{15} (0-0.30)
Grasses	6.4 ^{19} (1.9-14)	53 ^{19} (34-86)	22 ^{19} (3.7-43)	4.1 ^{9} (0.050-10)	4.0 ^{19} (1.6-7.2)	0.76 ^{17} (0.24-1.6)	0.70 ^{19} (0.25-1.4)	4.0 ^{19} (1.0-9.9)	2.1 ^{19} (0.45-5.7)	0.58 ^{17} (0.10-2.2)	0.31 ^{12} (0.020-2.8)
Forest biomass											
Tropical hardwood	27 ^{10} (12-68)	14 ^{10} (1.6-43)	24 ^{10} (10-35)	4.4 ^{6} (2.8-5.8)	5.5 ^{10} (0.50-8.5)	2.7 ^{10} (0.25-14)	2.2 ^{10} (0.22-8.3)	4.7 ^{10} (2.4-7.5)	3.2 ^{10} (0.87-6.5)	1.3 ^{10} (0.12-3.0)	0.33 ^{5} (0-0.96)
Temperate hardwood	38 ^{11} (18-65)	11 ^{11} (0.40-49)	17 ^{11} (9.5-27)	0.74 ^{3} (0.37-0.98)	8.2 ^{9} (0.15-17)	3.0 ^{11} (0.30-9.5)	1.5 ^{11} (0.20-8.5)	6.9 ^{11} (1.1-18)	2.9 ^{8} (2.0-4.0)	0.53 ^{11} (0.10-1.8)	0.13 ^{8} (0.020-0.30)
Softwood	32 ^{12} (9.5-51)	23 ^{12} (6.2-52)	10 ^{12} (7.3-17)	0.25 ^{6} (0.010-0.98)	2.8 ^{10} (1.9-4.2)	4.1 ^{11} (0.42-15)	3.2 ^{11} (0.74-9.3)	4.9 ^{12} (1.1-14)	4.8 ^{10} (0.86-13)	0.95 ^{12} (0.17-3.2)	0.51 ^{6} (0.080-1.2)
Temperate hardwood bark	64 ^{9} (47-76)	9.8 ^{9} (1.5-40)	5.9 ^{9} (2.6-8.0)	7.1 ^{1} (7.1-7.1)	2.0 ^{9} (0.30-3.8)	1.4 ^{9} (0-3.8)	1.2 ^{9} (0.30-2.9)	7.6 ^{9} (1.9-19)	1.6 ^{9} (0.60-3.2)	1.6 ^{9} (0.70-3.9)	0.10 ^{3} (0.10-0.10)
Softwood bark	59 ^{6} (41-74)	6.8 ^{6} (1.3-16)	6.0 ^{6} (4.1-7.6)	n.d.	3.2 ^{6} (2.2-4.8)	3.6 ^{6} (0-8.4)	2.3 ^{6} (0.30-5.0)	5.2 ^{6} (1.7-8.5)	2.0 ^{6} (1.3-2.6)	2.0 ^{6} (0.50-3.2)	0.13 ^{4} (0.10-0.20)
Wastes and residues											
Recovered wood	16 ^{4} (13-22)	39 ^{4} (19-58)	2.6 ^{4} (2.1-3.8)	n.d.	0.67 ^{4} (0.50-0.94)	9.5 ^{4} (5.0-16)	5.7 ^{4} (2.1-12)	14 ^{4} (2.6-46)	5.8 ^{4} (1.0-16)	2.0 ^{4} (1.1-2.4)	2.7 ^{4} (0.50-4.1)
Paper sludge	26 ^{8} (4.2-45)	37 ^{8} (23-61)	0.41 ^{7} (0.10-1.0)	0 ^{1} (0-0)	0.38 ^{6} (0.20-0.90)	23 ^{8} (16-29)	2.1 ^{8} (0.60-5.9)	4.7 ^{8} (1.8-7.8)	0.54 ^{3} (0.29-0.70)	0.49 ^{8} (0-1.1)	1.5 ^{7} (0.20-2.5)
Sewage sludge	15 ^{12} (4.7-22)	32 ^{12} (20-41)	1.7 ^{12} (0.84-3.4)	n.d.	14 ^{12} (2.0-23)	12 ^{12} (6.1-19)	13 ^{12} (3.6-27)	2.4 ^{12} (1.1-3.9)	2.2 ^{10} (0.26-5.3)	1.7 ^{12} (0.36-5.0)	0.99 ^{9} (0.35-1.4)
Municipal solid waste	19 ^{10} (9.1-51)	32 ^{10} (7.0-54)	3.6 ^{10} (0.88-16)	7.2 ^{7} (0.29-36)	1.3 ^{9} (0.34-3.9)	10 ^{10} (4.2-26)	6.4 ^{9} (0.80-14)	2.5 ^{10} (1.5-3.7)	5.8 ^{9} (1.3-20)	7.0 ^{10} (2.8-31)	1.4 ^{9} (0.31-2.3)

When organic matter is incinerated there is a concern that polychlorinated dibenzodioxins/dibenzofurans (PCDD/Fs) may form if Cl is present in the feedstock. Although PCDD/Fs in the feedstock are destroyed by relatively brief exposure to the temperatures within the combustion zone of a modern commercial furnace (Council, 2000; Wielgosiński, 2011), they can also be formed as the combustion gases cool as they leave the combustion zone, if appropriate organic substrates survive their transit through the furnace. There are three main pathways by which a range of PCDD/Fs can form (Altarawneh et al., 2009; Stanmore, 2004; Vermeulen et al., 2014; Zhang et al., 2017): gas phase formation at 400~800 °C (Altarawneh et al., 2009; Sidhu et al., 1995; Stanmore, 2004), and two surface catalysed pathways that typically occur at 200~400 °C (Altarawneh et al., 2009; Gullett et al., 1992; Huang and Buekens, 1995; Launhardt and Thoma, 2000). Production of precursor chlorophenols, and thus potentially PCDD/Fs, initially increases with Cl content of the feedstock at low Cl concentrations, but quickly becomes insensitive to Cl concentration (Kanters et al., 1996). However, transition-metal species associated with the ash particles, especially copper compounds, promote PCDD/Fs formation (Altarawneh et al., 2009; Gullett et al., 1992; Hinton and Lane, 1991; Qian et al., 2005).

Several current and proposed regulatory limits for PCDD/F concentrations are applied to combustion ashes, commonly defined in terms of toxic equivalents units (TEQs) based on specific toxic equivalency factors (TEFs) for individual compounds (International TEF values have been superseded by World Health Organisation TEF values, but the difference is very small and the TEQ values are comparable (BiPRO, 2005; UNEP, 2013)). Limits placed on PCDD/F concentrations are dependent on the intended end use or disposal method. EU limits on ash disposal methods place a limit of 15,000 ng TEQ/kg for disposal to landfill, and above this limit destruction or irreversible transformation of the PCDD/Fs is required (European Parliament, 2019). There is a recommendation that the EU limit for ash to be put directly onto or mixed with soil (e.g. road sub-bases, engineering fills, etc.) should be 1000 ng TEQ/kg PCDD/Fs (BiPRO, 2005). End of waste criteria have also been applied in the UK to ash from poultry litter incineration for application to land as a fertilizer at 20 ng TEQ/kg (EA-UK, 2012). These limits can be compared to PCDD/F concentrations determined in biomass combustion ashes as a way of determining to effect of PCDD/F content on the potential re-use or disposal pathways (Figure 2.2).

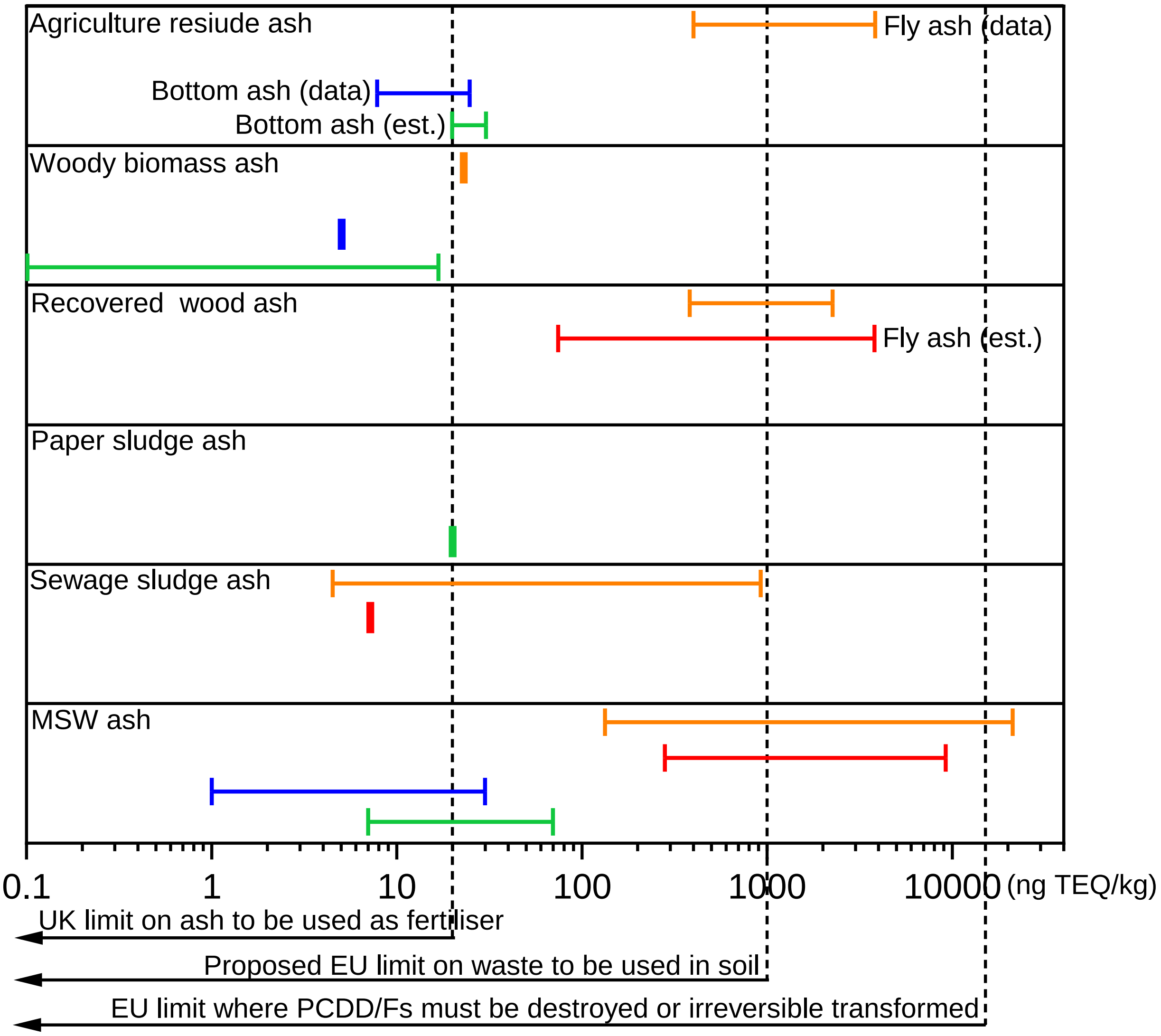


Figure 2.2. PCDD/Fs content in biomass ash and current regulations on PCDD/Fs content limits for ash management (blue line and orange lines are reported values of bottom ash and fly ash, respectively (Chang et al., 2011; Deng et al., 2009; He et al., 2004; Launhardt et al., 1998; Launhardt and Thoma, 2000; Robinson et al., 2004; Samaras et al., 2000; Shin and Chang, 1999; Swedish Environmental Protection Agency, 2011); dark green lines are estimates for bottom ash (MSW and paper sludge) or combined bottom and fly ash (agriculture residue ash and woody biomass ash) (UNEP, 2013); red lines are estimates for fly ash (UNEP, 2013)).

The mean PCDD/Fs concentrations reported in agricultural ashes deposited in the combustion chamber (4 to 5 separate trials per fuel) were 8, 24 and 12 ng TEQ/kg for triticale (whole crop), wheat straw and hay (from set aside land), respectively (Launhardt and Thoma, 2000). These feedstocks have low transition metal contents, but moderate to high Cl contents, yet combustion in modern furnace results in PCDD/F values in the bulk of the ash that are similar to end of waste criteria applied to poultry litter ashes (Launhardt and Thoma, 2000). This demonstrates potential for agricultural residue combustion ash re-use as fertiliser if combustion conditions are carefully controlled. Although, more than 90% of ash is deposited within the combustion chamber, ashes deposited in the heat exchanger or as chimney soot contain orders of magnitude higher PCDD/F concentrations (which vary between 250 and 4000 ng TEQ/kg (Launhardt and Thoma, 2000)) and these ashes must be consigned for disposal where PCDD/F concentrations are >1000 ng TEQ/kg.

2.2.2 Ash from forestry derived biomass

Hardwoods and softwoods are two common sources of forestry derived woody biomass, and more specifically, hardwoods include tropical hardwoods (referring those hardwoods grown in tropical areas such as Central and South America, West and Central Africa and Southeast Asia) and temperate hardwoods. Herein, 10 separate reports of tropical hardwood ash (Adeleke et al., 2020; ECN.TNO, 2020; Oladejo et al., 2020; Vamvuka and Zografos, 2004), 11 reports of temperate hardwood ash (Demirbas, 2004; ECN.TNO, 2020; Grammelis et al., 2006; Miles et al., 1995; Moilanen, 2006; Rahman et al., 2004; Zevenhoven-Onderwater et al., 2000) and 12 reports of softwood ash (Demirbas, 2005; ECN.TNO, 2020; Eseltine et al., 2013; Grammelis et al., 2006; Llorente and García, 2005; Miles et al., 1995; Thy et al., 2006; Wei et al., 2005) have been identified in the literature for relevant ash compositional analysis and the results are shown in Table 2.2. Tropical hardwood and temperate hardwood ash compositions are dominated by CaO (27% and 38%, respectively) and K_2O (24% and 17%, respectively), with moderate SiO_2 content (14% and 11%, respectively). In contrast, softwood ash contains similar amounts of CaO (32%), but more SiO_2 (23%) and less K_2O (10%) (differences between hardwood and softwood ash composition have been shown to be statistically significant (Zhai et al., 2021a)).

Chemical compositions of ashes from temperate hardwood bark (based on 9 separate records (Bryers, 1996; Theis et al., 2006)) and softwood bark (6 records (Bryers, 1996; Moilanen, 2006)) are reported in Table 2.2. Limited data were found for tropical hardwood bark ash, so its composition is not reported. Temperate hardwood bark ash and softwood bark ash have higher CaO content (64% and 59%, respectively) than the respective woody biomass. Temperate hardwood bark ash contains less K_2O content (6%) than temperate hardwood ash, whereas softwood bark ash has less SiO_2 content (7%) than softwood ash.

Figure 2.3 presents concentration of contaminant trace elements in 26 different wood/forest-residue combustion boiler ashes (Someshwar, 1996) (raw data in Appendix A; there is insufficient published data to consider different types of wood and forestry residue separately). The Swedish limits for ash as a forestry fertiliser (Swedish National Board of Forestry, 2002) are also shown for comparison. Generally, ash from burning of untreated wood and forest residues is thought to be relatively innocuous (Bramryd and Fransman, 1995; Demeyer et al., 2001; Meiwes, 1995), and the data in Figure 2.3 supports that position, with contaminant trace elements concentrations in most samples below the Swedish limits for all elements. However, 4 of the 26 samples exceed one or more of the Swedish limits for As, Cr and Ni content, and 5 of the 26 samples exceed one or more of the Finnish limits for ash use as a forest fertiliser for As, Pb, Cd and Hg (no samples exceed the Finnish limits for Cr and Ni as they differ slightly from the Swedish limits). Generally, the contaminant trace metal concentrations in woody biomass ash tend to be slightly higher than those in ash from agriculture residues, which may be associated with the lower ash content of woody biomass (Zhai et al., 2021a).

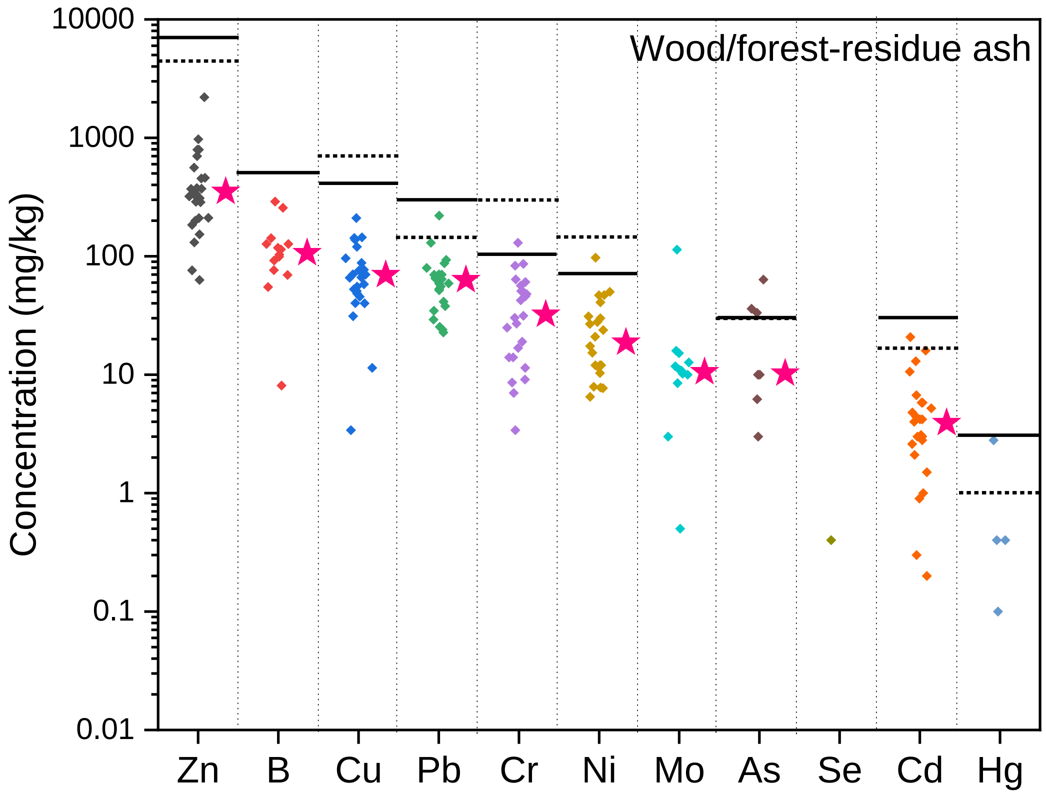


Figure 2.3. Concentration of contaminant trace elements in wood/forest-residue combustion ashes ((Someshwar, 1996) and references therein). The Swedish limits (black solid lines (Swedish National Board of Forestry, 2002)) and Finnish limits (black dotted lines (Dahl et al., 2010)) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median element concentration (median values of Se and Hg are both zero and therefore not shown).

The combustion of inland wood residue or wood fuel with very low levels of chloride content (<0.03%) has been reported to produce low PCDD/Fs content in the resultant wood ashes (Someshwar, 1996). However, PCDD/Fs concentrations in woody biomass ash differ greatly depending on where in the furnace it is collected. Spruce wood ash recovered from the main combustion chamber (>90% of total combustion residue by mass) contains 5 ng TEQ/kg PCDD/Fs (Launhardt and Thoma, 2000) making it suitable for fertiliser use by the same criteria applied to agricultural residue combustion ashes (EA-UK, 2012). Whereas PCDD/F concentrations in the chimney soot (61 ng TEQ/kg) and heat exchanger ashes (23 ng TEQ/kg) are about 12 and 5 times higher than the combustion chamber ash, and therefore may require controlled disposal to land.

Data for wood ash collected in the early 1990s indicates that the concentrations of other organics of environmental concern (e.g. polyaromatic hydrocarbons (PAHs), chlorobenzenes and chlorophenols) are negligible although insufficient data was available to draw a definitive conclusion (Someshwar, 1996). In recent years, some studies show that PAHs content in wood ash ranges from 0 (not detected) to 0.733 mg/kg (Rey-Salgueiro et al., 2016; Straka and Havelcova, 2012), which is within regulatory standards (e.g. in Sweden the preliminary PAHs limit is 2 mg/kg for ash utilisation as forestry fertiliser (Swedish National Board of Forestry, 2002) and in the Czech Republic the limit is 6 mg/kg for ash reuse in agriculture soil (Straka and Havelcova, 2012)). Therefore, organic contaminants in virgin woody biomass ash are unlikely to restrict its beneficial reuse.

2.2.3 Ash from energy crops

Currently, there is no available data to show the proportion of different energy crops that are grown around the world. However, the characteristics of ash from a selection of common energy crops (*Miscanthus giganteus*, *Pennisetum purpureum* and short rotation woody plants like *Salix* spp. (willow) and *Populus* spp. (poplar)) are herein reviewed.

In total, 19 separate reports of grass energy crop ash including 10 miscanthus ash (ECN.TNO, 2020; Wilén et al., 1996) and 9 pennisetum purpureum ash (Cui et al., 2015; Dayton et al., 1999; Miles et al., 1995; Srisittipokakun et al., 2013; Strezov et al., 2008; Yoshida et al., 2008) have been analysed to obtain the compositional results shown in Table 2.2. Like ashes from cereal crop residues, grass energy crop ashes have high SiO_2 (53%) and K_2O (22%) contents, and moderate CaO (6%) content. 25 separate reports of woody energy crop ash consisting of 11 willow ash (Miles et al., 1995; Moilanen, 2006; Zevenhoven-Onderwater et al., 2000) and 14 poplar ash (Miles et al., 1995; Misra et al., 1993; Rodrigues and Nunes, 2020; Wigley et al., 2007) have been identified for ash compositional analysis (Table 2.2). The composition of woody crop ash is dominated by CaO (42%) and K_2O (20%), with moderate P_2O_5 (9%) and MgO (6%) contents and some other minor elements (<3%). This composition is similar to that of temperate hardwood ash, although the mean SiO_2 content (4%) is lower, possibly reflecting the species of hardwoods used as energy crops or the age of the wood that is coppiced.

Trace elements of Pb, Cd, Cu and Hg in miscanthus ash are sometimes reported in the Phyllis2 database (ECN.TNO, 2020), and in total 30 separate records have been found (see Appendix A). Just one miscanthus ash exceeded the Swedish limits for ash use as forestry fertiliser (it exceeded the limit for Cu) (Swedish National Board of Forestry, 2002). Published information on trace elements in pennisetum purpureum ash is very limited, but pennisetum purpureum ash is likely to be similar to ash from miscanthus and cereal crops (i.e. other grasses) when it is grown on uncontaminated land. Trace elements in willow ash are not routinely reported with its chemical compositions but is likely to be non-hazardous like other wood ash samples (subsection 2.2.2). A case study (Rodrigues and Nunes, 2020) on the composition of ash from 9 short rotation coppice poplar clones (2 from central Portugal and 7 from Belgium) showed that heavy metals of Cd, Cr, Cu, Ni and Zn in this study frequently exceed Swedish limits for use of ash as forestry fertiliser (Swedish National Board of Forestry, 2002). However, no reason is given for why short rotation coppice poplar should accumulate more metals than other forestry products (such as contaminant metal levels in the soil), and therefore more case studies on energy crop ash are needed.

Information on potential organic contaminants in energy crop ashes is rarely reported and therefore is not discussed herein. However, discussions on potential organic contaminants in agriculture residue ashes (subsection 2.2.1) and forestry biomass ashes (subsection 2.2.2) may be used as a reference for grass energy crop ash and woody energy crop ash, respectively.

2.2.4 Ash from wastes and residues

Biomass derived waste materials are usually incinerated to recover the embedded energy and reduce their volume and weight. The resultant ash properties need a good understanding for safe ash management. Herein, four common ashes from wastes and residues (recovered wood ash, paper sludge ash, sewage sludge ash and municipal solid waste ash (Zhai et al., 2021b)) are reviewed.

Four separate reports of the chemical composition of recovered wood ash have been identified in the literature (Dunnu et al., 2010; ECN.TNO, 2020; Miles et al., 1995). These indicate that the composition of recovered wood ash is dominated by SiO_2 (39%), CaO (16%), MgO (14%), and Al_2O_3 (10%) (Table 2.2). This limited amount of data makes detailed comparison inappropriate, but the composition is generally similar to other wood ashes (particularly softwood ash), although mean data suggests that recovered wood may contain more MgO, Al_2O_3 and possibly SiO_2, and less K_2O and P_2O_5 than other wood ashes, possibly indicating the presence of soil and construction debris in the feedstock. Current information on heavy metal concentration and organic contaminants in the recovered wood ash is limited, although it has been suggested that waste wood (such as painted or impregnated wood) ash could potentially be highly contaminated with heavy metals (Demeyer et al., 2001). Recovered wood may be partially mixed with plastics and thus increase the potential of PCDD/Fs contamination of combustion ashes (Lavric et al., 2004). Chimney soot produced in a domestic heating system from painted wood and wood with 2-5% polyvinyl chloride contains PCDD/Fs at level of 380 to 2240 ng TEQ/kg, which is far higher than chimney soot from untreated natural wood (32 ng TEQ/kg) (Launhardt et al., 1998). If the combustion chamber ash exhibits a similar enhancement in PCDD/Fs it is likely to exceed the recommended EU PCDD/Fs content limit on waste to be used in soil (see Figure 2.2).

Eight reports of the chemical composition of paper sludge ash have been identified in the literature (ECN.TNO, 2020; Holbert and Lighty, 1998; Mun and Ahn, 2001; Toya et al., 2006; Tsai et al., 2002; Wajima et al., 2006; Wajima et al., 2004). The composition of paper sludge ash is dominated by SiO_2 (37%), CaO (26%) and Al_2O_3 (23%) (see Table 2.2). Addition of about 50% paper mill or 15% bleached kraft mill sludge to wood fuel (heat equivalents) results in bottom and fly ashes with heavy metal contents similar to that of the wood fuel (Someshwar, 1996). It is thus presumed that heavy metal concentrations in paper sludge ashes (whether bleached or not) are comparable to ashes from woody biomass. However, the ash from bleached kraft mill sludge could potentially contain more PCDD/Fs because of their chlorine content in the fuel mix compared to pure forest residues and wood (Someshwar, 1996).

Twelve reports of the chemical composition of sewage sludge incineration ash (SSIA) have been collated (Åmand et al., 2006b; Cyr et al., 2007; Donatello et al., 2010c; Dunnu et al., 2010; ECN.TNO, 2020) (Table 2.2). Their composition is dominated by SiO_2 (32%), CaO (15%), P_2O_5 (14%), Fe_2O_3 (13%) and Al_2O_3 (12%). It is noteworthy that SSIA has the highest mean P_2O_5 content of all the biomass ash types considered in this study, although there was considerable variation between different sources (2.0-23%).

Figure 2.4 shows the concentrations of contaminant trace elements in SSIA (full dataset in Appendix A) (Adam et al., 2009; Cyr et al., 2007; Donatello et al., 2010c; Fraissler et al., 2009; Herzel et al., 2016; Vogel and Adam, 2011; Vogel et al., 2013). Zn typically has the highest concentration (median value 1763 mg/kg; Swedish limit for use as a forestry fertiliser 7000 mg/kg), but this presents a smaller environmental risk than Cu and Cr where the median values (674 and 120 mg/kg, respectively) both exceed their respective Swedish limits for use as a forestry fertiliser (Swedish National Board of Forestry, 2002). Also, the Swedish limits for Pb, Ni, As and Hg are exceeded by several individual samples. There is less published information about organic contaminants and toxins in SSIA, but it has been reported that fly ash from fluidized-bed combustion of sewage sludge can contain 43 mg/kg PAHs (4.3 mg TEQ/kg) and 4.4 ng TEQ/kg PCDD/Fs (Deng et al., 2009). PCDD/Fs from sewage sludge incineration have been investigated using three different sludges (two from municipal wastewater one from industrial wastewater treatment) and the filter ash contained 9 - 909 ng TEQ/kg (Samaras et al., 2000) (an ash content of ~33 wt.% of dry solids of the fuel has been assumed (Marani et al., 2003; Samolada and Zabaniotou, 2014; Werther and Ogada, 1999)). Even the high value, which was for the industrial wastewater sludge and probably related to the high chlorine and copper content in this sample (Samaras et al., 2000), is below the proposed EU limit on waste to be used in soil (1000 ng TEQ/kg (BiPRO, 2005); see Figure 2.2), and therefore, PCDD/Fs content in sewage sludge ash is not the main factor restricting beneficial reuse.

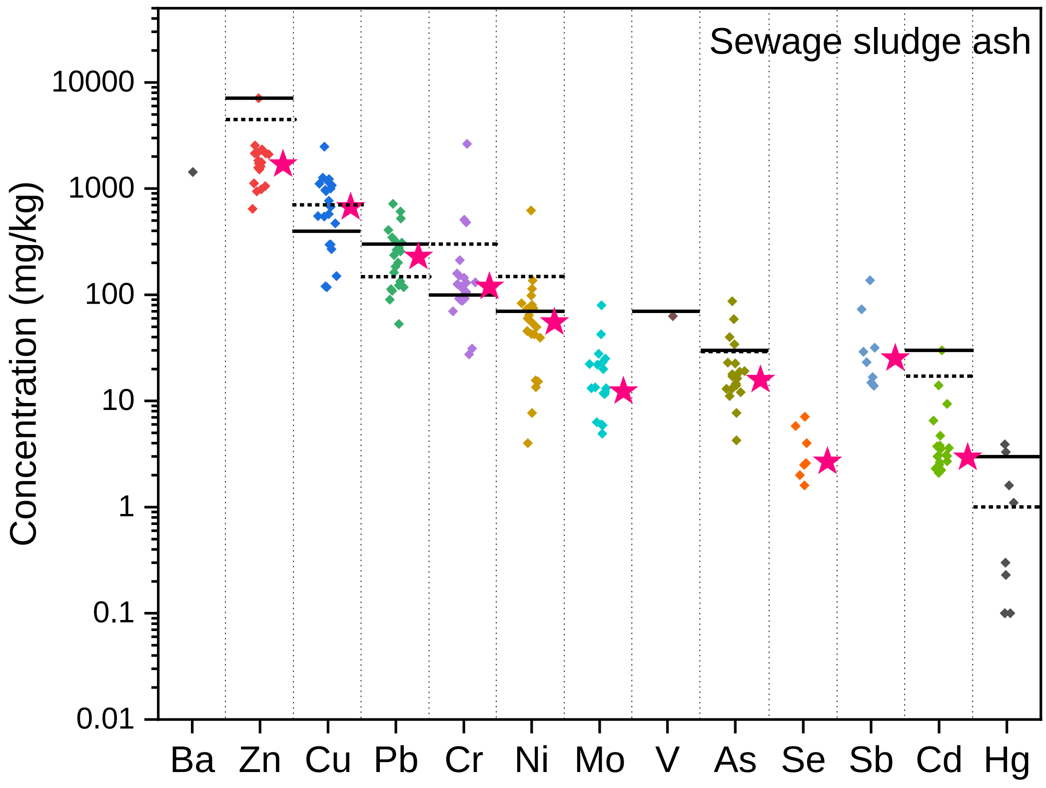


Figure 2.4. Concentrations of some reported trace elements in sewage sludge ashes. The Swedish limits (black solid lines (Swedish National Board of Forestry, 2002)) and Finnish limits (black dotted lines (Dahl et al., 2010)) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median value: median values of Ba and V are not shown because of only one available sample; median value of Hg is zero and therefore not shown).

Data from 10 separate studies has been used to analyse the major element composition of MSW ash (Dunnu et al., 2010; ECN.TNO, 2020; Fedje et al., 2010; Filipponi et al., 2003; Kirby and Rimstidt, 1993; Park and Heo, 2002; Rémond et al., 2002; Tang and Steenari, 2016; Tang et al., 2015). MSW ash mainly contains SiO_2 (32%), CaO (19%), Al_2O_3 (10%), Cl_2O (7%), Na_2O (7%) and Fe_2O_3 (6%) (Table 2.2). Contaminant trace element concentration in MSW bottom and fly ash are reported separately in Figure 2.5 (raw data in Appendix A) (Demirbaş, 2005; Fedje et al., 2010; Forteza et al., 2004; Hu, 2005; Huang et al., 2003; Kalmykova and Fedje, 2013; Li et al., 2007; Liu et al., 2005; Park and Heo, 2002; Rémond et al., 2002; Tang and Steenari, 2015; Tang and Steenari, 2016; Tang et al., 2015; Wei et al., 2011; Xue et al., 2010; Yan et al., 2014; Zhu et al., 2018). The median concentrations of Cu, Pb, Cr and Ni in bottom ash and the median concentrations of most contaminant trace elements in fly ash tend to exceed the Swedish limits for ash use as forest fertiliser (Swedish National Board of Forestry, 2002) (the median concentration of Hg in fly ash is just below the Swedish limit, but above the equivalent Finnish limit (Dahl et al., 2010)). The median concentrations of Zn, Pb, As, Sb, Cd and Hg are higher in MSW fly ash than in the bottom ash, whereas Cu, Cr and Ni have similar concentrations in the two ash fractions (Figure 2.5; the former are volatile at typical incineration temperatures (Belevi and Moench, 2000; Chang and Ku, 1998; Wu and Biswas, 1993; Zhang et al., 2008)).

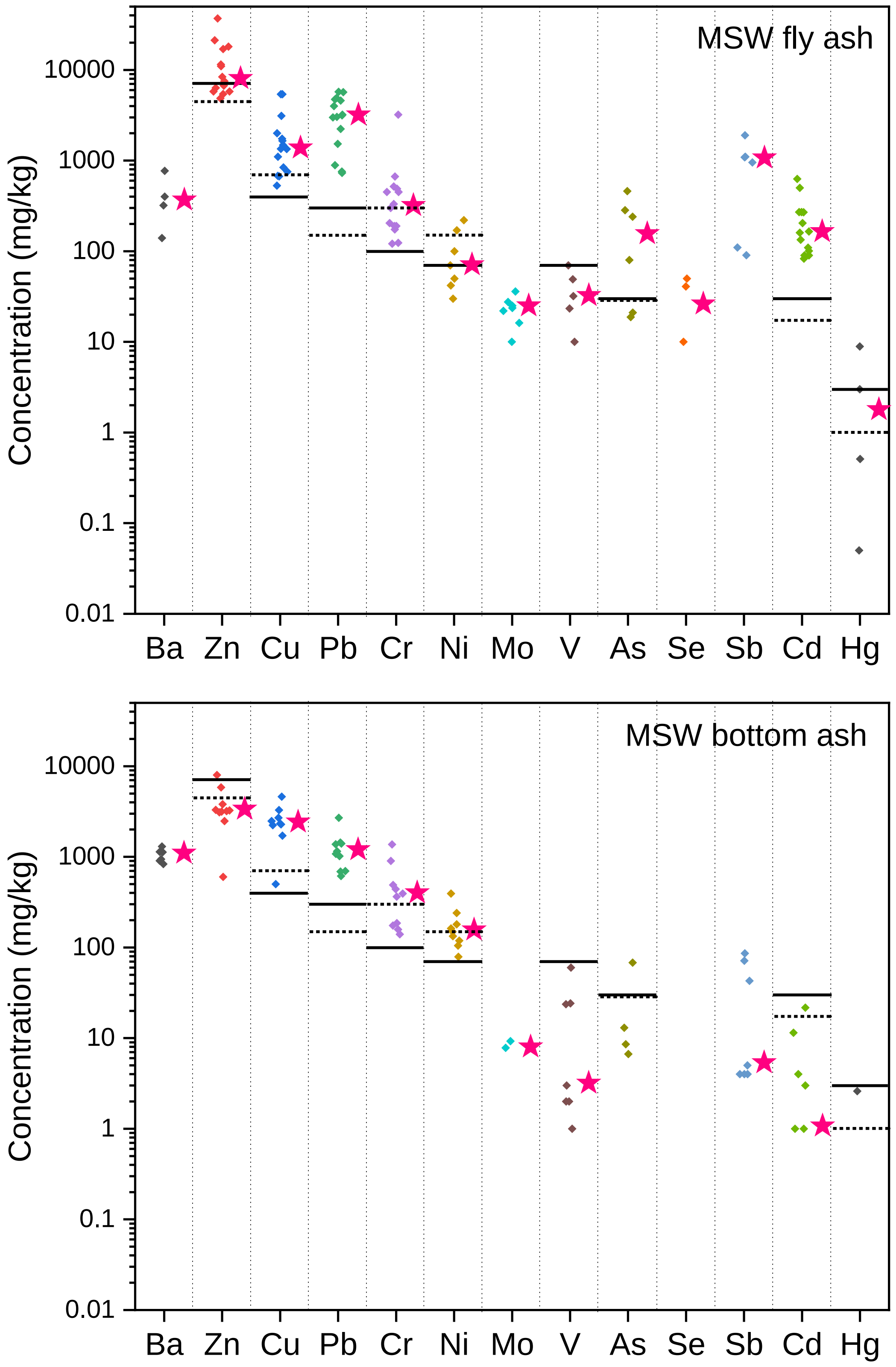


Figure 2.5. Concentrations of some reported trace elements in municipal solid waste ashes. The Swedish limits (black solid lines (Swedish National Board of Forestry, 2002))

and Finnish limits (black dotted lines (Dahl et al., 2010)) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median value: median value of As, Se and Hg in bottom ash is zero and therefore not shown).

PCDD/Fs concentrations in MSW fly ash ranged from 980 to 1500 ng TEQ/kg in Shanghai (He et al., 2004), 780-2860 ng TEQ/kg in Taiwan (Chang et al., 2011), 140 to 18,000 ng TEQ/kg in Sweden (Swedish Environmental Protection Agency, 2011), 130 to 21,000 ng TEQ/kg in Korea (Shin and Chang, 1999), and 1098 to 1839 ng TEQ/kg in UK (Robinson et al., 2004). The high variation of PCDD/Fs concentration in MSW fly ashes in different countries and regions may be caused by the differences in MSW composition, combustion technology and scale. However, the PCDD/F content of MSW fly ash frequently exceeds the proposed EU limit on waste to be used in soil (1000 ng TEQ/kg (BiPRO, 2005)), and sometimes exceeds the EU PCDD/Fs content limit for hazardous waste disposal in landfill, even after solidification (15,000 ng TEQ/kg (European Parliament, 2019)), and thus may require destruction or irreversible transformation of the PCDD/Fs prior to landfill disposal (see Figure 2.2).

2.3 Current practices on ash classification

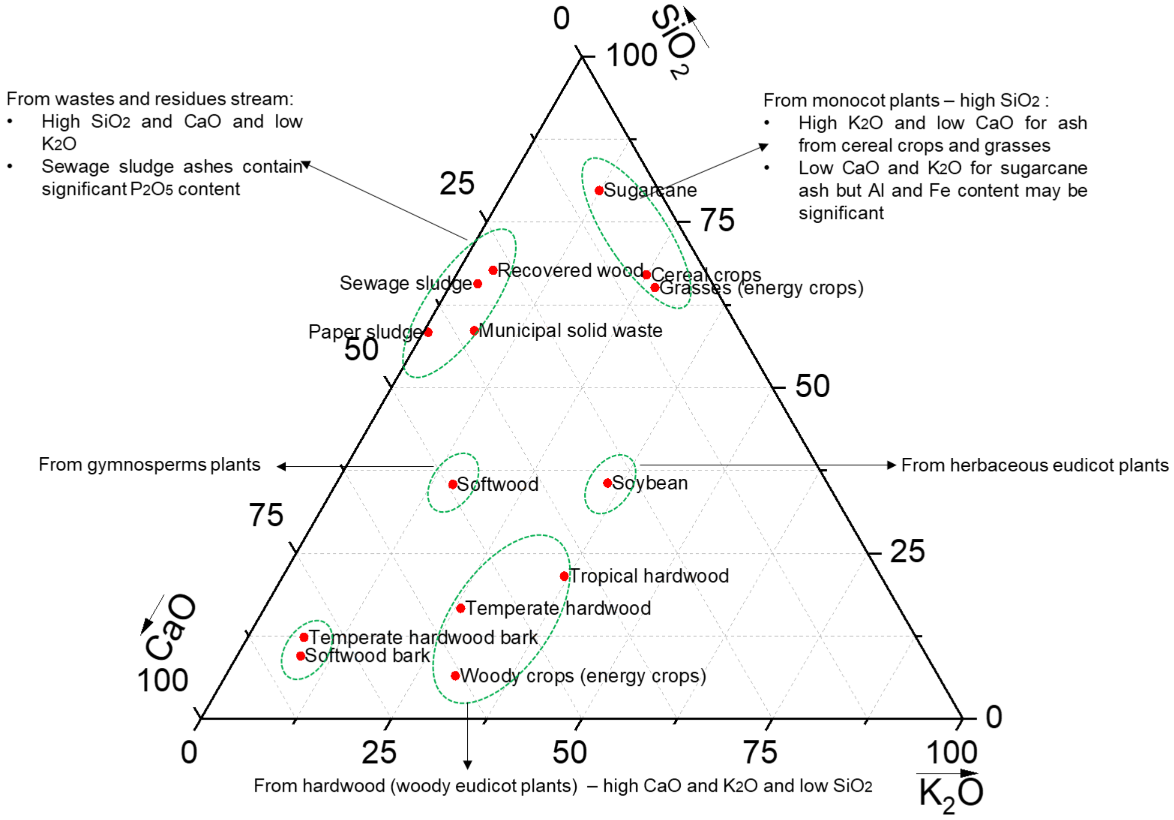
When burning biomass at a commercial scale, it is necessary to make rapid decisions about the feedstock to ensure supply security, and to adapt to seasonal availability and market forces. However, changes in feedstock can potentially affect the elemental composition of the ash produced. Ash composition controls the ash softening and melting temperatures (Zhai et al., 2021a), and thus slagging, fouling and corrosion within the furnace (Dunnu et al., 2010; Niu et al., 2016; Niu et al., 2010), which effect the thermal conversion efficiency of the furnace and determine its maintenance requirements. It also determines the hazards from, and the potential uses of the ash, and thus the ash reuse/disposal strategy. Therefore, an ash classification system based on elemental composition is a valuable tool that will assist in effective furnace management. It will allow furnace operators to understand which feedstocks produce similar ashes and determine the likely changes in ash composition from other feedstocks choices, and thus will facilitate dynamic decision-making at commercial scale.

Coal ash classification has been widely investigated and has proved to be a useful aid to ash reuse (Roy and Griffin, 1982; Vassilev et al., 1996; Vassilev and Vassileva, 2007), and thus biomass ash classification might prove useful in the future. Like coal ash, there is a proposal to characterise it using the relative proportions of three groups of ash-forming elements. For biomass ash the proposed groupings are (CaO+MgO+MnO) which are probably derived from oxalates and carbonates in plant matter, ($K_2O+P_2O_5+SO_3+Cl_2O$) which are probably derived from phosphates, sulphates, chlorides and nitrates in plant matter, and ($SiO_2+Al_2O_3+Fe_2O_3+Na_2O+TiO_2$), which are potentially derived from detrital material (Vassilev et al., 2012). Subsequently, a simplified version of this tripartite classification system was used that captures the statistically significant differences in composition of forestry and agricultural residues ash (Zhai et al., 2021a). This simplified system considers only the relative proportions of the most abundant constituent in each of the three groups (i.e. CaO, K_2O and SiO_2). This classification system was used to demonstrate that the chemical compositions of forestry and agricultural residue ashes reflect evolutionary differences between the feedstock plant species. Table 2.3 shows that the two most abundant elements in most types of biomass ash are either CaO, SiO_2 or K_2O (the only exception is sugarcane ash, which is SiO_2 rich, but Al_3O_2 is the second most abundant element, relegating K_2O to third place). This suggests that classification based on the relative abundances of CaO, K_2O and SiO_2 may be more widely applicable to biomass ash (Zhai et al., 2021b). The mean compositions of the biomass ashes (Table 2.2) have been used to calculate relative abundances of CaO, K_2O and SiO_2 and thus create the ternary diagram in Figure 2.6. This shows that there are compositional groupings amongst the biomass ash categories (Zhai et al., 2021b):

Table 2.3. Summary of abundant chemical components of biomass ash (mean value >5%, wt. %).

Ash origin	Main chemical components	Remarks
Agricultural residues		
Cereal crops residue	$SiO_2 > K_2O > CaO \approx Cl_2O$	Monocots plants (incl. maize, rice and wheat)
Sugarcane residue	$SiO_2 > Al_2O_3 \approx K_2O \approx Fe_2O_3 > CaO$	Monocots plant
Soybean residue	$SiO_2 \approx K_2O > CaO > MgO$	Herbaceous eudicot plant
Energy crops		
Grasses energy crops	$SiO_2 > K_2O > CaO$	Monocots plants (principally miscanthus and pennisetum)
Woody energy crops	$CaO > K_2O > P_2O_5 \approx MgO$	Woody eudicot plants (principally coppiced willow and poplar)
Forest biomass		
Tropical hardwood	$CaO > K_2O > SiO_2 > P_2O_5$	Woody eudicot plants (wood fuel)
Temperate hardwood	$CaO > K_2O > SiO_2 > P_2O_5 > MgO$	Woody eudicot plants (wood fuel)
Softwood	$CaO > SiO_2 > K_2O$	Gymnosperms (wood fuel)
Temperate hardwood bark	$CaO > SiO_2 \approx MgO \approx K_2O$	-
Softwood bark	$CaO > SiO_2 \approx K_2O \approx MgO$	-
Wastes and Residues		
Recovered wood	$SiO_2 > CaO \approx MgO > Al_2O_3 > SO_3 \approx Fe_2O_3$	Principally softwood; contaminated with construction debris
Paper sludge	$SiO_2 > CaO \approx Al_2O_3$	Paper fillers and flocculants used in sludge production affect ash composition
Sewage sludge	$SiO_2 > CaO \approx P_2O_5 \approx Fe_2O_3 \approx Al_2O_3$	Minerals entrained in the sewer and flocculants used in sludge production affect ash composition
Municipal solid waste	$SiO_2 > CaO > Al_2O_3 > Cl_2O \approx Na_2O \approx Fe_2O_3 \approx SO_3$	-

- Ash from monocot plants (cereal crops, sugarcane, and grasses energy crops) are generally dominated by SiO_2 content, which is taken up to support their growth.
- Ash from soybean (herbaceous eudicot plant) contains more CaO but less SiO_2 than the herbaceous monocot plants and does not group with them in Figure 2.6.
- Ash from hardwoods (temperate and tropical hardwood, and woody energy crops are all woody eudicots) is dominated by CaO and K_2O with more modest amounts of SiO_2.
- Ash from softwood (gymnosperms) contains more SiO_2 but less K_2O than hardwood ash and does not group closely with such ash (it has been demonstrated that the compositional differences between these ashes are significant (Zhai et al., 2021a)).



From wastes and residues stream:

- High SiO_2 and CaO and low K_2O
- Sewage sludge ashes contain significant P_2O_5 content

From monocot plants – high SiO_2 :

- High K_2O and low CaO for ash from cereal crops and grasses
- Low CaO and K_2O for sugarcane ash but Al and Fe content may be significant

From gymnosperms plants

From herbaceous eudicot plants

From hardwood (woody eudicot plants) – high CaO and K_2O and low SiO_2

Figure 2.6. Ternary diagram for the classification of biomass ash based on its CaO, K_2O and SiO_2 contents. Composition of different categories of biomass ash is based on the mean values as shown in Table 2.2.

- Ash from temperate hardwood and softwood bark have a much higher CaO and lower K_2O content than the parent wood ashes, and they form a distinct group in Figure 2.6.
- Perhaps surprisingly, ashes from disparate wastes and residues form a single group in Figure 2.6. Their composition is dominated by SiO_2 and CaO, and the K_2O content is modest. These ashes also contain more Al_2O_3 than other biomass ashes (with the exception of sugarcane ash). This probably reflects the similar elemental composition of non-combustible phases in these wastes (e.g. soil and construction debris in recovered wood, soil particles in sewage sludge, clay minerals from recycled paper, and the prevalence of paper/cardboard and glass in MSW).

2.4 Biomass ash management

Management of biomass wastes can include a range of options that include bulk re-use (with and without treatment), indirect recovery of valuable components and safe disposal. Assessment of these options is primarily directed by chemical composition of the ashes and their relative safety. This is a pre-requisite for cost-benefit analysis and should be used to inform policy improvements and business case for future ash management options. For example, during growth, plants take-up essential nutrients and use them to build biomass. The essential primary and secondary macronutrients for plant growth are N, P, and K and Ca, Mg and S, respectively (Barker and Pilbeam, 2015; White and Brown, 2010). P and K in soils are not replenished on human timescales by mobilisation from primary minerals or atmospheric deposition and must therefore be added in the form of organic matter (e.g. manure, digestate or compost) and inorganic fertilisers to maintain soil productivity (Bradshaw, 2000; Cleveland et al., 2013; Tipping et al., 2014). Ca, Mg and S can also be growth limiting in some soil types and are added to agricultural soils when required (Gransee and Führs, 2013; Oldham, 2019; Zhao et al., 1996). After combustion, most of these nutrients remain in the ash, providing an opportunity for their recovery and/or reuse in accordance with the waste hierarchy (European Commission, 2008) (see Table 2.4), but only if contaminant concentrations are acceptable for specific recovery options.

Table 2.4. Recommend resource recovery priorities for different combustion ashes (score based on utilisation potential).

Potential [a] / Ash type	Soil conditioner	K recovery	P recovery	Multicomponent recovery
Grass and cereal residue ash	++	++++	-	-
Eudicot residue ash	+++	++	-	-
Woody biomass ash	+++++	++	-	-
Forest residue ash [b]	++++	-	-	-
Recovered wood ash	-	-	-	-
Paper sludge ash	+	-	-	-
Sewage sludge ash	+	-	++++	-
MSW ash	-	-	+	+++

[a] beneficial reuse of combustion ashes in other applications like construction material production and zeolite synthesis is not listed in this table.

[b] only temperate hardwood bark and softwood bark ashes are considered in this study.

2.4.1 Ash from agricultural residues

2.4.1.1 Grass and cereal residue ashes

Ash derived from cereal crop residues is rich in potassium compounds (Table 2.2: mean 19%), contains modest amounts of phosphate and has very low levels of contaminants, so could potentially be used as a partial fertiliser replacement. A substantial proportion of the potassium is KCl, the common K-mineral phase in potash ore (Samadhi et al., 2019; Wang et al., 2017c; Wang et al., 2015). It thus has a comparable potassium grade to commercially exploited potash deposits (from 11% to 25% in operating potash mines) (Orris et al., 2014). This shows that there is potential for potassium recovery from cereal residue combustion ash. Ash from grass energy crops has similar chemical compositions to cereal crop residue ash and therefore is also a good source material for potassium recovery.

In addition to KCl, potassium in ash can also be present as carbonate and sulphates (Samadhi et al., 2019; Wang et al., 2017b; Wang et al., 2017c; Wang et al., 2015). All three are generally very soluble and can be extracted by hot water leaching. For example leachate from wheat straw ash contains KCl, K_2CO_3 and K_2SO_4 in a mass ratio of 12:9:5 (Wang et al., 2015), which is similar to commercial recovery of potassium from Cl bearing ores (Ciceri et al., 2017). Water leaching is preferable to H_2SO_4 acid leaching, even though K_2SO_4 is used in fertiliser mixtures (Idrees et al., 2004; IPNI), because the enhancement in K extraction is small and it may increase leaching of undesirable impurities (Wang et al., 2017b). Some challenges with water leaching of potassium from biomass ashes are: (1) unburnt carbon in ash can decrease K recovery by about 9-19% (Wang et al., 2017b); and (2) the proper disposal of residues and waste brines (Wang et al., 2017c).

Ash from grass and cereal crop residues is about 50% SiO_2 so its use as secondary pozzolan has been widely investigated. For example, wheat straw ash has been used as an alkali silicate binder in the production of novel inorganic composite boards (Dodson, 2011). Similarly, the use of rice husk ash (Yu et al., 1999) and miscanthus ash (Lojka et al., 2019) as cement substitutes, and wheat straw ash (Al-Akhras and Abu-Alfoul, 2002), rice straw ash (Sung and Kim, 2003), corn stalk ash (Aksoğan et al., 2016) as partial cement replacements in the manufacture of construction materials have also been investigated, and it has been proposed that sugarcane residue ash could be used for similar applications (Ganesan et al., 2007; Martirena et al., 2006). Initial research findings suggest that partial replacement of cement with agriculture residue ash may improve the engineering properties of concrete/mortar (compressive/tensile/flexural strength, splitting tensile strength, chloride/sulfate permeability, etc.), provided the amount of cement replacement is carefully managed (Agwa et al., 2020; Aksoğan et al., 2016; Al-Akhras and Abu-Alfoul, 2002; Ganesan et al., 2007; Yu et al., 1999), however, further work is still required to verify the long-term performance of such materials.

Amorphous and fine silica particles with large surface area are widely used in industry, for example in the production of adhesives, plastics, sealants, coatings, inks, toner, cosmetics, food additives and defoamers (Bartůněk et al., 2018), so recovery of SiO_2 from grass and cereal crop ash has also been investigated. Mesoporous silica has been recovered from miscanthus bottom ash (Dodson et al., 2013). Similarly, zeolites have been synthesised from wheat straw ash (Ali et al., 2018), sugarcane straw ash (Fungaro and da Silva Reis, 2014), and rice husk/hull/straw ash (Jesudoss et al., 2018). For some applications, like end-of-pipe CO_2 capture, biomass ash can be used as supportive precursor with alkali or alkali-earth metal oxides to synthesize the low-cost adsorbents (Guo et al., 2020), and meanwhile, it can capture/store atmospheric CO_2 simply by exposure to air (Vassilev and Vassileva, 2020; Vassilev et al., 2021).

While there has been much research on materials recovery from grass and cereal crop ash, the recovery of a single high-value product will be unattractive if it leaves a large volume residue whose disposal is more problematic than the original ash. There is little published work on multi-product recovery from ash, but a notable exception is the recovery of amorphous silica from grass straw ash using strong alkali, which is compatible with subsequent recovery of $CaCO_3$ leaving only a small volume of residue (Bartůněk et al., 2018), particular as the process appears to be compatible with an initial water extraction step for K_2O recovery.

2.4.1.2 Eudicot residue ashes

Herbaceous eudicot residue ashes have similar K_2O contents to grasses and cereal residues but higher CaO and lower SiO_2 contents (Table 2.2). Thus, eudicot residue ash is a good candidate for potassium recovery as, for example, the K-minerals in cotton straw ash are mainly KCl, K_2SO_4 and $KNaSO_4$ and ~70% is extractable by hot water leaching (Wang et al., 2017c). There has also been limited work on the use of herbaceous eudicot residue ashes as secondary pozzolans (work has been conducted on cotton straw, sunflower seed shell and soybean straw ashes), but the results have been mixed, possibly due to variability in the fine silica content (Agwa et al., 2020; Grubeša et al., 2019; Wang et al., 2017d). Alternatively, the high CaO content of herbaceous eudicot straw ash suggests that it should be suitable for lime addition to acidic soils, but little research has been published on this potential application.

2.4.2 Ash from forestry derived biomass

2.4.2.1 Woody biomass ashes

Ash from the three categories of woody biomass (temperate hardwood, tropical hardwood, and softwood) contains many nutrient elements required for plant growth in significant amounts, particularly Ca, K, P, and Mg (Table 2.2). It also contains relatively low levels of toxic trace elements and organic contaminants (as discussed in subsection 2.2.2). The principal component of all wood ash is CaO, which represents about a third of the ash averaged across all wood types. Hardwood ash also contains about 20% K_2O and just over 10% SiO_2 (differences between temperate and tropical hardwood ash are small). In contrast, nearly a quarter of softwood ash is SiO_2 and only about 10% is K_2O.

Currently the most common beneficial use of wood ash is as soil conditioner and fertilizer, rather than for recovery of specific valuable components (Demirbaş, 2001; Erich, 1991; Huang et al., 1992; Krejsl and Scanlon, 1996; Nkana et al., 1998; Ochecova et al., 2014; Park et al., 2005). Due to its high Ca content (as CaO, CaOH and $CaCO_3$), it is particularly suitable for application to acid soil, such as tropical and forest soils (Demeyer et al., 2001). Neutralising acidic soil reduces Al and Mn toxicity to plants by making lower solubility Mn species more stable and reducing phosphate fixation (fixation by Al and Fe reduces P availability to plants at low pH) (Demeyer et al., 2001; Fernando and Lynch, 2015; Hsu, 1965). Nutrient deficient soils, such as tropical red soils (Wilson et al., 2004; Zhang et al., 2009; Zhong and Cai, 2007), may also gain from other nutrients in the ash (e.g. P and Mg). In addition, modest ash additions can increase soil bacterial numbers and stimulate N-mineralization by reducing the pH stress on microbial communities (Bang-Andreasen et al., 2017; Santás-Miguel et al., 2020; Weber et al., 1985). However, excessive dosing needs to be avoided to prevent salinity build-up (particularly with tropical hardwood ash which has a higher Cl_2O content than other wood ashes) or overdosing with nutrients (Clapham and Zibilske, 1992; Etiegni et al., 1991; White and Brown, 2010), although the high solubility of the dominant phases in wood ash means that it will not persist in soil for long periods (Ulery et al., 1993).

The K_2O grade of hardwood ash is in the same range as commercially exploited potash deposits, while the K_2O grade of softwood ash is at the lower end of that range (Orris et al., 2014). Further, ~60% of the total potassium in softwood ash is rapidly soluble in water at room temperature, so there is potential to recover K_2O for use in fertiliser (Etiegni and Campbell, 1991). It has also been demonstrated that wood ash can be used as partial feedstock to form zeolites, exploiting the ash as a source of both potassium and alkalinity (Fukasawa et al., 2018; Fukasawa et al., 2017). Similarly, it has been demonstrated that wood ash can be used in the manufacture of construction materials (e.g. as partial replacement of lightweight aggregate or, exploiting their pozzolanic properties in cement blends or directly in mortars) (Abdullahi, 2006; Ayobami, 2021; Chowdhury et al., 2015; Siddique, 2012; Tosti et al., 2020). The mass percentage of wood ash in such products needs careful regulation as wood ash appears to be less suitable for such applications than fly ashes from coal (Wang et al., 2008). However, as the unburnt carbon content of wood ashes is one of the limiting factors (Siddique, 2012), the ash from modern commercial biomass power stations where there is careful combustion control may be more suitable than the ash used in many older studies. Another proposed application of wood ash that exploits its Ca-alkalinity is to produce sorbents for end-of-pipe CO_2 separation and capture (Guo et al., 2015; Wang et al., 2017a). Surface modification, such as surface coating by alkaline metal salts or amines, can enhance the CO_2 capture ability of wood ash (Guo et al., 2020; Wang et al., 2017a).

2.4.2.2 Forest residue ashes

There are only very modest differences between the composition of temperate hardwood bark ash and softwood bark ash (Table 2.2; there is very little data for tropical hardwood bark ash). Both materials contain ~60% CaO content (compared with an average value of just over 30% for wood), and as a result less SiO_2 and K_2O and (the average values for bark are ~10% and 6%, respectively). Thus, the principal value within bark ash is lime (CaO, $CaOH_2$ and $CaCO_3$), so given the low level of trace toxic elements and organic contaminants in residues direct from forestry, the most obvious beneficial use is as a soil conditioner for acidic soils (Pérez-Cruzado et al., 2011; Solla-Gullón et al., 2008; Solla-Gullón et al., 2006; Williams et al., 1996). Also, while its other principal components (SiO_2, K_2O and MgO) have value (the first as a pozzolan (Snellings et al., 2012) and the other two as plant nutrients (White and Brown, 2010)), their concentrations may not make their recovery an attractive proposition, however all are compatible with application to soil (Pérez-Cruzado et al., 2011; Solla-Gullón et al., 2008; Solla-Gullón et al., 2006).

There is less definitive data for ash from forestry residues like sawdust and wood chips, as the definition of these materials varies with source. However, as these are waste materials from sawmills and papermills, their ash is likely to be intermediate in composition between wood and bark ash (sawdust is likely to be similar in composition to the parent wood, but other waste materials are likely to contain bark). Thus, their beneficial use as a soil conditioner for acidic soils probably does not require additional verification. Research has been undertaken to demonstrate their suitability (due to their CaO and SiO_2 contents) as a cement replacement material (Elinwa and Mahmood, 2002; Ikponmwosa et al., 2020; Maschowski et al., 2020; Udoeyo and Dashibil, 2002).

2.4.3 Ash from wastes and residues

2.4.3.1 Recovered wood ash

Little has been published on the beneficial management of recovered wood ash, probably because resource recovery/extraction is currently limited by concerns over toxic trace elements in the ash from contaminants in the feedstock (e.g. paint, preservatives and construction debris) (Abouelela et al., 2020; Demeyer et al., 2001). Thus, while its composition is similar to virgin wood ash (it contains more SiO_2, MgO and Al_2O_3, possibly due to construction debris in the feedstock; Table 2.2), it is not used directly as a soil conditioner. It has been proposed that recovered wood should be co-combusted with sewage sludge (displacing other fuels added to ensure uniform combustion), as it will not change the ash disposal issues for either (contaminant metals being an issue for both ashes) (Åmand et al., 2006a).

2.4.3.2 Paper sludge ash

Paper sludge ash has a high CaO content (mean value 26%, Table 2.2) and could be used as a soil amendment via land spreading (Environment Agency, 2015; Nicholson et al., 2016). Paper sludge ash also contains high silica and alumina contents (mean nominal oxide value 37% and 23%, respectively; Table 2.2), which can be exploited in: (1) construction materials production (which also exploits the calcium content) (Ahmad et al., 2013; Bernal et al., 2014; Bui et al., 2019; Fava et al., 2011; Mengasini et al., 2021; Mozaffari et al., 2006); and (2) zeolite synthesis via the alkaline (NaOH) hydrothermal method (Mun and Ahn, 2001; Wajima, 2020; Wajima et al., 2006; Wajima et al., 2004). When paper sludge ash is used to replace cement in construction materials production, it can enhance the engineering properties if the replacement ratio is optimised (e.g. improved mechanical strength at 5% replacement ratio by weight (Ahmad et al., 2013; Bui et al., 2019; Fava et al., 2011) and enhanced sulfate attack resistance (Bui et al., 2019)). The major limitation to the use of paper sludge ash in zeolite synthesis is its high CaO content, which must either be removed by pre-treatment (Wajima et al., 2004), or the Si content must be supplemented (Wajima et al., 2006).

2.4.3.3 Sewage sludge ash

Much has been published on the beneficial reuse of SSIA, which probably reflects the current regulatory challenges associated with its safe disposal rather than easy opportunities for its exploitation. However, SSIA is regarded as potentially a good feedstock for phosphorus recovery (Tan and Lagerkvist, 2011), as it has a similar P content (typically ~14%) to commercially exploited phosphate minerals (5-40%, wt. % as P_2O_5 (Fang et al., 2018)). Also, it could be used as supplementary cementitious material due its high SiO_2 and Al_2O_3 contents (~30% and ~10%, respectively) (Cyr et al., 2007; Donatello and Cheeseman, 2013). However it is not suitable for application to land as there is concern about the contaminant trace element content (Cu and Cr contents typically exceed the Swedish limits, and Pb exceeds the Finnish limit for use as forestry fertilizer (Dahl et al., 2010; Swedish National Board of Forestry, 2002)).

Two main approaches to P recovery from SSIA have been proposed: wet chemical leaching and thermal chemical treatment. H_2SO_4, HCl, HNO_3, oxalic acid and citric acid have been used to dissolve P (Biswas et al., 2009; Fang et al., 2018; Fang et al., 2020; Franz, 2008; Liang et al., 2019; Oliver and Carey, 1976; Takahashi et al., 2001), but H_2SO_4 is the most common due to its low cost, wide availability and the subsequent ease with which unwanted Ca^{2+} can be removed from solution by gypsum precipitation ($CaSO_4 \cdot 2H_2O$) (Donatello and Cheeseman, 2013). Alkaline (NaOH) extraction of P from SSIA has also been attempted but recovery is lower than with HCl (Stark et al., 2006). The challenges that remain for P recovery from SSIA by leaching are: (i) selective separation of valuable phosphorus with impurity elements like heavy metals (Franz, 2008); and (ii) management of leaching residues and waste brines (Donatello and Cheeseman, 2013).

An alternative strategy is thermal treatment of SSIA to remove the heavy metals, so it can be used as a P-fertiliser (Li et al., 2015; Mattenberger et al., 2008; Mattenberger et al., 2010; Vogel and Adam, 2011; Vogel et al., 2013). Usually either inorganic chlorinating agents (HCl, KCl, $CaCl_2$ and $MgCl_2$) or organic chlorinating agents (polyvinylchloride) are added to the ash, and heavy metal chlorides are removed by evaporation. However, potential issues are: (1) detrimental transformation of P minerals that influence bioavailability (Vogel and Adam, 2011); (2) potential P loss (Mattenberger et al., 2008); and (3) the limited removal of largely non-volatile Cr and Ni (Mattenberger et al., 2008; Vogel and Adam, 2011). Another thermal method is to treat SSIA with sodium (K_2SO_4, Na_2CO_3 and NaOH) and potassium (KOH and K_2CO_3) under reducing conditions prior to removing the heavy metals by evaporation (Herzel et al., 2016), which has the advantage that the new P-bearing mineral phases have high bioavailability.

As SSIA contains reasonable amounts of SiO_2 and Al_2O_3 (Table 2.2), researchers have tried to exploit its pozzolanic properties in alternative construction materials, but it can cause decreased compressive strength, increased water demand and delays in cement hydration time, which limits the amount that can be added to such products (Cyr et al., 2007; Donatello and Cheeseman, 2013; Donatello et al., 2010a; Pan et al., 2003). There is also an ethical issue with direct use of SSIA in construction material production as it results in permanent loss of P (a valuable but finite resource (Donatello and Cheeseman, 2013; Neset and Cordell, 2012; Scholz et al., 2013; Tan and Lagerkvist, 2011)).

2.4.3.4 Municipal solid waste ash

Ferrous and non-ferrous metals (e.g. Al, Cu, Zn) are routinely recovered from the MSW bottom ash from waste to energy plants, leaving a material suitable for restricted use as aggregate (Abdulahi, 2009; Allegrini et al., 2014; Allegrini et al., 2015; Berkhout et al., 2011; Hjelmar et al., 2007; Lynn et al., 2017; Reid et al., 2008; Xia et al., 2017). Several studies have shown construction materials made with bottom ash and bottom ash reuse as aggregate in pavement applications meet the regulatory standards (Abdulahi, 2009; Li et al., 2012; Yan et al., 2014), but an environmental risk assessment is often required before use is permitted (Hjelmar et al., 2007). There has also been research into exploiting the pozzolanic properties of MSW bottom ash (Alderete et al., 2021; Li et al., 2012; Lynn et al., 2016; Tang et al., 2020; Yan et al., 2014). However, its use in cementitious materials is not straight-forward because it contains chlorides, sulfates, metallic Al and Cu, glass particles and possibly residual organics that are deleterious to cement hydration and the strength of the mortars (Loginova et al., 2019; Lynn et al., 2016; Sabbas et al., 2003; Tang et al., 2015; Wiles, 1996). Thus, further pre-treatment of bottom ash will probably be required before such use. Rare earth elements are also found in bottom ash but the concentrations are too low to recover based on current technology (Allegrini et al., 2014).

Heavy metal recovery from MSW fly ash is technically viable via thermal or hydrometallurgical methods (Geng et al., 2020; Kuboňová et al., 2013; Xue et al., 2010; Zucha et al., 2020). About 70% Cu, 80% Zn, >90% Pb and >92% Cd can be leached from the fly ash using HCl solution (Tang and Steenari, 2016), and the subsequent Cu separation from the acid leachate is viable but the Zn separation needs further refinement because of the co-extraction of Fe, Pb and Cd (Tang and Steenari, 2015). However, developing a reuse strategy for MSW fly-ash is far more challenging than it is for bottom ash, as modern waste-to-energy plants use sophisticated air pollution control (APC) equipment (dry, semidry or wet scrubbers; electrostatic precipitators; bag filters; fabric filters, and cyclones) to prevent pollutant release to atmosphere. The result is that the fly ash is often combined with other APC residues, and the product varies in composition depending the additives used from plant to plant (e.g. lime, activated carbon, etc.) (Quina et al., 2008). As a result APC residue is usually handled as a hazardous waste unless treated (Veolia, 2013) (recently developed commercial treatments involve either carbonation and incorporation into a binder (Chen et al., 2019; Sabbas et al., 2003; Veolia, 2013), or plasma treatment to extract hydrochloric acid and separate hazardous elements (Kourti et al., 2010; Tetronics; Wang et al., 2009), to produce secondary aggregates).

2.5 Conclusions

Biomass combustion produces ash with a composition dominated by two of three elemental oxides, SiO_2, CaO, K_2O, which typically forms >60% of ash from virgin biomass. Ash from biomass containing wastes typically contains more Al_2O_3 and Fe_2O_3 than ash from virgin biomass. The abundant nominal oxide phases (> 5 wt.%) in grass crop residues ash are SiO_2 > K_2O > CaO, in tropical hardwood ash are CaO > K_2O > SiO_2> P_2O_5, in temperate hardwood ash are CaO > K_2O > SiO_2 > P_2O_5 > MgO, and in softwood ash are CaO > SiO_2 > K_2O. The abundant nominal oxide phases (> 5 wt%) in biomass containing waste ashes are typically SiO_2 > CaO > Al_2O_3 > Fe_2O_3. In addition, recovered wood ash also contains nearly 15% MgO, sewage sludge incineration ash contains nearly 15% P_2O_5, whereas MSW ash also contains nearly 7% Cl_2O. Combustion of virgin biomass in modern well-run furnace can produce ash with negligible persistent organic pollutants (POPs), which makes direct application to land possible. Agricultural residue ashes contain abundant potassium, modest amounts of phosphate, and very low levels of contaminant metals so could potentially be used as a fertiliser additive. Forestry ashes are rich in CaO which is used as a soil conditioner, but their slightly higher contaminant metals levels may restrict their direct use to forestry soils. Other reuse and resource recovery options differ by ash category. Grass crop residues have pozzolanic activity and may be suitable as a cement replacement material. Other virgin biomass ashes have less pozzolanic activity but appear to be suitable for use a filler in cementitious materials. Potassium recovery has been demonstrated for several categories of ash, and silica recovery has been demonstrated for grass crop residues, but further work is required to ensure that the remainder after resource extraction has a viable use. Paper sludge ash may be suitable for restricted use as a soil conditioner and potentially a secondary pozzolan. Municipal solid waste bottom ash is routinely used as a construction aggregate for prescribed applications. Reuse of recovered wood ash and sewage sludge incineration ash are more challenging due to uncertainties associated with contaminant metals, and controlled disposal may be required.

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Chapter 3: Global biomass ash production and distribution

3.1 Introduction

There are two determinants for the estimation of ash amounts that can be produced from biomass incineration: ash content of biomass and the biomass amounts subjected to bioenergy production. Ash contents of biomass are influenced by biomass types (Vassilev et al., 2010; Zhai et al., 2021a), and for example, median ash contents of grass/eudicot straw (5.2/8.8%) and (eudicot) hardwood/softwood (1.6/1.0%) are significantly different (Zhai et al., 2021a). Meanwhile, biomass amounts used as sustainable biofuels are changing within recent decades as many nations are attempting to transition to a low-carbon economy (Bridge et al., 2013; Scarlat et al., 2015; Zhang, 2010). Therefore, national biomass ash production figures are not routinely published, and it is difficult to directly estimate the worldwide ash quantities. This is further complicated by national differences in how data is reported: for example, biomass ash figures from some countries include partial coal co-combustion with biomass (IEA Bioenergy, 2018). However, biomass ash amounts produced globally, if possible, should be estimated in a suitable way, so that: (1) policy-makers can acquire the information on biomass ash that should be concerned with considerations of both ash amounts and ash characteristics; (2) this can facilitate the research focus on the beneficial management of those ashes with large amounts or with problematic ash properties or with both; (3) and the changing trend of biomass ash amounts can be reflected to indicate the research needs in future.

Some attempts or initiatives have been made to estimate the biomass ash quantities. The Task 32 (Biomass Combustion) set out by the International Energy Agency (IEA) published the reports entitled “Options for increased use of ash from biomass combustion and co-firing” in 2018, which only reported the ash quantities in Austria, Canada, Denmark, Germany, Italy, The Netherland and Sweden (IEA Bioenergy, 2018). However, these directly reported ash data include different biomass sources for different countries and therefore a comparison is difficult. It was estimated in 2013 that approximately 7 billion tonnes (Gt) of biomass were burned annually for energy production (Vassilev et al., 2013). However, it appears to be based on an optimistic interpretation of data published between 2001 and 2010 (possibly to allow for growth in the biomass fuel usage in the intervening period). For example, it includes 3 Gt for forest residues, whereas the cited paper reports just under 2 Gt of forestry-based biofuels were produced worldwide in 2006 (Heinimö and

Junginger, 2009). Three separate sources were used to estimate the range for agricultural residues (between 1.1 and 3.1 Gt/yr (Abbasi and Abbasi, 2010; Heinimö and Junginger, 2009; Werther et al., 2000)), however a high-end figure is incorporated into the total. Typical ash production rate (mean ash yield at 6.8% of 86 biomass on dry basis (Vassilev et al., 2010)) was used to estimate that this biomass would have produced about 480 million tonnes of ash (Vassilev et al., 2013). It can be seen that the biomass amounts used for such estimate are based on those data over 10 years old, and moreover, the used ash yield of 6.8% neglects the difference in ash contents of different biomass, at least their differences in some biomass categories (e.g. agriculture residues and woody biomass). Therefore, such estimate of biomass ash quantities seems to be out of date and lack the significance on guiding ash management. Separately, it has been estimated that, globally, 43.5 – 56.5 EJ of energy was produced from biomass fuels in 2016 (Ritchie and Roser, 2018; World Bioenergy Association, 2019). If the energy content of fuel was similar to wood (the principal biomass fuel in use), then the total global usage of biomass is about 3 Gt/yr (assumption of 50 EJ/yr energy to be produced and the fuel energy content at 18 MJ/kg corresponds to 2.78 Gt/yr biomass to be utilised), which is less than half of the value used by Vassilev et. al.

However, no matter the 7 Gt/yr reported by Vassilev et al. or the 3 Gt/yr calculated from the global energy production, the biomass used for bioenergy generation accounts for only a very small parts of the total biomass created annually by terrestrial photosynthesis, as some is converted to root exudates, some remains below the ground as root material, some is lost as plant litter, and some is used as food, animal feed, construction materials and wood pulp for paper (Zhai et al., 2021b). A review in 2015 estimated the amount of carbon captured by terrestrial photosynthesis to be between 119 and 169 Pg C/year (Anav et al., 2015). Similarly, a best-estimate of 147 Pg C/year (range 131-163 Pg C/year) has been obtained from remote sensing of the near-infrared reflectance of vegetation (Badgley et al., 2019). Assuming that organic matter is 50% carbon (Pribyl, 2010), a factor of 2 is applied and this estimate (147 Pg C/year) of global net primary production corresponds very approximately to about 300 Gt/yr of organic matter. It can be seen that currently no more than 3% of the organic matter created annually by photosynthesis is used for bioenergy purpose.

To date, there is no practical biomass ash production data across the globe that can provide assistance on ash management for policy-makers, decision-makers and researchers. Although the total biomass amounts available for bioenergy generation is large, biomass supply can change in future: currently bioenergy from forestry sources is the largest contributor to global bioenergy supply, but it is estimated that the agriculture residues and dedicated energy crops will play a critical role in future bioenergy supply (Sims et al., 2006; World Bioenergy Association, 2019); also, with the increasing population growth and urbanization, more energy extraction by combustion of MSW and sewage sludge can be expected in the coming decades (Chen et al., 2016; Shaddel et al., 2019). Considering the biomass influence on ash content and ash characteristics, global biomass ash amounts will be helpful if they can be estimated specially based on the four major ash categories established in chapter 2: ashes from agriculture residues, forestry derived biomass, energy crops, and wastes/residues. In principle, global ash production data of this research is estimated from biomass production data (biomass amounts used for incineration), which is better recorded in most regions. The ash contents of specific biomass or biomass category are used to increase the pertinence and accuracy of the estimation.

3.2 Biomass supply and flow to incineration

A summary of biomass supply and its incineration rate based on current and maximum utilisation levels is shown in Table 3.1. Details on creating the table are discussed below.

Table 3.1. Global estimates of biomass supply, the current and maximum utilisation levels of biomass for incineration.

Fuel Source		Africa	Americas	Asia	Europe	Oceania	Total
Agriculture							
Agriculture residues	Amount produced (Mt/yr) [a]	624	3125	3244	998	67	8,058
	Current utilisation rate (%) [b]	4.1%	0.6%	1.1%	1.3%	0.7%	-
	Maximum utilisation rate (%)	50%	50%	50%	50%	50%	50%
Forestry							
Wood Fuel	Amount produced (Mt/yr) [c]	298	145	305	74	4	826
	Current utilisation rate (%)	100%	100%	100%	100%	100%	100%
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%
Wood chips, particles and residues	Amount produced (Mt/yr) [c]	1.0	49.8	54.1	57.8	5.7	168.4
	Current utilisation rate (%)	100%	100%	100%	100%	100%	100%
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%
Charcoal	Amount produced (Mt/yr) [c]	34.2	9.2	9.0	0.7	0.04	53.2
	Current utilisation rate (%)	100%	100%	100%	100%	100%	100%
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%
Wastes and residues							
Recovered wood	Amount produced (Mt/yr) [c]	-	-	0.8	26.4	-	27.2
	Current utilisation rate (%)	-	-	100%	100%	-	100%
	Maximum utilisation rate (%)	-	-	100%	100%	-	100%
Paper waste	Amount produced (Mt/yr) [d]	0.2	4.7	8.6	4.7	0.2	18.3
	Current utilisation rate (%) [e]	54%	54%	54%	54%	54%	54%
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%
Sewage sludge	Amount produced (Mt/yr) [f]	5.9	11.2	21	16.8	0.9	55.7
	Current utilisation rate (%) [g]	0%	15%	25%	24%	0%	-
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%
Municipal solid waste	Amount produced (Mt/yr) [h]	302.7	550.4	1165.3	599.4	28.7	2,646.4
	Current utilisation rate (%) [i]	0%	7%	26.40%	25.80%	1.50%	-
	Maximum utilisation rate (%)	100%	100%	100%	100%	100%	100%

[a] Source: (FAOSTAT, 2020; World Bioenergy Association, 2019).

[b] Source: (Cherubini and Ulgiati, 2010; Gravalos et al., 2016; Heinimö and Junginger, 2009; World Bioenergy Association, 2019).

[c] Source: (FAOSTAT, 2020; Forest Research, 2020).

[d] Source: (Haggith et al., 2018; Molina-Sánchez et al., 2018).

[e] Source: (van Ewijk et al., 2018).

[f] Source: (Bianchini et al., 2016; FAOSTAT, 2020; Yang et al., 2015).

[g] Source: (Bianchini et al., 2016; Christodoulou and Stamatelatou, 2016; Wei et al., 2020).

[h] Source: (FAOSTAT, 2020; Hoornweg and Bhada-Tata, 2012).

[i] Source: (Chi, 2017; Down To Earth, 2019; Habitat UN, 2010; Malinauskaite et al., 2017; Perrot and Subiantoro, 2018; US Energy Information Administration, 2019; Veolia, 2018).

3.2.1 Agriculture residues

The quantities of the principal agricultural residues suitable for biomass combustion (e.g. cereals crops and sugarcane) have been estimated by using United Nations (UN) agricultural production figures for 2018 (World Bioenergy Association, 2019) and average crop to residue ratios (FAOSTAT, 2020). Worldwide, agricultural residues contribute less than 3% to the total bioenergy production of 55.6 EJ in 2017 (World Bioenergy Association, 2019), which corresponds to usage of about 93 Mt/yr (an energy yield from agricultural residues by combustion of 18 GJ/t is assumed (Cherubini and Ulgiati, 2010; Gravalos et al., 2016; Heinimö and Junginger, 2009)). Regional data on energy from agricultural residues is not available, but if it is assumed to be 3% of bioenergy production in each region, then a rough estimate of the utilisation rate can be obtained (Table 3.1). The maximum sustainable utilisation of agricultural residues was assumed to be 50% as the remainder must be returned to the land for soil health (World Bioenergy Association, 2019). The median ash contents of (monocot) grass straw (5.2%) and eudicot straw (8.8%) are not significantly different (Zhai et al., 2021a), and meanwhile biomass production data do not support the accurate separation of both. Therefore, grass and cereal residue and eudicot residue quantities are not estimated separately.

3.2.2 Forestry derived biomass

An estimate of the amount of wood fuel used by region was obtained from the UN forestry production figures for 2018 (FAOSTAT, 2020) by assuming a wood density of 425 kg/m^3 for unit conversion from volume to mass (air dry stacked log wood has a density of 350-500 kg/m^3 (Forest Research, 2020)). As the amount of land used for forestry is relatively steady (globally it is changing by < 0.1% per annum), it is assumed that current usage is the maximum sustainable. Similarly, estimates of the amount of wood chips, particles, pellets and residues (excluding particleboard, fibreboard, wood pulp and similar forest products), and the amount of charcoal used by region were also obtained from the UN forestry production figures for 2018. A density of 250 kg/m^3 was used to calculate the mass of wood chips used from volume data (Forest Research, 2020). It is assumed that all forest residues quantified by the UN but not converted to a product are burnt. Similarly, it is assumed that all charcoal (100%) is burnt. As for forestry derived biomass estimation, hardwood and softwood are not further separated because the available forestry derived biomass data are not supportive for such purpose and moreover their median ash contents do not differ significantly (Zhai et al., 2021a), which means the estimated ash quantities below will not change significantly.

3.2.3 Energy crops

Perennial bioenergy crops are widely seen as viable source of renewable energy that can contribute to climate change mitigation by substituting for fossil fuels (Intelligent Energy Europe, 2009; Whitaker et al., 2018). Worldwide, the main perennial energy crops are grasses like miscanthus, switchgrass, reed canary grass and giant reed, and short rotation coppice crops like willow and poplar (Agostini et al., 2015). In addition, some dedicated energy crops are produced mainly for liquid biofuel and biogas production such as oil seed crops for hydrogenated vegetable oil/biodiesel, cereal crops for bioethanol/biogas, and sugar crops for bioethanol (Sims et al., 2006). Advocates of such crops believe that they can be a carbon neutral (and possibly even carbon negative) source of energy if grown on low grade soils, as a proportion of the litter, harvest residues, roots and root exudates are sequestered into recalcitrant soil organic matter (Agostini et al., 2015). However, there is also concern that widespread production will displace food crops (Intelligent Energy Europe, 2009; Vassilev et al., 2010). Global figures for perennial energy crop usage are not available, however 54 kt/yr were burnt in UK power stations in 2017/18 (Published 5th Dec. 2019). If the same per capital usage is assumed across Europe, it would represent ~0.2% of the amount of wood fuel burnt. It surmised that the current contribution of perennial energy crops to global energy usage is small, and therefore Table 3.1 does not cover the energy crops.

3.2.4 Wastes and residues

The quantities of post-consumer wood that are recovered in Europe and Asia are reported in the UN forestry production statistics (FAOSTAT, 2020). The collection of such data implies either a market for such materials, or regulation of their disposal. It is assumed that recovered post-consumer wood in regions where data is collected is used as fuel, with no burning of recovered wood in regions where no data is collected. This will over-estimate recovered wood combustion in regions where data is collected, as some wood may be returned to the construction sector, or sent to landfill, but will under-estimate recovered wood combustion in regions where no data is collected (in poorer regions the informal sector will recovery wood and some will be used as fuel).

The amount of dry solids in paper sludge has been estimated from global paper production figures (Haggith et al., 2018), and the assumption that paper sludge contains 4.5% air-dry solids (Molina-Sánchez et al., 2018). It is assumed that 54% of sludges are incinerated (the reported rate in 2012 (van Ewijk et al., 2018)).

The estimate of sewage sludge production around the world is based on the UN population data for 2018 (FAOSTAT, 2020). The amount of sewage sludge generated per capita depends on the proportion of wastewater treated centrally and the level of treatment undertaken, and therefore varies around the globe. Sewage sludge production in N. America, Europe and Oceania is calculated from the EU-27 average of 22.5 kg dry solids per person per year (Bianchini et al., 2016). Sewage sludge production for the rest of the world is calculated from the Chinese average of 4.6 kg dry solids per person per year (Yang et al., 2015). This approach is likely to overestimate production in regions where there is less centralised wastewater treatment than in China. The proportion of sewage sludge that is incinerated in the European Union (EU) member countries (the EU-27) is assumed for Europe (Bianchini et al., 2016), and the USA sewage sludge incineration rate (Christodoulou and Stamatelatou, 2016) is used for Americas. The average incineration rate of China in 2016-2019 (Wei et al., 2020) is assumed for Asia. Sewage sludge incineration is rare in Australia and New Zealand (Christodoulou and Stamatelatou, 2016) and thus there is no estimate for Oceania. No formal sewage sludge incineration is assumed for Africa.

The estimate of MSW production around the world is based on the UN population data for 2018 (FAOSTAT, 2020) and regional MSW production rates reported by the World Bank’s Urban Development and Local Government Unit of the Sustainable Development Network (Hoornweg and Bhada-Tata, 2012). The average MSW incineration rate in the EU-27 (Malinauskaite et al., 2017) is assumed for Europe. The MSW incineration rate for the USA (US Energy Information Administration, 2019) is used for N. America (excluding Caribbean and Central America) and no incineration is assumed in Latin America (Habitat UN, 2010). The population weighted average incineration rates for India (Down To Earth, 2019) and China (Chi, 2017) are used for Asia. Commercial incineration of MSW is not common practice in Oceania (Perrot and Subiantoro, 2018), so the overall incineration rate has been calculated by averaging the amount of incineration in Australia (Veolia, 2018) over the entire region. No formal MSW incineration is assumed for Africa.

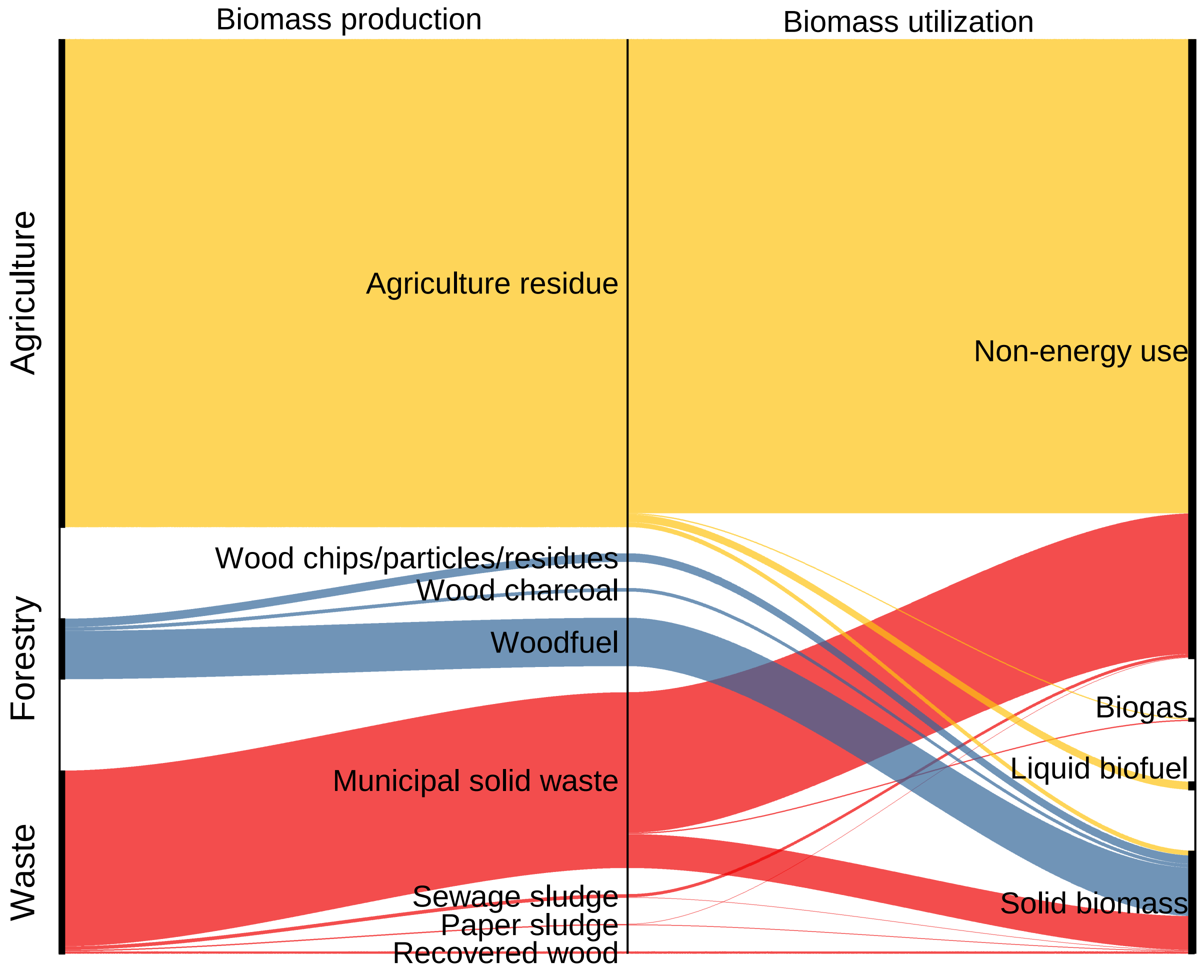

Figure 3.1. Global biomass production and utilisation (production is based on Table 3.1, and proportion of biomass used as a solid, liquid or gaseous fuel was determined from World Bioenergy Association data (World Bioenergy Association, 2019)).

Overall global biomass supply and the utilisation patterns are presented schematically in Figure 3.1. However, dedicated energy crops and some other wastes like animal manure and industrial waste are not shown in Figure 3.1 because the datasets are unavailable, although they contribute to bioenergy production. Current biomass/bioenergy supplies are from three sectors: agriculture, forestry and wastes; and only small proportions of agricultural and waste biomass are used for bioenergy purposes (thus there is great potential for future exploitation). In 2017 >90% of biomass used for energy production was burnt as solid fuel (World Bioenergy Association, 2019). Based on current biomass utilisation level (Table 3.1), only about 2 Gt/yr of biomass is subjected for bioenergy generation, but biomass usage has the potential to increase to around 8 Gt/yr in future if biomass utilisation is exploited to the maximum level. Current biomass utilisation of 2 Gt/yr based on Table 3.1 is close to the value (3 Gt/yr) calculated from the global energy production data as above mentioned but far lower than the 7 Gt/yr used by Vassilev et. al. However, the high estimation of 8 Gt/yr based on the maximum biomass utilisation level is very close to the value used by Vassilev et al.

3.3 Ash content of biomass

Ash content of biomass is the vital parameter to estimate the ash amounts, and the following values are applied to different biomass categories for this research:

- The ash content of agricultural residues is assumed at 6 wt.% (Gravalos et al., 2016; Llorente and García, 2005; Vassilev et al., 2010).
- The average wood ash content is assumed to be 1.5% (hardwood median 1.6%, softwood median 1.0% (Zhai et al., 2021a)); an ash content of 1.5% was assumed for forestry residues; loss of volatile wood components during charcoal production results in 75% mass loss (Ukrainian Biofuel Suppliers, 2020), so a charcoal ash content of 6% is assumed.
- The ash content of recovered wood is assumed to be similar to that of virgin woody biomass, assumed at 1.5 wt.% (Zhai et al., 2021a); although there is the potential contamination of such wood by soil and debris by which the ash content shall be increase, the total recovered wood quantities available for combustion is very small (<3% of the forestry derived biomass; Table 3.1) and such influence can be neglected.
- The ash content of paper sludge is assumed to be 25 wt.% of air-dry solids (ECN.TNO, 2020).
- The ash content of sewage sludge is assumed to be 33 wt.% of dry solids (Marani et al., 2003; Samolada and Zabaniotou, 2014; Werther and Ogada, 1999).
- The ash content of MSW is assumed to be 27.1% (Federal Highway Administration, 2016).

3.4 Ash production from incineration process and its global distribution

Based on the biomass amounts that can be used for incineration based on current and maximum utilisation levels (Table 3.1) and the associated ash content, the ash production data is calculated in Table 3.2 and schematically shown in Figure 3.2.

Table 3.2. Global biomass ash production estimates broken down by region based on current and maximum biomass utilisation level.

Ash amounts (Mt/yr)	Biomass utilisation level	Africa	Americas	Asia	Europe	Oceania	Total
Agriculture residue ash	Current	1.54	1.08	2.16	0.75	0.03	5.56
	Maximum	18.72	93.75	97.32	29.94	2.01	241.74
Wood fuel ash	Current	4.46	2.17	4.58	1.11	0.06	12.38
	Maximum	4.46	2.17	4.58	1.11	0.06	12.38
Wood chips, particles and residues ash	Current	0.02	0.75	0.81	0.87	0.08	2.53
	Maximum	0.02	0.75	0.81	0.87	0.08	2.53
Charcoal ash	Current	2.05	0.55	0.54	0.04	0.00	3.18
	Maximum	2.05	0.55	0.54	0.04	0.00	3.18
Recovered wood ash	Current	-	-	0.01	0.4	-	0.41
	Maximum	-	-	0.01	0.4	-	0.41
Paper sludge ash	Current	0.02	0.63	1.16	0.63	0.02	2.46
	Maximum	0.05	1.18	2.15	1.18	0.05	4.61
Sewage sludge ash	Current	0	0.54	1.76	1.31	0	3.61
	Maximum	1.95	3.70	6.93	5.54	0.30	18.42
MSW ash	Current	0	10.07	83.37	41.91	0.12	135.47
	Maximum	82.03	149.16	315.8	162.44	7.78	717.21

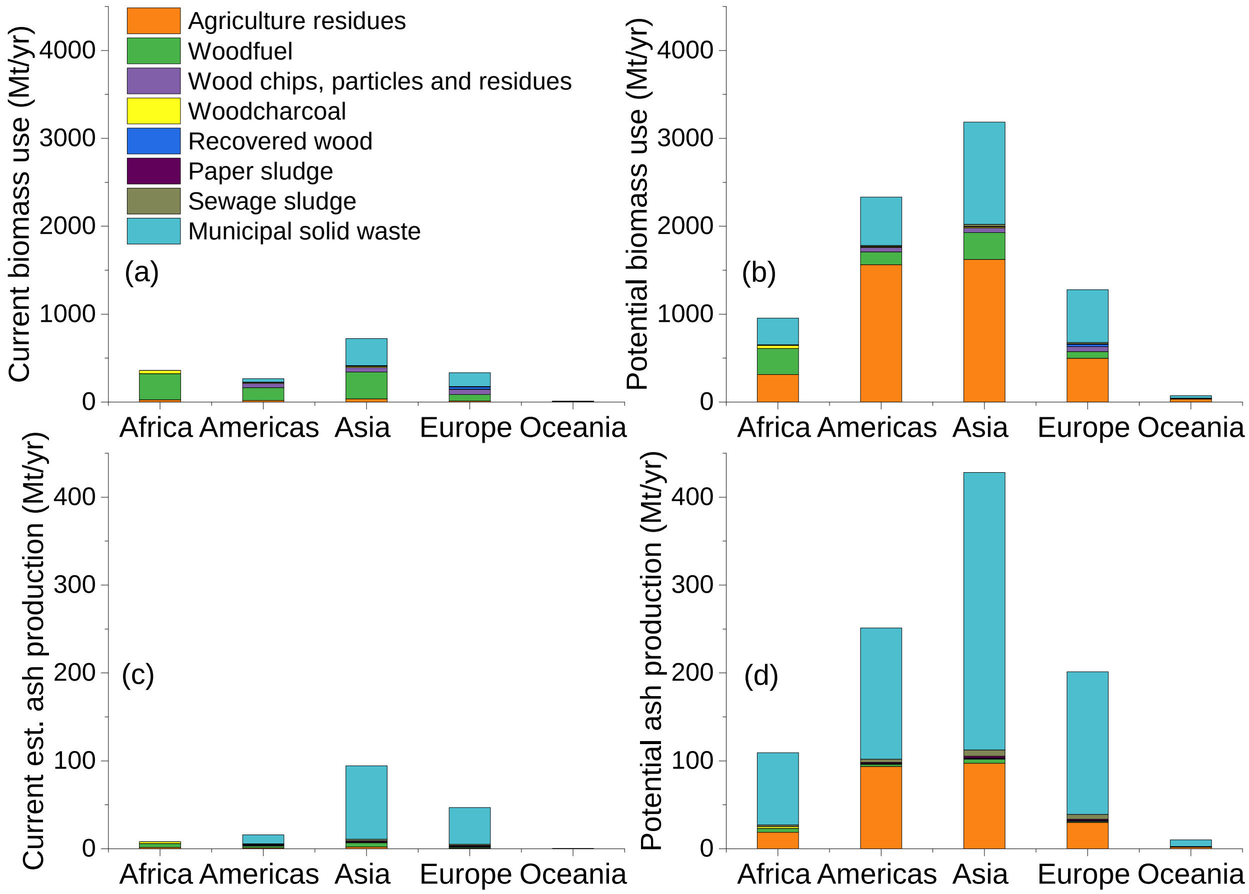

Figure 3.2. Current biomass utilisation level (a) and potential biomass utilisation if used to maximum level (b); current estimates of ash production (c) and potential ash production (d) if used to maximum level.

The breakdown of biomass utilisation by geographic region (Figure 3.2a) shows that wood fuel is the main biomass feedstock used in Africa, where it is used for traditional cooking and heating (World Bioenergy Association, 2019), and therefore wood ash is the primary biomass type in Africa. In Europe, large volumes of MSW are burnt to generate energy, whereas in Asia and Americas, main bioenergy supplies are from wood fuel, MSW and wood chips, particles, and residues. The pattern of biomass ash production (Figure 3.2c) differs markedly from that for fuel use due to the differing ash contents. Currently, MSW incineration is the main source of biomass ash in Americas, Asia, and Europe due to its high ash content. Ash from forestry derived biomass ranks the second place of global biomass ash production (Table 3.2). Agricultural residue utilisation is now low (World Bioenergy Association, 2019), but there is great potential for future bioenergy supply (Figure 3.2b), and similarly there is scope for increased recovery of energy from MSW

(Chen et al., 2016). Thus, future biomass ash production is likely to be dominated by MSW and agricultural residue ash. In addition, sewage sludge ash is projected to increase by more than 4 times than the current level, reaching to a similar level as ash from forestry derived biomass (Table 3.2). As sewage sludge ash contains valuable P that can be recovered or beneficial reused and meanwhile problematic trace toxic elements to be properly managed as discussed in Chapter 2 (see subsections 2.4.3.3 and 2.2.4 respectively), more research on its P recovery or trace metal removal via bioleaching or technology with low energy input should be given.

In summary, it is estimated that a total of ~170 Mt/yr of ash are currently produced globally by biomass combustion to produce energy, and in future, this figure could potentially rise to a maximum of ~1000 Mt/yr.

3.5 Conclusions

This section focused on estimations of worldwide biomass ash amounts and their distribution. Biomass quantities subjected to incineration as sustainable fuels and the ash content of biomass are the two factors for determination of global biomass ash amounts produced. It is found that current utilisation of biomass for bioenergy purpose only accounts for very limited fractions (< 3%) of total biomass created annually by terrestrial photosynthesis. It is estimated that about 2-3 Gt/yr of biomass is currently used globally for energy production, which is less than the previous estimate of 7 Gt/yr, and most (>90%) is used as a solid fuel, generating ~170 Mt of ash each year. However, biomass usage has the potential to increase to around 8 Gt/yr, producing to ~1000 Mt of ash each year, if all currently available biomass is exploited. Currently, municipal solid waste ash and wood ash are the two major ash types of concern with larger amounts than other ash types. However, agriculture residue has great potential to be utilised in future bioenergy supply and more agriculture residue ash is projected to be produced. Additionally, sewage sludge ash amount is also expected to increase by more than 4 times than the current level so its proper treatment for P recovery or heavy metal removal should be explored. Municipal solid waste ash generally has troublesome characteristics, and large amount of such ash means that more studies on its value recovery and safe disposal should be given as well.

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Chapter 4: Plant phylogenetic influences on biomass ash categorisation

4.1 Introduction

Combustion of biomass within power stations is a more sustainable way to generate electricity/heat than the use of fossil fuels provided the feedstock is sustainably grown (Cherubini et al., 2011; Vassilev et al., 2010). However, effective reuse of the resultant biomass combustion ashes or, as an absolute minimum, their safe disposal is essential to the environmental sustainability of using biomass fuels. To achieve this, biomass ash substrate characteristics must be well understood. Biomass ashes are mainly composed of the inorganic constituents of the feedstock, together with some unburned organic phases. They have been characterised as a heterogeneous poly-component inorganic–organic mixture with variable compositions, which contain non-crystalline (amorphous) semi-crystalline and crystalline phases (Vassilev et al., 2013a). In a review of ash from 120 different sources, 229 phases or minerals have been identified in biomass ash (Vassilev et al., 2013a), with quartz, calcite, sylvite, arcanite, anhydrite, char, glass, lime, periclase and hematite as the common mineral phases. Further, there are usually compositional differences between the fly and bottom ash from the same feedstock, as volatile phases vaporised in the furnace (particularly salts and heavy metals) can condense onto the fly ash (Dahl et al., 2009, 2010; Rajamma et al., 2009). Similarly, different furnace technologies (e.g. grate furnace with the maximum bed temperature of 1000-1200 ℃ or fluidised bed furnace with that generally below 900 ℃) also affect ash composition due to differences in the furnace temperature (Rajamma et al., 2009). Such a detailed review of biomass ash composition by Vassilev et al. is not helpful when attempting to identify different potential reuse strategies for an industrial by-product. It implies that detailed knowledge of the biomass composition and the combustion technology are necessary to reliably predict the characteristics of the ash. Whereas practical and commercial considerations, such as seasonal availability and supply security, may necessitate rapid decisions about feedstock. Thus, there is a pressing need for more general guidance on how ash characteristics vary with type of feedstock.

The elemental constituents of an ash must be derived from the elemental constituents of the biomass, and while there is loss of organic matter and phase changes in the furnace, and fractionation of volatile constituents between the ash fractions, the bulk characteristics of the ash are likely to be correlated with the composition of the feedstock. Many different types of biomass are used worldwide to provide heat on a domestic scale, but commercial biomass combustion for electricity/heat generation requires large volumes of consistent feedstock, so primary fuels are forestry or agricultural residues. Their sources can thus be classified as softwood, hardwood, grasses (which includes all cereal crops), and other crop residues. Crops grown and harvested specially for biomass combustion, such as willow (hardwood) and miscanthus (grass) also fall in one of these categories. Thus, primary biomass fuels are all derived from land plants (Embryophyta), but these plants fall into three distinctly different groups from an evolutionary standpoint (Figure 4.1). All the extant softwoods are gymnosperms (they have unenclosed seeds) and taxonomically they are grouped in a single division Pinophyta in the order Pinales (Sharma, 1993; Stace, 1991). The gymnosperm lineage separated from flowering plants (angiosperms) about 270-330 Myr ago (Hedges et al., 2015; Kumar et al., 2017; Savard et al., 1994; Scutt et al., 2006). Similarly, all grasses are from the family Poaceae within the monocotyledon (monocot) clade of the angiosperms, whereas the majority of hardwoods that are used as a commercial fuel are Rosids (e.g. oak, beech, walnut, willow) within the eudicotyledon (eudicot) clade of the angiosperms (the remainder are Asterids also within the eudicot clade of the angiosperms) (Erdtman, 1986; Sharma, 1993). Other crop residues used as biomass fuels (e.g. rapeseed, sunflower, alfalfa) also belong to the eudicots (rapeseed and alfalfa are Rosids and sunflower is an Asterids). The eudicot lineage separated from the monocot (grasses) lineage around about 143-157 Myr ago (Chaw et al., 2004; Magallón, 2009).

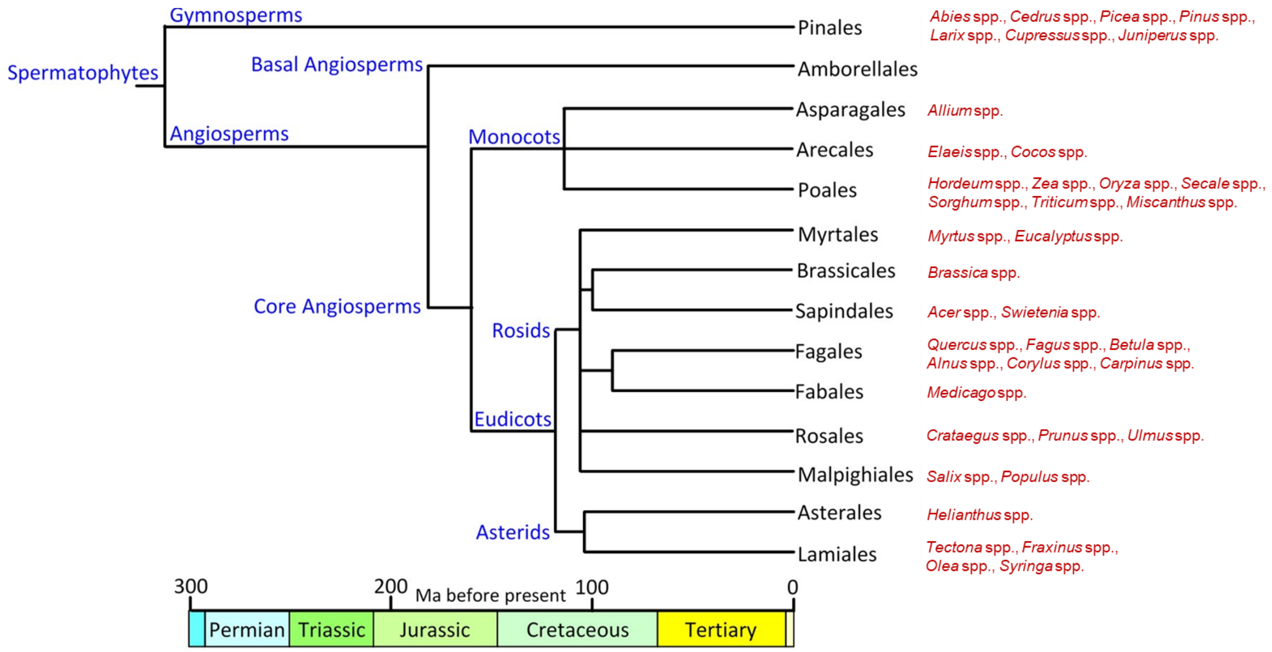

Figure 4.1. Approximate phylogeny of spermatophytes (seed plants) determined using TimeTree(Kumar et al., 2017; Timetree, 2020). TimeTree estimates phylogenetic relationships and species divergence times from the synthesis of all available molecular clock analyses (Kumar and Hedges, 2011). Potential biomass fuels are shown next to the order to which they belong.

These evolutionary differences are reflected in the structural differences between softwood, hardwood, herbaceous eudicot and monocot stems (biomass fuels that are burnt commercially are overwhelmingly plant stems, such as straw, stalks, and wood). Between node points (e.g. buds, leaves, and branching points), the stems of gymnosperms and eudicots typically consist of a ring of vascular bundles (for the transport of water and food) between outer and inner regions of ground tissue, whereas the vascular bundles in monocots are arranged in more than one ring or are scattered throughout the cross-section (Esau, 1977). Wood is formed during the secondary (lateral) growth by most gymnosperms (softwoods) and by woody eudicots (hardwoods). It is composed of secondary xylem tissue produced within the vascular bundles (Etchells et al., 2015), which in hardwood contain vessels for the transport of sap but not in softwood where sap is transported by evolutionarily more primitive tracheid cells (Britannica, 2019). Thus, the distribution of organic tissues within the stem of plants is determined by evolution. The inorganic constituents that remain after biomass combustion will reflect the composition of the organic tissues from which they originate, so there are likely to be systematic differences in the composition of the ashes produced by combustion of different feedstocks.

The supposition that the taxonomy of the feedstock will influence the composition of biomass ash is supported by systemic differences in the silicon content between taxonomically distinct groups of plants, and variation in the amount of ash produced by different categories of feedstocks (grasses produce far more ash than woody biomass (Vassilev et al., 2010)). Deposition of Si in plants mostly occurs in epidermal cells, and is thought to be an evolved defensive response to pathogens and pests (Deshmukh et al., 2017). Hodson et al. (2005) undertook meta-analysis of the data from 735 different species of land plants which showed variations in the shoot Si concentration with taxonomic grouping, with high Si accumulation in the taxonomic families that contain grasses and palms, and to a lesser extent in the families that include common hardwoods (including oak, beech, birch, alder, hazel, hornbeam, walnut, hawthorn, cherry, elm, willow, poplar).

This research reviews 168 database records reporting the major element chemical composition of biomass combustion ash from different feedstocks and proposes an evolutionary-based system for categorising biomass derived ash into four categories: hardwood ash, softwood ash, eudicot straw ash and grass straw ash. Systematic differences in the ash properties between these categories are qualitatively and quantitatively determined. Finally, guidance is offered to commercial generators of electricity/heat from biomass to help them make rational decisions about feedstock variation.

4.2 Methodology

Biomass ash sample characterisation data was recovered from the Energy Research Centre of the Netherlands (ECN) Phyllis2 classification database (https://phyllis.nl/Browse/Standard/ECN-Phyllis#). The Phyllis2 databases are designed and maintained by the Netherlands Organization for Applied Scientific Research for the Netherlands Government. Phyllis2 contains around 3000 compositional data records from biomass fuels organised based on a mixture of plant physiology and practical considerations. Of these data records, 168 contain the major element chemical composition of their corresponding combustion ashes and these were selected for the present study. These records also contain incomplete details of other relevant ash properties such as trace metal composition and ash melting temperatures, which were also complied and included in the present study. No data on organic contaminant composition of ashes (e.g. PCBs, dioxins) were available in the Phyllis2 database. The ash composition data consisted of data from both hardwood and softwood samples and a wide range of crop straws ashes (Table 4.1). All the extracted data, along with their corresponding Phyllis2 database ID numbers, is provided in the Appendix B.

Table 4.1. Number of ash data records based on biomass types used in this study.

Hardwood ash (24)	Softwood ash (28)	Eudicot straw ash (26)	Grasses straw ash (90)
Beech (1)	Fir (3)	Rapeseed (11)	Barley (12)
Birch (1)	Pine (12)	Sunflower (6)	Maize/corn (8)
Oak (4)	Spruce (4)	Alfalfa (9)	Rice (15)
Willow (14)	Mixed fir/pine/spruce (4)		Rye (2)
Poplar (4)	Unspecified (5)		Sorghum (8)
			Wheat (45)

Major element data was transformed to nominal oxide format prior to use (e.g. elemental Ca data was converted to CaO wt. %, etc.), and any data reported as below laboratory detection limits were given a value of zero. In addition, when the nominal oxide compositions are reported on ternary diagrams, the oxides being reported were normalized to 100% on a total oxide composition basis.

Ash composition data were analysed to test the null hypothesis that there was no significant difference in median elemental composition between the four ash types using a Kruskal-Wallis test. Dunn's post-hoc test was then used to test pairwise differences in the median values between the different ash types where significance was apparent ($p < 0.05$). The two-tailed Spearman rank correlation of Cu, Pb and Cd with CaO content and Pearson correlation tests of ash fusion behaviour with ash chemical composition were analysed by treating all the ash samples as a single dataset. All analyses were undertaken in IBM SPSS v24.

4.3 Results

4.3.1 Ash content derived from biomass

The median ash content produced by each biomass type (Table 4.2) indicates that eudicot straw (median 8.8%) and grass straw (5.2%) tend to produce more ash upon burning than either hardwood (1.6%) or softwood (1.0%). Kruskal–Wallis analysis of the ash contents indicates that there are two or more separate populations within the overall dataset (Table 4.2; $p < 0.001$), and while the pairwise comparisons show that there is no significant difference between the hardwood and softwood ash contents or between the eudicot straw and grass straw ash contents, woody biomass (hardwood or softwood) has significantly lower ash content than straw biomass (eudicot straw and grass straw) ($p < 0.001$).

Table 4.2. Median and range of biomass feedstock properties (wt. % of biomass). K-W *H* shows the Kruskal-Wallis *H* statistic with level of significance (** denotes p <0.001; * denotes p <0.05: degrees of freedom = 3 for all tested items in the left-hand column). Different superscript letters in a row indicate a significant difference in median value between sample populations based on post-hoc pairwise comparisons (Dunn's Test with Bonferroni correction, p <0.05).

Item	Hardwood	Softwood	Eudicot Straw	Grass Straw	K-W *H*
Ash content	1.6 (0.3-4.6) ^{a}	1.0 (0.1-5.2) ^{a}	8.8 (2.9-12.9) ^{b}	5.2 (2.7-22.1) ^{b}	78.7**
Volatile matter	83.6 (78.6-86.2) ^{a}	81.9 (73.0-87.5) ^{ab}	77.7 (73.9-79.2) ^{bc}	76.5 (65.7-81.2) ^{c}	28.7**
Fixed Carbon	15.4 (12.3-19.3) ^{a}	17.3 (10.9-24.0) ^{b}	17.7 (16.7-19.7) ^{ab}	17.5 (14.1-19.3) ^{b}	13.3*
Carbon	50.3 (48.5-51.7) ^{a}	51.5 (48.8-55.0) ^{a}	50.3 (40.4-62.5) ^{a}	49.1 (46.6-53.4) ^{b}	49.8**
Hydrogen	6.1 (5.9-8.1) ^{a}	6.0 (4.8-6.4) ^{a}	5.8 (4.6-7.4) ^{a}	6.0 (4.6-6.6) ^{a}	6.6
Nitrogen	0.58 (0.03-1.12) ^{ab}	0.13 (0.06-0.94) ^{a}	2.07 (0.08-5.39) ^{c}	0.68 (0.25-1.74) ^{b}	59.3**
Sulphur	0.05 (0.01-0.13) ^{a}	0.01 (0.01-0.42) ^{a}	0.22 (0.03-2.21) ^{b}	0.11 (0.02-0.46) ^{c}	46.8**
Oxygen	43.1 (40.3-44.9) ^{ab}	42.2 (38.7-45.1) ^{a}	39.6 (27.8-54.2) ^{a}	43.7 (41.4-50.4) ^{b}	36.7**

A subset of the biomass ash database records considered in this study also report biomass feedstock data (Table 4.2). Hardwoods contain significantly more volatile matter (median 84%) than eudicot straw (78%) and grass straw (77%). Softwoods also have higher volatile content than grass straw, but are not significantly different from either hardwoods or eudicot straw. Hardwoods contain less fixed carbon (median 15%) than either softwoods or grass straw (17-18%). Ultimate analysis of biomass (the relative proportions of the major components, including carbon, hydrogen, nitrogen, oxygen and sulphur), again indicates only very modest, albeit significant differences between some of the biomass categories. Hardwood, softwood and eudicot straw have slightly higher C content (medians 50-52%) than grass straw (49%), while there is no significant difference in H content across biomass categories. Grass straw has a higher O content (median 44%) than softwood and eudicot straw (40-42%) but is similar to hardwood (43%). Eudicot straw has a significantly higher S content (median 0.22%) than grass straw, hardwood and softwood, with grass straw (0.11%) having a significantly higher S content than hardwood or softwood (0.01-0.05%). N content follows a similar pattern being significantly higher in eudicot straw (median 2%) than any other biomass categories.

4.3.2 Ash chemical compositions

Table 4.3 presents the statistical results of chemical compositions (in the form of common oxide) of four ash categories. The abundant oxide phases in hardwood ashes (median concentration > 5% w/w) are $CaO > K_2O > P_2O_5$, whereas in the softwood ashes they are $CaO > SiO_2 > K_2O$. The abundant oxide phases in eudicot straw ashes are $K_2O > CaO > P_2O_5 > Cl_2O$, and in grass straw ashes they are $SiO_2 > K_2O > CaO$.

Table 4.3. Median and full range of ash composition data (wt. % of ash). K-W *H* shows the Kruskal-Wallis *H* statistic with level of significance (** denotes p <0.001; * denotes p <0.05: degrees of freedom = 3 for all tested items in the left-hand column). Different superscript letters in a row indicate a significant difference in median value between sample populations based on post-hoc pairwise comparisons (Dunn's Test with Bonferroni correction, p <0.05). For example, a population labelled ^{a} is significantly different ^{b}, ^{c} or ^{d}, while ^{ac} would not be significantly different from a population annotated as ^{a} or ^{c}, but would be significantly different from those labelled ^{b} or ^{d}.

Item	Hardwood	Softwood	Eudicot Straw	Grass Straw	K-W *H*
CaO	37.4 (10.9-65.0) ^{a}	32.0 (8.8-51.2) ^{a}	20.1 (6.6-66) ^{ab}	8.7 (0.5-26.5) ^{c}	108.0**
MgO	4.1 (0.1-18.4) ^{a}	4.9 (0.6-13.5) ^{a}	2.5 (0.6-16) ^{ab}	2.4 (0.6-6.1) ^{b}	37.2**
K_2O	14.7 (4.6-26.5) ^{a}	8.5 (1.0-23.9) ^{b}	28.0 (8.0-44.2) ^{c}	14.3 (2.0-41.0) ^{ad}	42.6**
P_2O_5	9.3 (0.2-17.0) ^{a}	2.9 (0.1-11.6) ^{b}	5.9 (0.7-40.9) ^{a}	2.9 (0.4-11.6) ^{b}	36.6**
SO_3	2.3 (1.1-4.0) ^{a}	1.8 (0.1-13.5) ^{a}	3.8 (0.8-14.0) ^{a}	2.5 (0.3-11.1) ^{a}	9.5*
Cl_2O	0.7 (0.1-0.9) ^{a}	0.1 (0.01-0.21) ^{a}	5.4 (1.5-11.3) ^{b}	3.7 (0.2-18.0) ^{b}	19.8**
SiO_2	2.7 (0.4-27.4) ^{a}	20.1 (2.8-57.2) ^{a}	4.2 (0.3-30.5) ^{a}	50.7 (16.2-93.3) ^{b}	114.7**
Al_2O_3	1.1 (0.1-11.1) ^{a}	4.1 (0.4-14.7) ^{b}	0.3 (0.1-3.8) ^{c}	0.8 (0.1-4.4) ^{ac}	50.3**
Fe_2O_3	0.5 (0.2-2.9) ^{a}	2.1 (0.4-9.3) ^{b}	0.3 (0.1-51) ^{ac}	0.7 (0.1-7.1) ^{ac}	42.9**
Na_2O	0.9 (0.1-3.1) ^{a}	0.8 (0.2-23.5) ^{a}	0.4 (0.1-6.8) ^{a}	0.5 (0.1-10.5) ^{a}	7.6
TiO_2	0.1 (0.1-0.3) ^{a}	0.3 (0.1-1.2) ^{b}	0.1 (0.1-0.7) ^{ab}	0.1 (0.1-0.2) ^{a}	29.1**

Kruskal–Wallis analysis of the elemental oxide contents indicates that there are significant differences in sample medians between ash types for each of the oxides reported except Na_2O (Table 4.3; $p < 0.05$ for SO_3 and $p < 0.001$ for other oxides). Pairwise comparisons of the CaO content indicate there is no significant difference between the hardwood ash and softwood ash (the pairwise elemental oxide comparisons are reported using superscript letters in Table 4.3), but both have a significantly higher CaO content than grass straw ash. Eudicot ash also has significantly higher CaO than grass straw but is not significantly different from hardwood or softwood ash. Similar pairwise comparisons indicate that the eudicot straw ash has a significantly higher K_2O content than the hardwood ash and the grass straw ash, which in-turn have significantly higher K_2O contents than the softwood ash (but there is no significant difference between the hardwood and grass straw ash). Also, the grass straw ash has a significantly higher SiO_2 content than the other three ashes. The SO_3 and Cl_2O contents of the ash are important indicators of the amount of volatile sulphur and chlorine in the feedstock, which can result in acid gas emissions that cause high temperature corrosion and may require additional air-pollution control measures. There are no significant differences in SO_3 content between the ash categories in pairwise comparisons (the overall median value across all ash categories was 3.0%, range: 0.1-14.0%). In comparison, the median Cl_2O contents of the eudicot and grass straw ashes were similar and both were significantly higher than either hard or soft wood ashes, which had similarly low Cl_2O values. However, the small sample size for softwood and hardwood Cl_2O data must be noted ($N = 4$ for both). Lastly, the hardwood and eudicot straw ashes have significantly higher P_2O_5 contents than the softwood and grass straw ashes. Statistical analysis of the other main elemental oxides can be found in Table 4.3.

4.3.3 Trace metal concentration in biomass ash

Contaminant trace metal concentrations are reported in a subset of the data records considered in this research (Figure 4.2). The median Cu concentrations in biomass ashes are 90, 329, 72, and 42 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. The median Pb concentrations in the biomass ashes are 135, 29, 3, and 4 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. The median Cd concentrations in the biomass ashes are 10, 1, 0, and 0.1 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. For comparison, the Finnish limits for ash use as a forest fertiliser are 700, 150 and 17.5

mg/kg for Cu, Pb and Cd respectively (Dahl et al., 2010). The equivalent Swedish limits are 400, 300 and 30 mg/kg, respectively (Forestry, 2002). The Cu concentration in softwood ash is significantly higher than in either straw ash (Table 4.4), but the difference between the two straw ashes is not significant (contaminant trace metal concentrations were reported for insufficient hardwood ash samples for statistical inference). Similarly, the Pb and Cd concentrations in softwood ash are significantly higher than in eudicot straw ash, although grass straw ash is not significantly different from either softwood ash or eudicot straw ash. Hg concentrations are only reported for three softwood samples, but all three values are non-zero (median value 1.7 mg/kg), so these values are significantly higher than the zero (i.e. below detection limit) values reported for the two straw ashes. Cr concentrations are only reported in three data records so no inference can be drawn from the data.

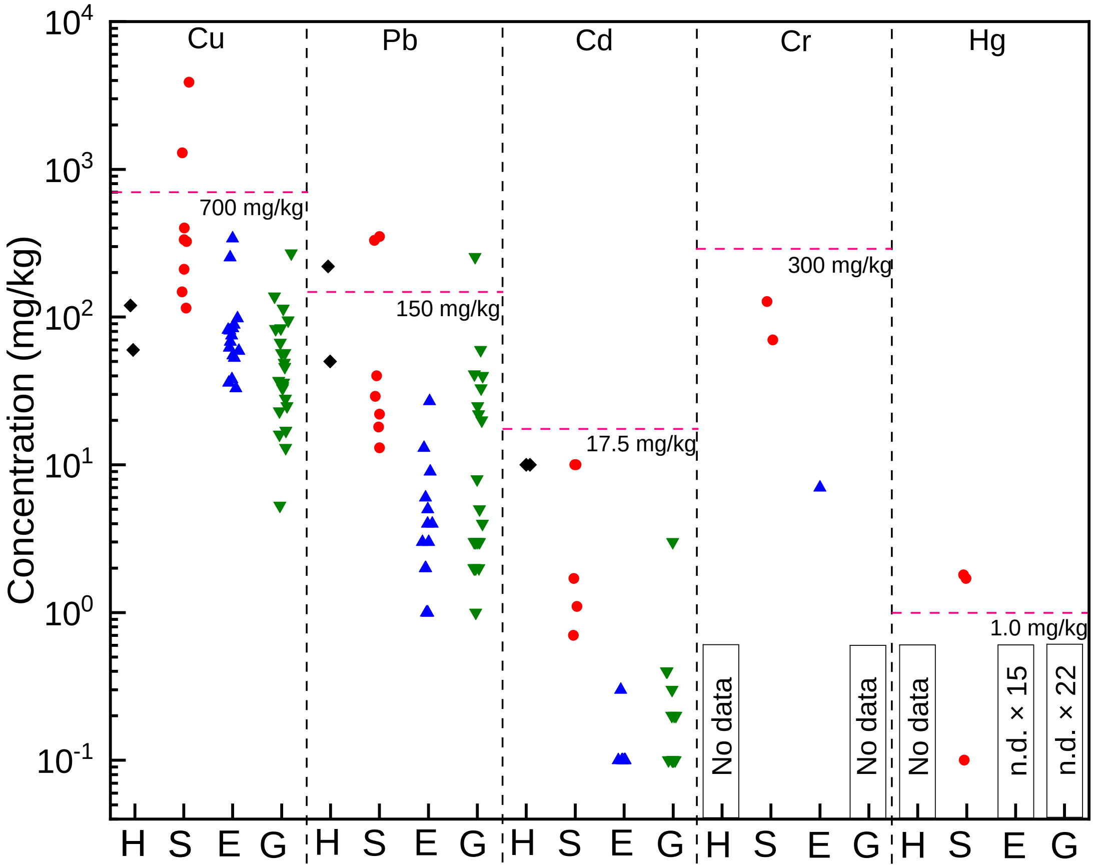

Figure 4.2. Contaminant trace metal concentrations in four different biomass ashes (n.d. x n – not detected in n samples; pink dotted line – Finnish limits for ash to be used as a forest fertiliser (Dahl et al., 2010); H – hardwood ash; S – softwood ash; E – eudicot straw ash; G – grasses straw ash).

Table 4.4. Median and range of contaminant trace metal concentrations (mg/kg) for ashes derived from different types of biomass. K-W H shows the Kruskal-Wallis H statistic with level of significance (** denotes $p < 0.001$; * denotes $p < 0.05$: degrees of freedom = 3 for all tested items in the left-hand column). Different superscript letters in a row indicate a significant difference in median value between sample populations based on post-hoc pairwise comparisons (Dunn's Test with Bonferroni correction, $p < 0.05$).

Item	Hardwood	Softwood	Eudicot Straw	Grass Straw	K-W *H*
Cu	90 (60-120) ^{ab}	329 (115-3879) ^{b}	72 (33-340) ^{a}	42 (5-270) ^{a}	20.5**
Pb	135 (50-220) ^{ab}	29 (13-350) ^{a}	3 (0-27) ^{b}	4 (1-255) ^{ab}	16.1*
Cd	10.0 (10.0-10.0) ^{a}	1.4 (0-10) ^{a}	0.0 (0.0-0.3) ^{b}	0.1 (0.0-3.0) ^{ab}	16.1**
Cr	No data	99 (70-127)	7 (7-7)	No data	1.5
Hg	No data	1.7 (0.1-1.8) ^{a}	0.0 (0.0-0.0) ^{b}	0.0 (0.0-0.0) ^{b}	38.9**

4.3.4 Ash fusion temperatures

Figure 4.3 reports initial deformation temperature (IDT), softening temperature (SOT), hemispherical temperature (HT) and fluid temperature (FT) of the four ash types (these temperatures are important in evaluating ash slagging, fouling and corrosion effects on the boiler and thus its conversion efficiency (Dunnu et al., 2010; Niu et al., 2016; Niu et al., 2010).

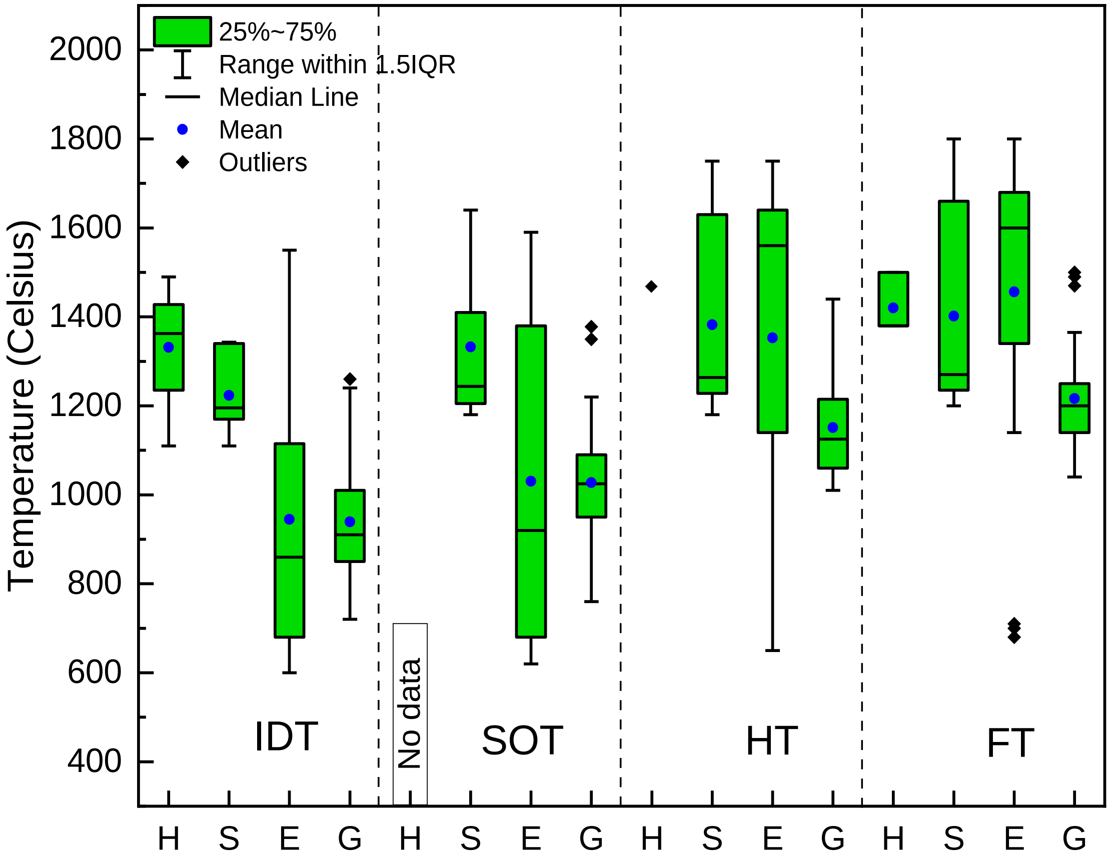

Figure 4.3. Variation in the initial deformation temperature (IDT), softening temperature (SOT), hemispherical temperature (HT) and fluid temperature (FT) of ashes derived from different types of biomass (H – hardwood ash; S – softwood ash; E – eudicot straw ash; G – grasses straw ash).

Hardwood and softwood ashes have significantly higher IDTs (medians 1363°C and 1196°C, respectively; Table 4.5) than the eudicot straw and grass straw ashes (860°C and 910°C, respectively), but the difference between the wood ashes and the difference between the straw ashes are not significant. Softwood ash has a significantly higher SOT (median 1244°C) than the eudicot straw and grass straw ashes (920°C and 1025°C, respectively), but the difference between the straw ashes is not significant (no data is reported for hardwoods). It is harder to discern the trends in HT and FT data, but both the mean and median HT and FT of grass straw are lower than those of the other ashes (Figure 4.3 and Table 4.5).

Table 4.5. Median and range of the initial deformation temperature (IDT), softening temperature (SOT), hemispherical temperature (HT), fluid temperature (FT), for ashes derived from different types of biomass (all °C). K-W H shows the Kruskal-Wallis H statistic with level of significance (** denotes $p < 0.001$; * denotes $p < 0.05$: degrees of freedom = 3 for all tested items in the left-hand column). Different superscript letters in a row indicate a significant difference in median value between sample populations based on post-hoc pairwise comparisons (Dunn's Test with Bonferroni correction, $p < 0.05$).

Item	Hardwood	Softwood	Eudicot Straw	Grass Straw	K-W *H*
IDT	1363 (1110-1490) ^{a}	1196 (1110-1343) ^{a}	860 (600-1550) ^{b}	910 (720-1260) ^{b}	27.3**
SOT	No data	1244 (1180-1640) ^{a}	920 (620-1590) ^{b}	1025 (760-1378) ^{b}	14.1*
HT	1470 (1470-1470) ^{ab}	1264 (1180-1750) ^{b}	1560 (650-1750) ^{b}	1125 (1010-1440) ^{a}	17.2*
FT	1380 (1380-1500) ^{ab}	1271 (1200-1800) ^{a}	1600 (680-1800) ^{a}	1200 (1040-1500) ^{b}	22.3**

4.4 Discussion

4.4.1 Biomass categorisation

A wide range of factors can affect the chemical composition of potential biomass feedstock, such as plant species, soil characteristics, nutrition and stresses during growth, plant maturity, timing of the harvest, plant component being harvested, etc. (Demirbas, 2005; McKendry, 2002; Obernberger et al., 1997; Olanders and Steenari, 1995; Someshwar, 1996; Vassilev et al., 2010; Werkelin et al., 2005), but it is impossible to recognise all these factors in any functional system for classifying the ash produced by biomass combustion. This complexity has meant that most published work has tended to use only very broadly defined categories to characterise biomass ash properties, such as "herbaceous and agricultural biomass (HAB)" and "wood and woody biomass (WWB)" (Vassilev et al., 2017), which provide the user with very little information except the likely ash content.

The hypothesis underlying the statistical analyses presented in this research is that the biomass feedstock will be a major factor in determining the inorganic elements within a biomass ash, and that feedstocks will exhibit systematic differences due to evolutionary divergence. The statistical analyses of database records clearly support this hypothesis. The four biomass categories proposed consistently divided into two or more statistically significant groups based on their content of each abundant elemental oxide, and their ash content. Specifically, the biomass ash categories considered in this study divide into those that have a comparatively high or low CaO content, those which have a comparatively high or low SiO_2 content, those that have a comparatively high or low P_2O_5 content, those that have a comparatively high, intermediate or low K_2O content, and those that have a comparatively high or low ash content. The four biomass ash categories can be clearly differentiated by considering even a subset of these measures in combination. Hardwood ashes have relatively high CaO and P_2O_5, intermediate K_2O and relatively low SiO_2 and ash contents. Softwood ashes have relatively high CaO, but relatively low SiO_2, K_2O, P_2O_5 and ash contents. Eudicot straw ashes have relatively high K_2O, CaO, P_2O_5 and ash, but relatively low SiO_2 contents. Grass straw ashes have relatively high SiO_2 and ash, intermediate K_2O, but relatively low CaO and P_2O_5 contents.

4.4.2 Chemical composition classification

Vassilev et al. proposed a chemical classification system for biomass based on its inorganic composition (Vassilev et al., 2012). They identified that the ash-forming elements are either authigenic or detrital in origin (either elements required for plant growth, or fine mineral grains that become associated with plant matter), and grouped the inorganic elements into three major elemental associations:

- Ca-Mg-Mn - Elements probably derived from plant matter that form oxalates and carbonates
- K-S-P-Cl - Elements probably derived from plant matter that form phosphates, sulphates, chlorides and nitrates
- Si-Al-Fe-Na-Ti - Elements that are potentially derived from detrital material associated with the biomass

While the rationale behind these elemental groups needs further confirmation (e.g. Si deposition by plants can be a defensive response to pathogens, pests and grazers; (Deshmukh et al., 2017), and Al uptake and localised sequestration can be a plant adaptation to Al-toxicity (Bojórquez-Quintal et al., 2017)), representing their relative proportions on a ternary diagram has been shown to differentiate between ashes from markedly different fuels (e.g. HAB and WWB) (Vassilev et al., 2010, 2013a, b; Vassilev et al., 2012). Presenting the data collated in this research on a “Vassilev” style ternary diagram (Figure 4.4(a)) confirms its utility and, despite some scatter, supports the biomass ash categorisation proposed in this study (each ash category plots in a distinct region of the diagram). Most of the 90 grass straw ashes plot in the low CaO + MgO + MnO areas of the diagram, the 28 softwood samples plot in the low K_2O + P_2O_5 + SO_3 + Cl_2O areas of the diagram, whereas the 24 hardwood and 26 Eudicot straw ashes plot in the low SiO_2 + Al_2O_3 + Na_2O + TiO_2 areas of the diagram.

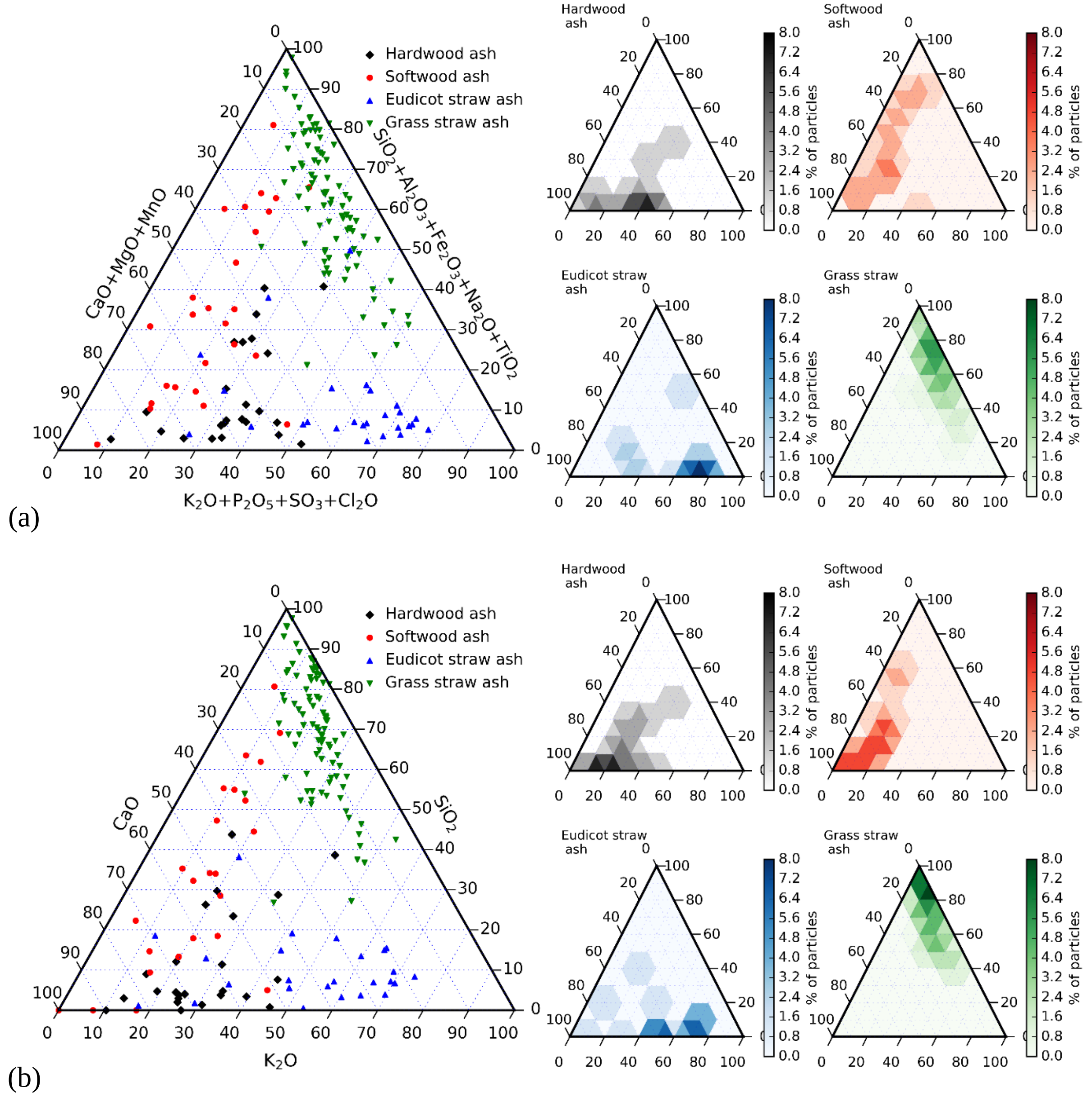

Figure 4.4. Ternary diagrams for the classification of biomass ash based on inorganic constituents: (a) Using ($CaO + MgO + MnO$), ($K_2O + P_2O_5 + SO_3 + Cl_2O$) and ($SiO_2 + Al_2O_3 + Fe_2O_3 + Na_2O + TiO_2$) as the end members (Vassilev et al., 2012) and (b) using CaO, K_2O and SiO_2 as the end members. Note: The Mn concentration is rarely reported in the Phyllis2 database, so is assumed to be negligible when plotting (a). The main ternary diagrams plot the chemical composition of all the ash samples, while the smaller graphs contain interpolated heat maps showing the percentage of samples for each ash category within each compositional bin.

Review of the data in Table 4.3 suggests that the “Vassilev” style ternary diagram shown in Figure 4.4(a) could be simplified by plotting only the most abundant constituent in each of the three groups: CaO, SiO_2 and K_2O (see Figure 4.4(b)). On the revised ternary diagram, data from hardwood ash, softwood ash and grass straw ash exhibit closer grouping than in Figure 4.4(a), with very little difference in the grouping of eudicot straw ash.

Although P_2O_5 was the third most abundant nominal oxide in hardwood ash and eudicot straw ash and Cl_2O was the fourth most abundant nominal oxide in eudicot straw ash, the decision was made to omit them from the simplified ternary diagram (Figure 4.4(b)). This is because the Kruskal–Wallis analysis clearly indicates that the biomass categories group differently on the basis of their K_2O, P_2O_5 and Cl_2O contents (hardwood ash groups with grass straw ash for K_2O content, with eudicot straw ash for P_2O_5 content, and with softwood ash for Cl_2O content), so it is not appropriate to sum them on a classification diagram. Therefore, K_2O alone was selected from this group of elemental oxides as it is more abundant than the other two in all four categories of ash.

All the hardwoods included in the data analysis are Rosids (part of the eudicot clade of angiosperms; see Figure 4.1), as are alfalfa and rapeseed (the remaining eudicot grass is an Asterid). However, the herbaceous eudicots ashes form a single group that is distinct from the woody eudicot ashes (see Figure 4.4). The principal difference between woody and herbaceous eudicots is that there is far more secondary growth in the stems of the former (i.e. wood) and this is composed of secondary xylem tissue (Etchells et al., 2015). The xylem is a critical part of the Ca^{2+} delivery system in plants (White, 2001), and this probably accounts for the higher CaO in woody eudicot ash than in herbaceous eudicot ash.

4.4.3 Contaminant trace metal associations

All the eudicot straw ashes were below the Finnish and Swedish limits on Cu, Pb and Cd content for use as a forest fertiliser (data was available for 48 samples) . Similarly, almost all of the monocot grass straw ashes were below these same limits (1 of 66 samples failed to meet the more stringent Finnish limit for Pb content). Whereas a noteworthy proportion of the softwood ashes exceeded both the Finnish and Swedish limits on for either Cu content, Pb content, or both (contaminant trace metal concentrations are reported for insufficient hardwood samples for further comment). Part of the reason why softwood ashes tend to contain more contaminant trace metals than either eudicot straw or grass straw ash may be associated with the lower ash content of woody biomass, as the estimated mean Cu content of the original biomass is similar for three biomass types (Table 4.6), and as are the estimated mean Pb and Cd contents of the original softwood and grass straw (interestingly, the estimated trace metal contents of unburnt biomass are similar to those reported elsewhere in the literature; Adriano, 2013; Fergusson, 1990; Jung, 2008). However, other explanations, such as differences in metal uptake mechanism by different plant types or more stringent limits on the soil metal contents for agriculture than forestry cannot be discounted.

Table 4.6. Calculated trace metal concentration in the different biomass feedstocks estimated from the concentrations in the ash samples and the ash content (μg trace metal per g dry weight biomass).

Item	Mean trace metal concentration in biomass (μg/g)				Literature values
	Hardwood [a]	Softwood	Eudicot straw	Grass straw	(μg/g)
Cu	1.7	11	7.4	4.9	5-20 [b]
Pb	2.6	1.5	0.40	2.1	0.01-3.85 [b, c]
Cd	0.19	0.05	0.005	0.02	<1 [b, d]

[a] Note: Trace metal concentrations are only reported for 2 hardwood ash samples within the dataset.
[b] Jung (2008)
[c] Fergusson (1990)
[d] Adriano (2013)

Uptake of metals not required by, and potentially harmful to plants is likely to be an artefact of nutrient uptake, and for example, uptake of a divalent contaminant metal might be via the Ca^{2+} uptake pathway (Diatloff et al., 2006; Lu et al., 2010; Peralta-Videa et al., 2009). The correlation of Cu, Pb and Cd with CaO content was analysed by treating all the ash samples as a single dataset and the results are shown in Table 4.7. There is considerable scatter in the data (see Appendix B), which is to be expected as contaminant metal uptake must be affected by soil concentrations, but there are modest but significant positive correlations between Cu and Ca (Spearman's Rank $r_s = 0.59$, $p < 0.001$), Cd and Ca ($r_s = 0.30$, $p = 0.046$) and Pb and Ca ($r_s = 0.35$, $p = 0.016$).

Table 4.7. Spearman rank correlation analysis results of Cu, Pb and Cd concentration against CaO content.

Trace metal	Spearman Rank correlation coefficient	P value	Confidence level
Cu	0.59	<0.001	99%
Pb	0.35	0.016	95%
Cd	0.30	0.046	95%

4.4.4 Associations of ash fusion behaviour and ash chemical composition

While this research is focussed on the chemical composition of biomass ash (which determines whether the ash can be put to beneficial use and/or issues associated with disposal), commercial operators of biomass power stations need to balance multiple constraints when making decisions about feedstock composition (Baxter et al., 1998). In addition to concerns with availability, cost and calorific value, operators need to consider the ash fusion characteristics of different feedstocks, as fusing of ash particles can result in slagging, fouling and corrosion within the furnace, and thus thermal conversion efficiency and maintenance requirements for a biomass power station (Niu et al., 2016; Werther et al., 2000; Yin et al., 2008).

The temperature at four defined points (IDT, SOT, HT and FT) are used to characterise the ash melting process and thus the likelihood that ash particles will fuse together (Niu et al., 2016; Tambe et al., 2018), but there still debate about which best correlates with the ash fusion characteristics of biomass (Liu et al., 2018; Magdziarz et al., 2016; Wang et al., 2012). The softening temperature (SOT) is generally used as the index of coal ash fusion behaviour, but initial work on biomass ash suggests that the initial deformation temperature (IDT) may be the better index for biomass (Niu et al., 2010). IDT is also the most widely reported of these indices in the Phyllis2 data records considered in this study (it is reported in 80/168 records), and as IDT is the temperature at which melting is first recorded, it is the lowest of the four defined temperature points.

The obvious pattern is that wood ashes have a significantly higher IDT than straw ashes, however four of the elemental oxide contents also show a statistically significant correlation with two or more of the defined temperature points (IDT correlates with all four of these nominal oxides). IDT, SOT, HT and FT are all positively correlated with the CaO content (confidence 99%; Table 4.8), and 36% of the variance in IDT can be explained by the CaO content. IDT and SOT are both negatively correlated with both the K_2O and Cl_2O contents (conf. 99%); 18% of the variance in IDT can be explained separately by the K_2O and Cl_2O contents. IDT, HT and FT also exhibit a weak negative correlation with the SiO_2 content (conf. 95%, 95% and 99%, respectively), but SiO_2 can only explain 4% of the variance in IDT. Thus, IDT increases as CaO content increases, but decreases as K_2O, Cl_2O, and to a lesser extent SiO_2 increase.

Table 4.8. Some significant correlation coefficient values (r) at 99% confidence level via Pearson correlation analysis (80 samples for IDT, 54 samples for SOT, 64 samples for HT and 78 samples for FT; * at 95% confidence level).

Item	CaO	MgO	MnO	K_2O	P_2O_5	SO_3	Cl_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2
IDT	0.60	0.42	n.c.	-0.42	n.c.	n.c.	-0.43	-0.22*	0.33	n.c.	n.c.	0.31
SOT	0.49	n.c.	n.c.	-0.51	n.c.	n.c.	-0.40	n.c.	n.c.	0.31*	n.c.	n.c.
HT	0.37	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	-0.30*	n.c.	n.c.	n.c.	n.c.
FT	0.34	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	-0.35	n.c.	n.c.	n.c.	n.c.

n.c.: no correlation.

4.5 Conclusions

Statistical analysis of the chemical composition of 168 biomass combustion ashes from different feedstocks shows that the plant taxonomy of the feedstock has a strong influence on the major element chemical composition of the ash produced. The biomass feedstocks that are burnt commercially for electricity/heat generation can usefully be categorised as hardwood, softwood, grass crop residues (e.g. straw from cereal production), and non-grass crop residues. The abundant nominal oxide phases in hardwood ashes are CaO > K_2O > P_2O_5, whereas in the softwood ashes they are CaO > SiO_2 > K_2O. The abundant nominal oxide phases in eudicot straw ashes are K_2O > CaO > P_2O_5 > Cl_2O, and in grass straw ashes they are SiO_2 > K_2O > CaO. SO_3 and Cl_2O composition are important for high temperature corrosion effects in furnaces and environmental emission control. Cl_2O content was significantly higher in eudicot and grass straw ash than softwood and hardwood ash, while SO_3 content was variable but not significantly different between ash classes.

Other properties depend principally on whether the feedstock is herbaceous (eudicot straw and grass straw) or woody (hardwoods and softwoods). Herbaceous feedstocks produce significantly more ash (typically 5–9%) than woody feedstocks (typically 1–2%)

but, possibly as a result, the ashes generally contain lower concentrations of contaminant trace metals. Also, the initial deformation temperature (IDT) of ash from herbaceous feedstocks (typically 860–910 ◦C) is significantly lower than that of woody feedstocks (typically 1196–1363 ◦C), which is an indicator that such ash has a higher potential to form slag and foul the biomass furnace.

Operational decisions about the specific choice of feedstock for use in a commercial biomass combustion power station depend on a range of practical and business-related considerations. For example, seasonal availability and supply security may necessitate occasional, and sometimes rapid, feedstock changes. However, the ash reuse or disposal strategy will always be an important consideration when managing such change. The data in this research indicate how the ash characteristics are likely vary with the type of feedstock, and thus can facilitate dynamic decision-making. An alternative fuel within the same feedstock category is likely to cause only a modest change in the ash's physical and chemical characteristics, whereas a change between categories (e.g. from cereal crop residues to wood-pellets from coniferous forestry) is likely to have a more substantial impact of ash's physical and chemical characteristics. Finally, it is noted that incomplete data on contaminant trace metals and organics hinder the beneficial reuse of biomass ash as in the absence of data regulators often make conservative decisions regarding approval of new ash reuse proposals.

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Chapter 5: Biomass ash characteristics and implications for ash management: from laboratory ash to industrial ash

5.1 Introduction

It has been shown in Chapter 4 that biomass ash characteristics depend on the taxonomy of feedstock, and ash derived from virgin biomass has been classified as hardwood ash, softwood ash, grass straw ash and eudicot straw ash. Ash management options must be consigned based on biomass ash characteristics, among which ash bulk chemical composition is the first consideration. The elemental compositions of biomass ash often make their resource recovery or beneficial reuse possible: for example, potassium recovery from wood/agriculture residue ash (Etiegni and Campbell, 1991; Samadhi et al., 2019; Wang et al., 2017; Wang et al., 2015), phosphorus recovery from sewage sludge ash (Fang et al., 2018; Liang et al., 2019; Takahashi et al., 2001), and ash reuse as soil fertiliser/amendment (Huang et al., 1992; Park et al., 2005). However, the leaching behaviour of biomass ash is also an important factor in decision makings of ash management, which have been less studied. In this aspect, ash mineral or phase compositions are a more useful indicator as they represent the existing form of elements in biomass ash (whether easily soluble/extractable or not). This also applies to trace toxic elements in biomass ash. Although some regulatory limits on trace toxic elements control have been put forward to guide ash management (based on the bulk concentration of trace metals in ash; e.g. the Swedish and Finnish limits for ash to be used as forestry fertiliser (Dahl et al., 2010; Swedish National Board of Forestry, 2002)), their leaching behaviour needs more clarification (e.g. how will they change with the value extraction process? how will the leachate influence the environment in the process of ash beneficial reuse?). As biomass types and ash generation methods may have considerable influence on ash characteristics, there is increasing interest to study their possible influence on potential ash management strategies.

This research focuses on the study of biomass influences on ash characteristics (including several laboratory and industrial ash samples derived from different biomasses), which are characterised by ash bulk chemical composition, X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and water leaching test. It is hoped from this comparative study that more evidence can be given to resource recovery from, and beneficial management of biomass ash.

5.2 Materials and methods

5.2.1 Materials

Five woody biomasses from different plant orders are prepared for laboratory ash production (Table 5.1). The obtained raw woods were first split (using bandsaw) to blocks with a size below 5×5×5 cm, and then subjected to Retsch SM300 Cutting Mill to finally mill the sample less than 1 mm for subsequent laboratory ashing procedure.

Table 5.1. Details on the woody biomass prepared for producing laboratory ash.

Biomass label [a]	*Cedrus* spp.	*Alnus* spp.	*Crataegus* spp.	*Fraxinus* spp.	*Salix* spp.
Biomass English name	Cedar	Alder	Hawthorn	Ash	Willow
Biomass order	Pinales	Fagales	Rosales	Lamiales	Malpighiales
Biomass clade	Gymnosperms	Angiosperms	Angiosperms	Angiosperms	Angiosperms
Biomass type	Softwood	Hardwood	Hardwood	Hardwood	Hardwood
Biomass source	Purchased from Druidswood	Purchased from Amazon (provided by reservoir logs)	Purchased from Druidswood	Purchased from Druidswood	Leeds local

[a] Biomass Latin name is used to label studied biomass in this research

A further six biomass ash samples were also obtained for this study (Table 5.2). There are three industrial wood ash samples (Lynemouth ash, CFA and CBA), two laboratory rice husk ash samples (RHA-1 and RHA-2) and one industrial straw ash sample (Aarhus ash).

Table 5.2. Details on six biomass ash samples included in this study.

Ash name	Lynemouth ash	CFA	CBA	RHA1	RHA2	Aarhus ash
Origin	Lynemouth power station	Cumbria	Cumbria	Germany	Germany	Aarhus power station
Feed	White wood pellets	Woodchip	Woodchip	Rice husk	Rice husk	Straw
Colour	Black	Black	Black	Grey	Black	Grey
Collection methods	Electrostatic precipitator	Cyclone ash	Grate discharged ash	Electrostatic precipitator	Electrostatic precipitator	Electrostatic precipitator

5.2.2 Laboratory ashing procedure

For each ashing test, 50 g biomass were placed into two 250 mL porcelain crucibles and placed in muffle furnace (AAF 11/18 manufactured by Carbolite). The muffle furnace was set to increase its temperature to 580 ℃ at a ramping temperature of 3 ℃ and then kept at this temperature for 2.5 hours. The as-obtained ash was cooled overnight in desiccator and weighed to calculate the ashing ratio (ash content determined by residual mass/initial mass) of each biomass.

5.2.3 Chemical composition determination

Bulk chemical compositions of ash samples were determined by classical wet chemical digestion method (detailed procedure can been seen in Appendix C). Briefly speaking, silica in ash was extracted with NaOH to solution and determined by colorimetry. Another solution was prepared by treating ash samples with HF, HCl and H_2SO_4 so that other elements can be dissolved for concentration determination (phosphorous determined by colormetric method, and Ca, Mg, K, Al, Fe and Na determined by atomic absorption spectroscopy - AAS). And moreover, such solution of five laboratory wood ash samples is used to determine trace toxic elements contents in ash: inductively coupled plasma - optical emission spectrometry (ICP-OES; Thermo iCAP 7400) for measurement of As, B, Ba, Cd, Co, Cr, Cu, Ni, Pb, V and Zn; and inductively coupled plasma - mass spectrometry (ICP-MS; Thermo iCAP Qc) for measurement of Hg. The contents of related trace toxic elements in Lynemouth ash, CFA, CBA, RHA-1, RHA-2 and Aarhus ash were determined from their microwave-assisted (Microwave Digestor/Reactor- Anton Parr Multiwave 3000) digestion solution. In addition, loss on ignition (LOI) value of each biomass ash was determined at 900 ℃ for 2 hours.

5.2.4 X-ray diffraction (XRD)

Identification of potential mineral-phases present in ash was conducted via X-ray diffraction (XRD) analysis. The equipment used was Bruker D8 equipped with a LynxEye detector and a 90-position auto sampler. During the XRD tests, Cu Kα was used as radiation sources and the powder samples were mounted on silicon slides scanned between 2theta 2° and 70°. Finally, an International Centre for Diffraction Data (ICDD) database for indexing patterns using specialised software package EVA® was adopted to identify what components are present.

5.2.5 Fourier Transform infrared spectroscopy (FTIR)

An attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) machine manufactured by Perkin Elmer was used to obtain the FTIR spectroscopy of each biomass (the powder ash samples are used directly). The exported spectra data were processed using Thermo Scientific Omnic and Origin 2018b software.

5.2.6 Water leaching procedure

Biomass ash water leaching test was conducted at a solid to liquid (deionised water - DIW) ratio of 1:100 (e.g. 1 g Lynemouth ash samples with 100 ml DIW; Figure 5.1). The mixture was sealed in plastic bottles or vials and then shaken for 2 hours at 700 rpm on vertical laboratory shaker. After this, the separation of the leachate and the residue was performed via vacuum flask using a paper membrane with a pore size of 0.65 μm. The leachate was subjected to pH and conductivity measurement; the elemental compositions of leachate were measured by ion chromatography (IC for measurement of Ca^{2+}, K^{+}, Cl^{-}, NO_3^{-}, PO_4^{3-} and SO_4^{2-}; Thermo Scientific ICS5000), ICP-OES (Thermo iCAP 7400) for measurement of As, B, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn; and ICP-MS (Thermo iCAP Qc) for measurement of Rb and Hg. The total dissolved solids (TDS) value was converted from the conductivity value via the web-link: https://www.lenntech.com/calculators/conductivity/tds_engels.htm. The residue after water leaching was dried in an oven until the weight kept in a constant value and weighed to calculate the water leaching ratio.

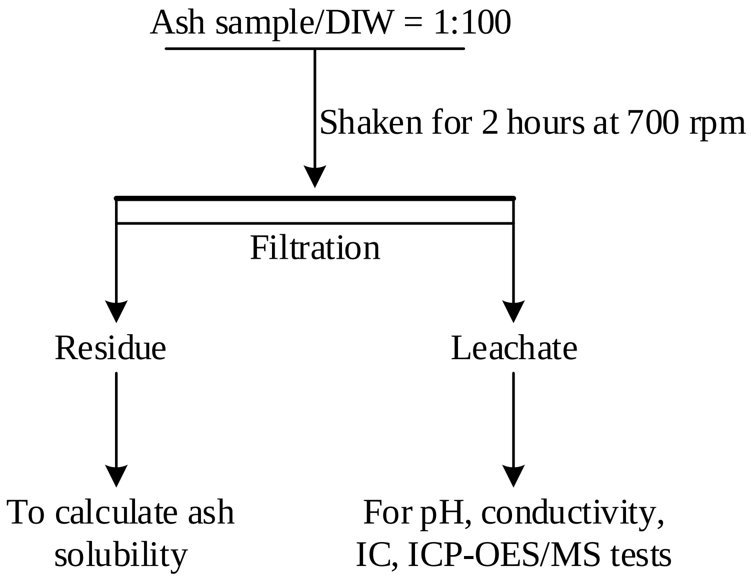

Figure 5.1. Detailed flowsheet for ash water leaching.

5.3 Results

5.3.1 Ash content of different woods

Woods have different ash contents (Table 5.3). *Cedrus* spp. has the highest ash ratio (~5%) among five woods. The other four woods (*Alnus* spp., *Crataegus* spp., *Fraxinus* spp. and *Salix* spp.) have a similar ash content of ~1%.

Table 5.3. Ash content (wt. %) of five woody biomasses (mean value ± standard deviation).

Biomass	*Cedrus* spp.	*Alnus* spp.	*Crataegus* spp.	*Fraxinus* spp.	*Salix* spp.
Ash ratio	4.56±0.08%	1.07±0.07%	1.44±0.03%	0.81±0.04%	1.41±0.04%

5.3.2 Ash chemical composition

Ash chemical compositions (Table 5.4) show that CaO and K_2O are the two primary components (> 5%) in laboratory wood ash: CaO is the most abundant composition (31-

37%) in ashes from *Alnus* spp., *Cedrus* spp., *Crataegus* spp. and *Salix* spp., whereas *Fraxinus* spp. ash just contains about one third of CaO content of above-four ashes; K_2O content is the highest (41%) in *Fraxinus* spp. ash, which is about 2, 3, 4 and 6 times higher than *Salix* spp. ash, *Cedrus* spp. ash, *Alnus* spp. ash and *Crataegus* spp. ash, respectively; P_2O_5 content is higher (6-7%) in *Alnus* spp. ash and *Salix* spp. ash than three other ashes (2-3%). As for three industrial wood ash samples, CaO (~15-30%), SiO_2 (~15-30%) and K_2O (~5-15%) are the primary components. As for three other ash samples, SiO_2 (90-95%) is dominating in both rice husk ashes and K_2O (~50%) is the primary component of Aarhus ash. Three industrial wood ash, in most cases, contain much higher trace toxic elements than laboratory wood ash.

Table 5.4. Chemical compositions of biomass ash (LOD – Limit of Detection; LOQ – Limit of Quantification).

Item	Laboratory wood ash					Industrial wood ash			Other ashes		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash
Major elements (wt. %)											
CaO	36.36	36.77	36.02	11.98	31.53	19.28	17.11	30.36	0.58	0.76	0.39
MgO	1.88	3.46	2.17	4.08	4.31	4.07	3.19	5.43	0.30	0.37	0.10
K_2O	15.9	10.84	7.2	41.37	18.6	6.25	13.24	12.53	1.49	2.06	46.46
P_2O_5	2.3	6.8	2.5	2.4	6.1	3.05	3.11	5.06	0.58	0.77	0.16
SiO_2	0.08	1.29	1.17	0	0.18	21.28	16.49	31.41	94.22	90.37	1.06
Al_2O_3	0	0.26	0.24	0	0.02	1.59	3.21	4.11	0.12	0.65	0.08
Fe_2O_3	0.06	0.67	0.29	0.14	0.23	0.59	1.31	1.53	0.08	0.34	0.68
Na_2O	0.59	0.47	2.30	0.51	0.43	1.55	1.63	2.11	0.82	0.32	0.85
LOI	36.6	28.6	34.8	34.8	37	40.27	25.94	7.04	1.60	3.77	33.55
Trace toxic elements (ppm; mg/kg)											
As	<LOQ	2.1	1.5	0.44	1.4	33	16	10	<LOD	<LOQ	6.2
B	32	43	197	109	49	283	812	514	<LOD	<LOD	<LOQ
Ba	26	13	14	17	69	1,381	1,729	2,121	44	51	32
Cd	1.2	3	5.3	0.15	35	5.9	138	1.0	<LOQ	<LOQ	2.7
Co	0.49	11	2.3	0.59	3.7	7.9	9.7	13	0.95	1.6	0.28
Cr	8.3	20	12	8.9	19	296	125	142	7.9	102	24
Cu	26	104	124	70	103	157	290	272	8.5	16	33
Hg	0.06	0.04	0.04	0.05	0.11	0.23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ni	52	27	45	16	13	108	47	61	1.9	27	3.5
Pb	1.8	29	68	1.8	5.5	21	632	55	<LOD	18	26
V	1.1	5	9	0.83	0.91	12	32	44	0.58	4.4	0.42
Zn	154	1,078	817	116	1,698	975	5,358	130	68	76	447

5.3.3 XRD

The XRD results (Table 5.5 and raw spectra in Appendix C) indicate that the common mineral phases are calcite ($CaCO_3$), fairchildite ($K_2Ca(CO_3)_2$) and arcanite (K_2SO_4) in laboratory wood ash. *Alnus* spp. ash, *Cedrus* spp. ash, *Crataegus* spp. ash and *Salix* spp. ash are all dominated by calcite phase, with minor arcanite and hydroxylapatite ($Ca_5(PO_4)_3(OH)$). *Cedrus* spp. ash and *Salix* spp. ash also contain moderate fairchildite. Fairchildite is the main phase of *Fraxinus* spp. ash, together with some calcite, arcanite, larnite (Ca_2SiO_4) and polyhalite ($K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$). As for industrial wood ash, Quartz (SiO_2) and calcite exist in three industrial wood ash samples, and lime (CaO) is identified in Lynemouth ash and CBA. Lynemouth ash also contains some kalsilite (KAl_2SiO_4) and gypsum ($CaSO_4{\cdot}2H_2O$), and CBA has some periclase (MgO) and sodium calcium silicate ($Na_2Ca_3Si_2O_8$). In addition, arcanite and sylvite (KCl) are identified in CFA. Although both rice husk ash samples are mainly composed by SiO_2, cristobalite is the main mineral phase in RHA-1 with less quartz, whereas RHA-2 sample is mainly composed by quartz. On both samples, there is some amorphous content, but sample RHA-2 has a greater amount of this. As for Aarhus ash, sylvite, arcanite and less kalicinite ($KHCO_3$) are identified. In general, the XRD patterns of biomass ash are consistent with the changes in ash chemical compositions.

Table 5.5. Summary of mineral phases identified by XRD for each biomass ash (score based on XRD peak height).

Item	Laboratory wood ash					Industrial wood ash			Other ashes		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash
Arcanite (K_2SO_4)	+	+	+	+	+		++				++
Calcite ($CaCO_3$)	+++	+++	+++	++	+++	++	++	++			
Cristobalite (SiO_2)									+++		
Fairchildite ($K_2Ca(CO_3)_2$)	++	+		+++	++						
Gypsum ($CaSO_4 \cdot 2H_2O$)						++					
Hydroxylapatite ($Ca_5(PO_4)_3(OH)$)	+	+	+		+						
Kalicinite ($KHCO_3$)	+	+		+	+						++
Kalsilite (KAl_2SiO_4)						+					
Kaolinite ($Al_2Si_2O_5(OH)_4$)				+							
Larnite (Ca_2SiO_4)				++							
Lime (CaO)						++		+++			
Periclase (MgO)								+			
Polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$)	+	+		++	+						
Quartz (SiO_2)						+++	+++	+++	+	+++	
Sodium calcium silicate ($Na_2Ca_3Si_2O_8$)								++			
Sylvite (KCl)	+						++				+++

5.3.4 FTIR

The main characteristic bands of biomass ash are recorded from 2000 to 500 cm^{-1} (Table 5.6 and raw spectra in Appendix C). The FTIR results indicate the presence of carbonate/bicarbonate (e.g. calcite, fairchildite and kalicinite), sulfate (e.g. arcanite and gypsum), and/or silicate/aluminosilicate (e.g. quartz, kalsilite and larnite) in ash, which are in consistence with the XRD results of each biomass ash.

Table 5.6. Summarized FTIR bands (cm $^{-1}$) and associated distributions of biomass ash.

Item	Laboratory wood ash					Industrial wood ash			Other ashes		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash
C-O [a]	1416/870	1415/875	1445/877	1445/1393/871	1394/871	1400/873	1412/875	1408/874	--	--	1400/1372
S-O [b]	1120	1113	1116	1124	1114	1115	1108	--	--	--	1115/982
Si-O-Si/Al [c]	1062	1042	--	1058/845	1040	1034	--	1026	1068/792/620/460	1068/798/451	1282/832
Series Me-O bonds [d]	711/619/571	712/618/571	711/619/571	704/671/619	712/618/570	712/620	713/616	712	--	--	703/663/620

[a] Carbonate or bicarbonate; Source: (Abraham et al., 2013; Bakovic et al., 2006; Mozgawa et al., 2014).

[b] Sulfate; Source: (Abraham et al., 2013).

[c] Silicate or aluminosilicate; Source: (Criado et al., 2007; Mozgawa et al., 2014; Tang et al., 2015; Wang and Ren, 2005; Zhang et al., 2012).

[d] Ca-O, Mn-O, etc; Source: (Abraham et al., 2013).

5.3.5 Water leaching

Water leaching tests show that biomass ash samples are alkaline in nature (Table 5.7; leachate pHs of both the laboratory and industrial wood ashes are within the range ~11-12 whereas three other ashes are between ~8-9). As for laboratory wood ash, leaching ratio (weight loss/initial mass of dry solids) of *Fraxinus* spp. ash (~70%) is almost 2.5 and 4 times higher than that of *Cedrus* spp./*Salix* spp. ash and *Alnus* spp./*Crataegus* spp. ash, respectively; and accordingly, leachate conductivity of *Fraxinus* spp. ash (~9 mS/cm) is about 2 and 4 times higher than that of *Cedrus* spp./*Salix* spp. ash and *Alnus* spp./*Crataegus* spp. ash. As for industrial wood ash, CFA has more soluble fractions (~30%) than Lynemouth ash and CBA (~10-15%). As for three other ashes, both rice husk ashes have few soluble fractions (< 6%) but Aarhus ash is almost all soluble (> 95%) in water.

Table 5.7. Water leaching properties of biomass ash (average value ± standard deviation; N = 4).

Item	Laboratory wood ash					Industrial wood ash			Other ashes		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash
Leachate pH	11.22± 0.22	10.81± 0.24	11.04± 0.21	11.02± 0.30	11.15± 0.30	12.38± 0.05	11.82± 0.17	12.35± 0.24	9.38± 0.09	9.57± 0.14	8.90± 0.06
Leachate conductivity (mS/cm)	4.49± 0.06	2.44± 0.15	2.83± 0.04	8.72± 0.37	4.51± 0.03	4.54± 0.37	4.19± 0.25	4.76± 0.19	0.106± 0.026	0.244± 0.022	12.78± 0.37
Leachate TDS (ppm)	2,875± 35	1,560± 99	1,810± 28	5,580± 240	2,885± 21	2,903± 240	2,680± 165	3,047± 125	68±16	156± 14	8,177± 238
Leaching ratio (wt. %)	30.16± 2.69	19.07± 1.40	19.45± 1.02	72.99± 3.71	30.71± 1.18	12.72± 2.83	28.48± 0.55	10.76± 2.09	4.11± 2.20	5.66± 0.15	97.41± 0.88

Table 5.8 gives the elemental compositions of leachates. Potassium (K^+), calcium (Ca^{2+}) and sulfate (SO_4^{2-}) are the most abundant constituents in wood ash leachates. As for other ashes, all major elements are in low level (< 100 ppm) in both rice husk ashes, but K^+ (5344 ppm) is dominating in Aarhus ash leachate, followed by Cl^- (2061 ppm), SO_4^{2-} (1778 ppm) and Ca^{2+} (1615 ppm). As for potassium of extraction interest, five laboratory wood ash, Lynemouth ash, CFA and Aarhus ash contain water soluble potassium: all with 100% soluble potassium except for *Alnus* spp. ash (~90% potassium extraction ratio), which can be due to the dissolution of fairchildite/arcanite rich particles (laboratory wood ash), kalsilite (Lynemouth ash) or arcanite (CFA) rich particles, and sylvite/arcanite/kalicinite rich particles (Aarhus ash). Rb is found in high concentration in leachate than many other trace toxic elements: wood ash from ~400-2500 ppb and Aarhus straw ash at 3825 ppb. For comparison, the human body typically contains about 5 ppm Rb (Yamagata, 1962). Current guideline values on biomass ash management do not include Rb, probably due to its non-toxic property to environment and humans (Royal Society of Chemistry, 2022).

Table 5.8. Elemental compositions of leachates from water leaching tests of biomass ash (LOD – Limit of Detection; LOQ – Limit of Quantification).

Item	Laboratory wood ash					Industrial wood ash			Other ashes		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash
Major elements (ppm; mg/L)											
Ca^{2+}	569	299	320	1,056	478	510	881	1,245	9.3	42	1,615
K^{+}	1,535	781	728	3,481	1,615	786	1,053	259	29	82	5,344
Cl^{-}	137	39	26	104	49	77	189	55	5.7	15	2,061
NO_3^{-}	52	20	15	113	44	41	58	32	0.31	0.90	120
PO_4^{3-}	n.d.	n.d.	44	n.d.	n.d.	51	n.d.	47	15	27	n.d.
SO_4^{2-}	293	594	589	468	455	352	1,264	182	5.8	22	1,778
Trace elements (ppb; ug/L)											
As	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
B	1,467	875	2,017	8,525	1,658	525	1,175	508	500	517	629
Ba	<LOD	<LOQ	73	92	<LOQ	48	583	517	<LOQ	<LOD	141
Cd	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOQ	<LOD	7.6
Co	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ
Cr	<LOQ	27	31	<LOQ	<LOQ	283	200	350	<LOD	333	151
Cu	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	64
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3.8	<LOD
Mo	53	<LOQ	43	<LOQ	<LOD	30	108	73	<LOQ	13	37
Ni	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD
Rb	758	842	492	1,200	2,117	2,275	2,525	425	60	53	3,825
Sb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zn	11	<LOQ	<LOQ	<LOQ	13	7.0	217	<LOQ	6.2	12	341

5.4 Discussion

5.4.1 Biomass influences on ash characteristics

Biomass type has remarkable influence on associated ash chemical composition. CaO content is usually the first component (typically ~30-40%) in woody biomass ash (Vassilev et al., 2013; Zhai et al., 2021a; Zhai et al., 2021b), which is supported by *Alnus* spp. ash, *Cedrus* spp. ash, *Crataegus* spp. ash, *Salix* spp. ash and CBA. Ash from *Alnus* spp., *Crataegus* spp. and *Salix* spp. (three hardwoods) situates within the reported hardwood ash region (Figure 5.1). *Cedrus* spp. ash falls within the softwood ash range but at the edge of the range, possibly reflecting more data required to perfect softwood ash distribution pattern (softwood ash data background in Figure 5.1 are primarily based on ash from fir, pine and spruce). *Fraxinus* spp. ash falls in the part of the diagram normally associated with non-woody eudicots, rather than with the other hardwoods. *Fraxinus* spp. ash surprisingly contains much higher potassium content (K_2O; ~40%) than other wood ashes (5-20%), and similar biomass with high potassium content in ash is sunflower straw (Phyllis 2 database) (ECN.TNO, 2020). A recent document also reported that teak ash produced at 815 ℃ contains high potassium content (K_2O; ~20%) (Adeleke et al., 2020). In general, higher ashing temperature will volatilize more volatile chemical components like potassium, and thus it is presumed that teak ash would contain much higher potassium content that might be comparable with *Fraxinus* spp. ash and sunflower straw ash. Therefore, high potassium content in Asterids derived biomass ash might be more common than other woody biomasses (*Fraxinus* spp. and teak belonging to Lamiales order and sunflower belonging to Asterales order; Lamiales and Asterales diverged from Asterids (Zhai et al., 2021a)).

Lynemouth ash and CBA locate within softwood ash region, probably indicating a proportion of softwood involved in their biomass sources. Silica is the primary component (SiO_2; >90%) in both rice husk ashes, which agrees with other reports (Pode, 2016; Vassilev et al., 2010). Aarhus ash is the straw fly ash and a reasonably high potassium content is identified in the form of sylvite (KCl), arcanite (K_2SO_4) and kalicinite ($KHCO_3$), which is due to the condensation of volatile constituents like K, Na, Cl and S onto fly ash particles (Niu et al., 2016; Yin et al., 2008).

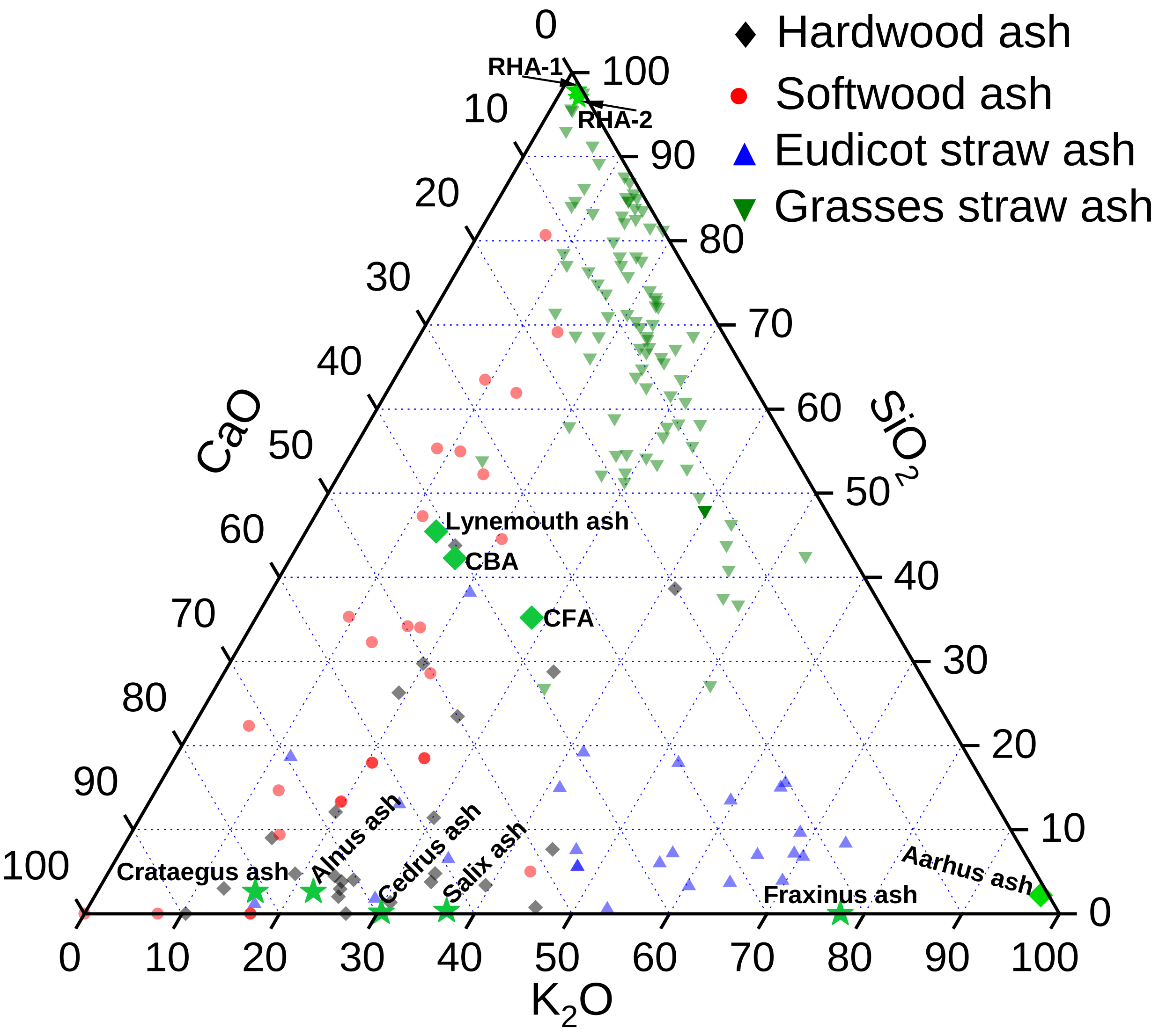

Figure 5.1. Distribution of 11 ash samples in a K_2O-SiO_2-CaO ternary diagram modified from Zhai et al. (2021a).

Ash generation procedure can also influence ash characteristics. A comparison of bulk chemical compositions of five lab-obtained wood ashes and three industrial wood ashes (Table 5.4) shows that industrial wood ash tends to contain more trace toxic elements than laboratory wood ash. Although the underlying reasons are not clear, the contamination introduction during biomass processing for industrial power/heat plant usage, and the trace toxic element levels in soil where plant grows can be part reasons. It is noted that Cd in *Salix* spp. ash is higher than Lynemouth ash and CBA. Studies have indicated that *Salix* spp. tends to accumulate more Cd from soil and is suitable for Cd phytoextraction from Cd-contaminated soil (Dimitriou et al., 2012; Greger and Landberg, 1999; Robinson et al., 2000), which may be the reason for the high Cd content in *Salix* spp. ash. Although CaO content in wood ash is high, their existing form in ash differs greatly: calcite for laboratory wood ash and CFA, and lime plus calcite in Lynemouth ash and CBA. This may be due to the different ashing temperature (laboratory ashing at 580 ℃ in this study), and calcite generally decomposes into CaO and CO_2 within ~700-800 ℃ (Bilton et al., 2012; Karunadasa et al., 2019). Rice husk ash samples also confirm that even the bulk chemical compositions are similar (Table 5.4), their mineral phase composition can vary greatly (Table 5.5).

5.4.2 Biomass ash leaching behaviour

All biomass ashes in this study are alkaline (liming effect) in nature, which may be caused by the dissolution of oxide, carbonate, salt and hydroxide of calcium and potassium (Pöykiö et al., 2009). The general leachate pH values are sequenced as: industrial wood ash (pH at ~12) > laboratory wood ash (~11) > rice husk ash (~9.5) > straw ash (~9).

The leachate also contains some trace toxic elements that may arise environmental concerns (Table 5.8). WHO guideline values (World Health Organization, 2022) and USEPA limits (USEPA, 2022) for drinking water quality control (listed in Appendix C) are referred to compare the trace toxic elements in leachate. Here, if the trace toxic elements in leachate are below the WHO guideline values or USEPA limits, it is regarded that the leachate will not pollute the environment. It appears that trace elements of environmental concern in leachate are: Cr in leachates of Lynemouth ash, CFA, CBA, RHA-2 and Aarhus ash, Mo in leachates of CFA and CBA, B in *Fraxinus* spp. ash leachate and Cd in Aarhus ash leachate.

Totally released trace toxic elements from ash water leaching tests can also provide some other indications on ash property. Based on water leachable trace toxic element amounts, EU waste acceptance criteria (WAC) lists three waste types at landfill: inert waste, non-hazardous waste and hazardous waste (Council Decision, 2003). The compliance water leaching test (BS EN 12457-3) includes first stage leaching at L/S of 2 and second stage leaching at L/S of 8 with a sum L/S of 10 that can be compared to WAC landfill limits to determine whether a waste is inert, non-hazardous or hazardous. In this research, water leaching test was conducted at a L/S of 100, from which it is hoped that the trace toxic elements can be released at a maximum level. Water leaching results can thus be used to make prudent comparisons with WAC landfill limits. Table 5.9 shows that five ash samples are affected by Cr, cautiously resulting in Lynemouth ash, CFA, CBA, RHA-2 and Aarhus ash as hazardous waste at landfills. Mo and Hg also cautiously leads CFA and RHA-2 to hazardous waste, respectively.

Table 5.9. Comparison of water leachable trace toxic elements with waste acceptance criteria at L/S = 10 l/kg (Council Decision, 2003); all reported values here are mg/kg ash (LOD – Limit of Detection; LOQ – Limit of Quantification).

Item	Ash type											WAC landfill limit		
	Cedrus spp. ash	*Alnus* spp. ash	*Crataegus* spp. ash	*Fraxinus* spp. ash	*Salix* spp. ash	Lynemouth ash	CFA	CBA	RHA-1	RHA-2	Aarhus ash	Inert	Non-hazardous	Hazardous
As	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	0.5	2	25
Ba	<LOD	<LOQ	7.3	9.2	<LOQ	4.8	**58.3**	**51.7**	<LOQ	<LOD	14.1	20	100	300
Cd	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOQ	<LOD	**0.76**	0.04	1	5
Cr	<LOQ	**2.7**	**3.1**	<LOQ	<LOQ	***28.3***	***20***	***35***	<LOD	***33.3***	***15.1***	0.5	10	70
Cu	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	**6.4**	2	50	100
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	***0.38***	<LOD	0.01	0.2	2
Mo	**5.3**	<LOQ	**4.3**	<LOQ	<LOD	**3**	***10.8***	**7.3**	<LOQ	**1.3**	**3.7**	0.5	10	30
Ni	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.4	10	40
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	0.5	10	50
Sb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.06	0.7	5
Se	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.1	0.5	7
Zn	1.1	<LOQ	<LOQ	<LOQ	1.3	0.7	**21.7**	<LOQ	0.62	1.2	**34.1**	4	50	200

5.4.3 Implications for ash beneficial management

In order to guide waste management in a possibly sustainable way, five basic steps including prevention, reuse, recycling, recovery and disposal have been put forward in European waste hierarchy (European Commission, 2008). While applying this idea into biomass ash management, the priority can be characterised as ash reduction, ash reuse, ash value recovery and disposal.

Ash reduction in bioenergy generation can be realised by biomass selection as biomass type has significant influence on biomass ash content (Vassilev et al., 2010; Zhai et al., 2021b). This study shows that *Cedrus* spp. (softwood) contains higher ash content than *Alnus* spp., *Crataegus* spp., *Fraxinus* spp. and *Salix* spp., which means that using *Cedrus* spp. as the biofuel would produce more ash than the other four samples. However, no significant difference was found in statistical analysis of ash content of hardwood (median value 1.6 with a range of 0.3-4.6) and softwood (median value 1.0 with a range of 0.1-5.2) (Zhai et al., 2021a). Other factors, like biomass availability, biomass supply and volume/mass reduction advantage by incineration in waste biomass management, must be balanced in decision-making of which biomass to be used. Increasing combustion temperature can decrease ash production (Etiegni and Campbell, 1991; Zając et al., 2019), and also decrease the volatile toxic elements (e.g. Cd, Pb and Zn) content in bottom ash (Zając et al., 2019). Therefore, to ensure the highly efficient combustion of biomass in furnace is not only important in ash reduction, but also to reduce the ash contaminants level.

Biomass ash recirculation to soil as fertiliser material or soil amendment will promote the sustainable development of bioenergy utilisation and have received many studies (Demeyer et al., 2001; Krejsl and Scanlon, 1996; Ochecova et al., 2014; Park et al., 2005). However, trace toxic elements in ash may restrict such purpose. Some guideline values on trace elements control for ash reuse have been put forward: for example, Finnish limit (Dahl et al., 2010) and Swedish limit (Swedish National Board of Forestry, 2002) on ash to be used as forestry fertiliser, and UK limit on poultry litter ash (PLA) to be used as a fertiliser (EA-UK, 2012). These guideline values (listed in Appendix C) are compared with ash bulk chemical composition of trace toxic elements. Table 5.10 indicates that some environmental concerns may be raised if just using ash bulk contents of trace toxic elements to evaluate ash reuse: for example, CBA and Aarhus ash are within Finnish limits but could be hazardous waste as affected by leachable Cr. Therefore, when making decisions on whether biomass ash can be returned to soil, not only the bulk chemical composition of trace toxic elements in ash should be compared to guideline values, but also the leaching behaviour of such ash should be studied.

Table 5.10. Summary of potential trace toxic elements of environmental concern on ash management in relation to Finnish, Swedish and PLA limits (based on bulk chemical composition; within bounds representing within related guideline limit values) and WCA landfill limit (based on ash leaching behaviour).

Item	Finnish limit	Swedish limit	PLA limit	WCA landfill limit
Laboratory wood ash				
Cedrus spp. ash	Within bounds	Within bounds	Excessive Ni	Mo: non-hazardous; others: inert
Alnus spp. ash	Within bounds	Within bounds	Excessive Ni	Cr: non-hazardous; others: inert
Crataegus spp. ash	Within bounds	Within bounds	Excessive Cd and Ni	Cr and Mo: non-hazardous; others: inert
Fraxinus spp. ash	Within bounds	Within bounds	Within bounds	Inert
Salix spp. ash	Excessive Cd	Excessive Cd	Excessive Cd	Inert
Industrial wood ash				
Lynemouth ash	Excessive As	Excessive As, Cr, Ni	Excessive As, Cd, Cr and Ni	Cr: hazardous; Mo: non-hazardous; others: inert
CFA	Excessive Cd, Pb and Zn	Excessive B, Cd, Cr and Pb	Excessive Cd, Cr, Ni, Pb, V and Zn	Cr and Mo: hazardous; Ba and Zn: non-hazardous; others: inert
CBA	Within bounds	Excessive B and Cr	Excessive Co, Cr, Ni and V	Cr: hazardous; Ba and Mo: non-hazardous; others: inert
Other ashes				
RHA-1	Within bounds	Within bounds	Within bounds	Inert
RHA-2	Within bounds	Excessive Cr	Excessive Cr and Ni	Cr and Hg: hazardous; Mo: non-hazardous; others: inert
Aarhus ash	Within bounds	Within bounds	Within bounds	Cr: hazardous; Cd, Cu, Mo and Zn: non-hazardous; other: inert

Potassium recovery from biomass ash, if possible, is attractive before ash disposal. Potassium in wood ash (except CBA) is easily extractable (K extraction ratio of ~90% for *Alnus* spp. ash and ~100% for others). K extraction ratios of both rice husk ash samples are low (<50%) but Aarhus ash contains very easily soluble potassium (almost all soluble). Potassium content in ash also impacts the feasibility of potassium recovery, and taking this into consideration, *Cedrus* spp. ash, *Fraxinus* spp. ash, *Salix* spp. ash CFA and Aarhus ash are in high potential for potassium recovery. The leachate elemental composition shows that the extracted potassium is highly likely to be a mixture of KCl, K_2SO_4, K_2CO_3 with some calcium salts, which is in line with other studies (Wang et al., 2017; Wang et al., 2015). However, potassium recovery leachate from *Fraxinus* spp. ash, Lynemouth ash, CFA and Aarhus ash should be monitored as they may contain excessive trace toxic elements compared to the WHO guideline values and USEPA limits for drinking water quality control.

Although least favoured in waste hierarchy, currently landfill disposal is the most common fate of most biomass ash (Carević et al., 2020; IEA Bioenergy, 2018). This study shows that Lynemouth ash, CFA, CBA, RHA-2 and Aarhus ash are cautiously regarded as hazardous waste at landfill (Table 5.9), which means that more money will be spent on their landfill than inert and non-hazardous ash. Controlling Cr and Mo contents in biomass feedstocks may be useful in ash beneficial management and reduce the landfill costs by ash conversion from hazardous waste to non-hazardous waste or from non-hazardous waste to inert waste.

5.5 Conclusions

In total 11 biomass ash samples were studied in this research and their physiochemical properties were characterised. It is found that biomass type and ash generation procedure have significant influence on ash major chemical compositions and their existing mineral phases. All biomass ashes in this research are alkaline in nature and their water leachate pH at L/S of 100 can range from ~9 (Aarhus ash) to ~12 (three industrial wood ashes). To reduce possible environmental risks, ash beneficial reuse as fertiliser material or soil amendment should not only take bulk chemical compositions of trace toxic elements into consideration, but also consider the leaching behaviour of trace toxic elements in ash. Potassium is easily soluble in most ash samples and therefore potassium recovery from biomass ash is of enormous interest, but potassium recovery leachates from *Fraxinus* spp. ash, Lynemouth ash, CFA and Aarhus ash should be monitored as they may contain excessive trace toxic elements compared to WHO and USEPA guideline values for drinking water quality control. Finally, different destinations are assigned to 11 biomass ash samples in comparison with EU WAC landfill limits: inert waste landfills for *Fraxinus* spp. ash, *Salix* spp. ash and RHA-1, cautiously non-hazardous waste landfills for *Alnus* spp. ash, *Cedrus* spp. ash and *Crataegus* spp. ash, and cautiously hazardous waste landfills for Lynemouth ash, CFA, CBA, RHA-2 and Aarhus ash.

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Chapter 6: Effect of persistent organic pollutants (POPs) content on potential reuse options for biomass combustion ash

6.1 Introduction

Combustion of biomass within power stations is a more sustainable way to generate electricity than the use of fossil fuels because the half-life of the emitted CO_2 in the atmosphere is shorter provided the feedstock is sustainably grown (Cherubini et al., 2011). As a result, global bioenergy electricity generation has increased from 164 terawatthours (TWh) in 2000 to 718 TWh in 2020, and it is projected that a 7% annual increasing rate is required to meet the predictive value of over 1400 TWh in 2030 within the net zero emissions scenario by 2050 (IEA, 2021). However, if this rate of increase is to continue, beneficial uses or safe disposal options must be found for the increasing volumes of ash that are generated. Combustion of virgin biomass produces between 1-2% ash (woody feedstocks) and 5-9% ash by weight (herbaceous feedstocks) (Zhai et al., 2021a). Such ashes are rich in macronutrients needed for plant growth (e.g. potassium, calcium, phosphorus, magnesium, sulphur (Barker and Pilbeam, 2015)) and silica (a major constituent of soil), with only very low contaminant metals concentrations (Zhai et al., 2021a) making reuse as a fertiliser feasible (Dahl et al., 2010; Swedish National Board of Forestry, 2002). Waste biomass tends to produce a larger proportion of ash (sewage sludge, MSW and paper sludge produce around 30% ash by dry weight (Zhai et al., 2021b)) and such ashes can contain higher contaminant metal concentrations, making their reuse more difficult, but the extraction of embedded energy as electricity, volume reduction and removal of degradable organics before disposal are themselves seen as important environmental benefits (Chang et al., 1998; Fytili and Zabaniotou, 2008; Zekkos et al., 2013), and the bottom ash may be suitable after processing for restricted use as aggregates (Allegrini et al., 2014; Hjelmar et al., 2007; Lynn et al., 2017; Reid et al., 2008). However, whenever organic matter is incinerated, there is always the potential to form persistent organic pollutants (POPs) during combustion, as POPs and POP precursor molecules can form from unburnt carbon moieties in the combustion gases as they cool (Altarawneh et al., 2009; Gullett et al., 1992; Launhardt and Thoma, 2000; Stanmore, 2004).

POPs are those organic compounds that are resistant to photolysis, biological and chemical degradation to varying degrees (Ritter et al., 1995). POPs have two notable characteristics (Kelly et al., 2007; Ritter et al., 1995; Walker, 2008; Wania and Mackay, 1996; World Health Organization, 2020): (1) they are often halogenated compounds with low water solubility and high lipid solubility, which lead to their bioaccumulation and biomagnification in fatty tissues; and (2) they are semi-volatile which facilitates their long-range transport through the atmosphere, and results in their wide distribution around the world, even in those regions where they have never been used. Human exposure to POPs, whether acute or chronic, can lead to many health problems including the immune system alteration, increased cancer risk, endocrine disruption, neuro-behavioural impairment, and death (Ritter et al., 1995; World Health Organization, 2016, 2020). Due to the effect of POPs on human and environmental health, the United Nations held the Stockholm Convention on Persistent Organic Pollutants in 2001, with the intention of eliminating or severely restricting their production (UNEP, 2001). Twelve POPs were initially agreed as causing harmful impacts on humans and the ecosystem, but another eighteen have subsequently been added to the list (see Table 6.1).

Table 6.1. List of POPs.

Item	Annex A (Elimination)	Annex B (Restriction)	Annex C (Unintentional production)	Reference
UN Stockholm Convention 12 original POPs	Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene, Polychlorinated biphenyls (PCB)	DDT	Hexachlorobenzene (HCB), Polychlorinated biphenyls (PCB), Polychlorinated dibenzo-p-dioxins (PCDD), Polychlorinated dibenzofurans (PCDF)	(UNEP, 2001)
UN Stockholm Convention 18 additional POPs	Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Chlordecone, Decabromodiphenyl ether (Commercial mixture, c-DecaBDE), Dicofol, Hexabromobiphenyl, Hexabromocyclododecane, Hexabromodiphenyl ether and heptabromodiphenyl ether (Commercial octabromodiphenyl ether), Hexachlorobutadiene, Lindane, Pentachlorobenzene, Pentachlorophenol and its salts and esters, Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds, Polychlorinated naphthalenes, Short-chain chlorinated paraffins (SCCPs), Technical endosulfan and its related isomers, Tetrabromodiphenyl ether and pentabromodiphenyl ether (Commercial pentabromodiphenyl ether)	Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF)	Hexachlorobutadien, Pentachlorobenzene, Polychlorinated naphthalenes	(UNEP, 2001)
Other POPs of Concern			Polycyclic aromatic hydrocarbon (PAHs)	(El-Shahawi et al., 2010; European Environment Agency, 2021; Lammel et al., 2013; Liu et al., 2019)

The POPs currently listed in the Stockholm Convention can be classified into three groups (UNEP, 2001): substances whose production and use should be eliminated (Annex A) , substances whose production and use should be restricted (Annex B), and substances that are produced unintentionally (Annex C). Annex A and B substances are mainly pesticides and industrial chemicals, whereas Annex C substances are by-products of other processes.

The main anthropogenic production of unintentional POPs is from the production and use of industrial chemicals and the combustion of organic matter (El-Shahawi et al., 2010; European Environment Agency, 2021). As bioenergy is set to increase its share of future energy supply, biomass combustion is projected to produce more unintentional POPs, either emitted with flue gases or associated with the biomass combustion residues or both (Chagger et al., 1998; El-Shahawi et al., 2010; Lammel et al., 2013; Zhang et al., 2017). However, with increasingly stringent gas emission regulations, the amount of POPs emitted to atmosphere is generally controlled to meet very low regulatory limits by using sophisticated air-pollution control technology (Brunner and Rechberger, 2015; European Environment Agency, 2021). In contrast, the POPs that are retained in the biomass ash have received less attention, with more focus to date on toxic trace metals, the other barriers to beneficial reuse of biomass ash (Demeyer et al., 2001; Someshwar, 1996; Vassilev et al., 2013). This deficit impacts on current ash management practices and restricts potentially beneficial reuse of the ash. The POPs that cause most concern when they are present in biomass combustion ash are those listed in Annex C of the Stockholm Convention (Bundt et al., 2001; Chagger et al., 1998; Freire et al., 2015; Swedish Environmental Protection Agency, 2011). They can be grouped into three categories: polychlorinated biphenyl (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (UNEP, 2001). Although not listed as POPs in the Stockholm Convention, polycyclic aromatic hydrocarbons (PAHs) are a similar unintentional by-product of inefficient combustion that are toxic to many organisms and potentially mutagenic and carcinogenic to humans (El-Shahawi et al., 2010; European Environment Agency, 2021; Lammel et al., 2013; Liu et al., 2019), and therefore also have a major impact on the ash disposal strategy if they are present in biomass ash (Bundt et al., 2001; Freire et al., 2015; Košnář et al., 2019; Sarenbo, 2009).

To date, there is no systematic work on the POPs content of biomass combustion ash, or differences in the POPs distribution with feedstock and between ash fraction, or the implications POPs have for the management and beneficial reuse of biomass ash. This study addresses this knowledge gap by statistical analysis of published data on the PAHs, PCDDs, PCDFs and PCBs contents of biomass combustion ash from different feedstocks. The main objectives are: (1) to determine the differences in the POPs contents of biomass ash from different feedstocks and between ash size fractions; (2) to compare POPs distributions with current regulatory limits and guidelines and thereby to identify potential ash management strategies.

6.2 Methodology

6.2.1 Data source

Google scholar, ScienceDirect and Web of Science were used to find papers and articles that report the PAH, PCB and PCDD/F contents of biomass ash. The search terms that were used were “persistent organic pollutants”, “PAHs”, “PCBs”, “PCDD/Fs”, “dioxins”, “biomass ash”, “agriculture residue ash”, “wood ash”, “waste wood ash”, “paper sludge ash”, “sewage sludge ash” and “MSW ash”. The dataset used in this study is summarised in an excel datasheet that is include within Appendix D. A reference link is provided with each record wherever the data is extracted from a journal paper or web-document. In total, 63 journal papers, 4 web-documents, and “The Handbook of Biomass Combustion and Co-firing” were used to obtain the data reported in this study. In addition, some PCDD/Fs data in biomass ash are calculated from their default emission factors outlined by the UNEP (UNEP, 2013) (details on the conversion from default emission factors to associated PCDD/Fs content in ash can be found in Appendix D).

6.2.2 Data compilation

The dataset on the POPs content of biomass ash is divided into six categories (Zhai et al., 2021b): agriculture residue ash, wood ash, waste wood ash, paper sludge ash, sewage sludge ash and MSW ash (Table 6.2 reports the number of data records associated with each type of biomass ash). It is further subdivided into the POPs content of bulk ash and fly ash (fly ash typically represented about 10~30% mass percentage of the ash produced from biomass combustion (Obernberger and Supancic, 2009; Wiles, 1996)). There was limited data on the POP content of paper sludge ash, so paper sludge fly ash is excluded from in this study.

Table 6.2. Details on biomass ash categories and fractions for this study and sample numbers of each POP.

Ash abbreviation	Ash type	Number of samples		
		PAHs	PCDD/Fs	PCBs
AR-FA	Agriculture residue fly ash	8	10	1
AR-BA	Agriculture residue bottom/total ash	4	15	5
W-FA	Wood fly ash	14	17	4
W-BA	Wood bottom/total ash	30	46	26
WW-FA	Waste wood fly ash	0	9	0
WW-BA	Waste wood bottom/total ash	0	5	3
PS-BA	Paper sludge bottom/total ash	0	1	0
SS-FA	Sewage sludge fly ash	5	4	0
SS-BA	Sewage sludge bottom/total ash	2	0	0
MSW-FA	MSW fly ash	18	50	38
MSW-BA	MSW bottom/total ash	15	13	11

A number of data records were found during the search that report only a data range for the principal POPs and fail to report TEQ values for PCBs and PCDD/Fs. These data recorded were excluded from all further analysis (the Appendix D reports both the raw data collected, and the dataset used for analysis). Differences in analytical methods used to determine the PAH content and regulatory standards being used to evaluate the data mean that different studies report the total PAH content based on sum of different numbers of PAH-congeners. Here, the reported total PAHs content values are used to compare the different categories of biomass ash (e.g., in Table 6.4 and Figure 6.1). However, when comparing the PAH-congeners produced by different ashes (Figures. 6.2 & 6.3), only the 16 US EPA priority PAHs (Table 6.3: ring-number from 2-6) are used to ensure comparability. As a result, this comparison can only be made for agriculture residue ash, wood ash and MSW ash (Figures. 6.2 & 6.3).

Table 6.3. List of US EPA 16 PAHs (modified from Lerda, 2011).

PAH - congener	Ring numbers in structure
Naphthalene	2
Acenaphthylene	3
Acenaphthene	3
Fluorene	3
Phenanthrene	3
Anthracene	3
Fluoranthene	4
Pyrene	4
Benz[a]anthracene	4
Chrysene	4
Benzo(b)fluoranthene	5
Benzo(k)fluoranthene	5
Benzo(a)pyrene	5
Dibenzo[a,h]anthracene	5
Indeno[1,2,3-c,d]pyrene	6
Benzo[g,h,i]perylene	6

6.2.3 Statistical analysis

The median value and data range of each POP in each ash category were calculated. An Independent-Samples Kruskal-Wallis Test was then conducted for those ash categories/size fractions with no less than 5 data records, with a null hypothesis that there was no significant difference in PAHs, PCBs and PCDD/Fs contents between the ash categories/size fractions. When there are at least two ash categories or ash fractions showing different POP distribution trends, the null hypothesis is rejected, and then pairwise comparison was conducted based on Dunn's post-hoc test to test if difference is significant ($p < 0.05$, adjusted using the Bonferroni correction). Bivariate two-tailed Pearson correlation tests of POPs contents in biomass ash are conducted by treating all the ash types and fractions as a single dataset to test if there are significant correlations between any two POPs. All the statistical analyses were performed using IBM SPSS Statistics Version 27.

6.3 Results

6.3.1 PAHs content in biomass ash

Statistical analysis of POPs content in biomass ash (Table 6.4) indicates a significant PAHs content distribution difference between agriculture residue fly ash (median PAHs content 12 mg/kg) and wood bottom/total ash (0.42 mg/kg). There is no evidence of a significant difference between the other pairs (Table 6.4). The limited data of PAHs content in bottom/total ash from agriculture residue and sewage sludge seem to show a much lower level of PAHs content in bottom/total ash than their respective fly ash (Figure 6.1). Also, for every ash for which there is data, the PAHs content of the fly ash exhibits a far larger range and higher median value than the associated bottom/total ash (Table 6.4 and Figure 6.1).

Table 6.4. Median and full range of POPs content (PAHs mg/kg ash; PCDD/Fs and PCBs ng TEQ/kg ash) in biomass ash. Kruskal-Wallis test statistic is listed with level of significance (K-W analysis was only conducted where n≥5 indicated by bold type); ** denotes p ≤ 0.001: degrees of freedom = 5, 7 and 3 for PAHs, PCDD/Fs and PCBs, respectively. Different superscript letters in a column indicate a significant difference between sample populations based on pairwise comparisons. For example, a population labelled a is significantly different from b or c, while ac would not be significantly different from a population labelled as a or c, but would be significantly different from b.

Item	AR-FA	AR-BA	W-FA	W-BA	WW-FA	WW-BA	PS-BA	SS-FA	SS-BA	MSW-FA	MSW-BA	K-W Test Statistic
PAHs	**12 ^{b} (0.13-160)**	0.095 (0.069-0.3)	**2.3 ^{ab} (0.015-1757)**	**0.42 ^{a} (0.025-18)**	No data	No data	No data	**0.20 ^{ab} (0.011-43)**	0.0055 (0.002-0.009)	**1.5 ^{ab} (0.05-117)**	**2.3 ^{ab} (0.48-6.9)**	**20.40 ****
PCDD/Fs	**63 ^{ac} (1.3-3976)**	**5.5 ^{ab} (0.02-71)**	**121 ^{bc} (0.48-1740)**	**2.3 ^{a} (0.050-11000)**	**3133 ^{c} (75-98570)**	**22 ^{ac} (6.1-70)**	20 (20-20)	8.3 (4.4-130)	No data	**645 ^{c} (32-31100)**	**11 ^{ab} (4-69)**	**105.89 ****
PCBs	0.04 (0.04-0.04)	**0.18 ^{a} (0.03-2.2)**	25 (0.028-120)	**0.14 ^{a} (0.018-58)**	No data	3 (0.6-9)	No data	No data	No data	**22 ^{b} (0.2-790)**	**0.46 ^{a} (0.06-5.6)**	**43.84 ****

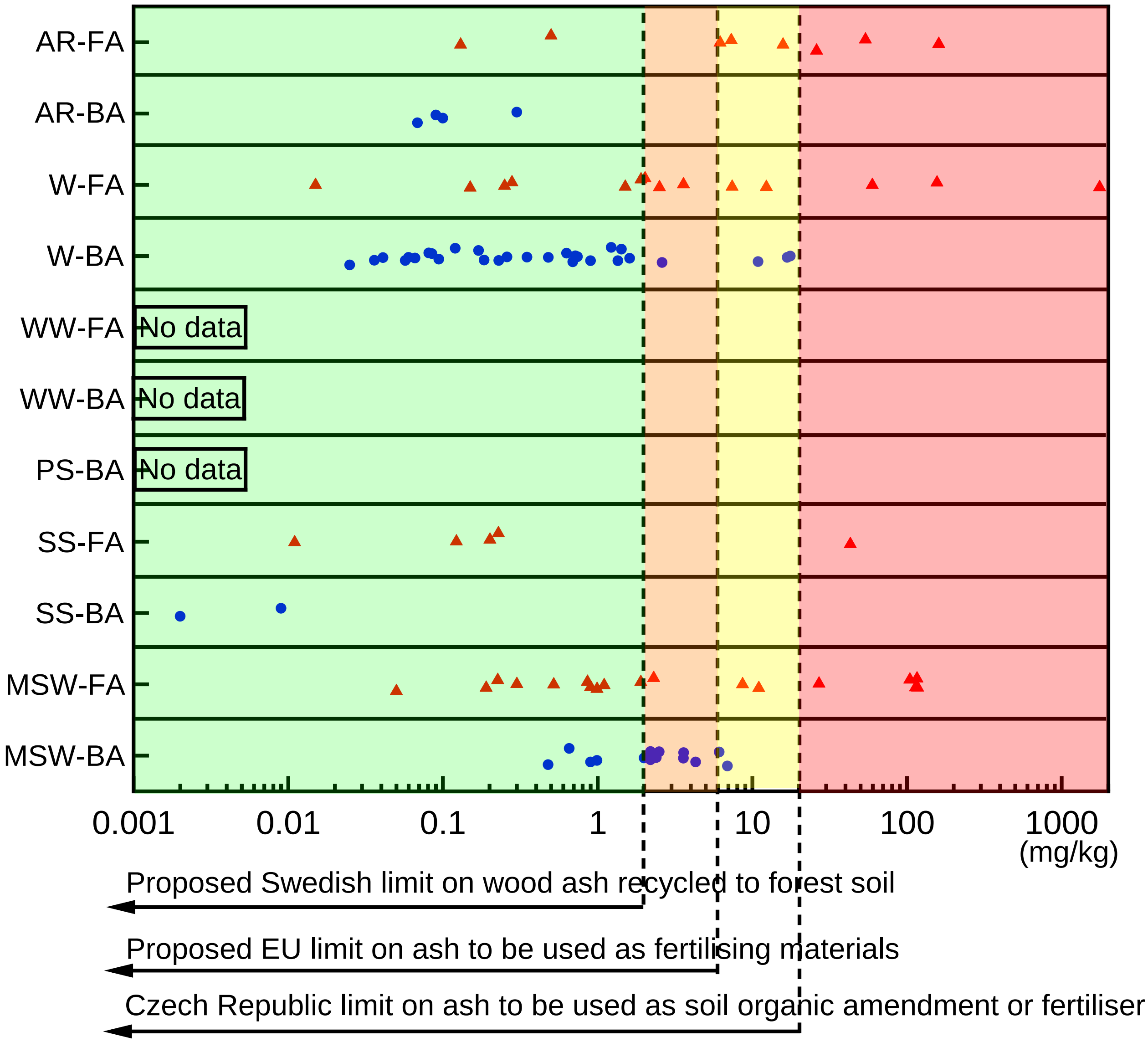

Figure 6.1. PAHs content (mg/kg) distribution based on biomass ash categories and ash fractions.

6.3.2 PAHs profile in biomass ash

The PAH contents of wood and MSW ash (based on the 16 US EPA priority PAHs) are dominated by PAHs containing low (2 or 3) and medium (4) numbers of rings (Figure 6.2). Agriculture residue ash, for which there were only 3 datasets, has a similar profile (Figure 6.3). Adequate data (n≥9) for comparison is only available for wood and MSW ash (Figure 6.2) but both the mean and median values indicate that wood ash tends to contain a larger proportion of 2-ring PAHs than MSW ash. Conversely, the proportion of 3- and 4-ring PAHs combined tends to be lower in wood ash than MSW ash (these ashes only contain a small proportion of 5- and 6-ring PAHs). Interestingly there are only modest differences in the proportion of 2-, 3- and 4-ring PAHs between the bottom/total ash and fly ash for each ash type, although the wood bottom/total ash may contain a slightly higher proportion of 2- and 3-ring PAHs and a smaller proportion of 4-ring PAHs than wood fly ash.

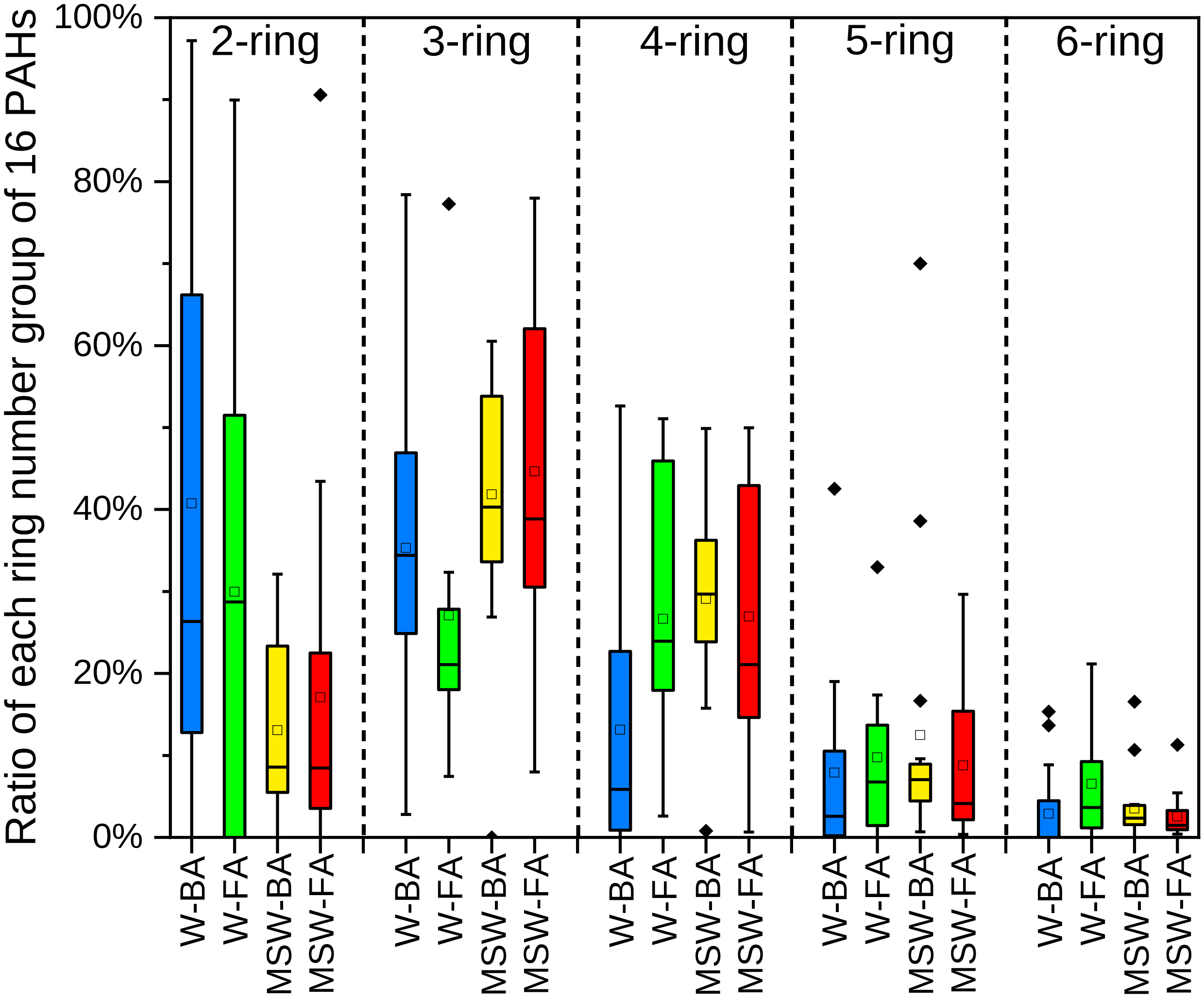

Figure 6.2. Box chart of each ring number group of US EPA 16 PAHs in wood ash and MSW ash (shaded boxes show the median values and interquartile range; tails indicate 1.5 × IQR; □ mean value; ♦ outliers).

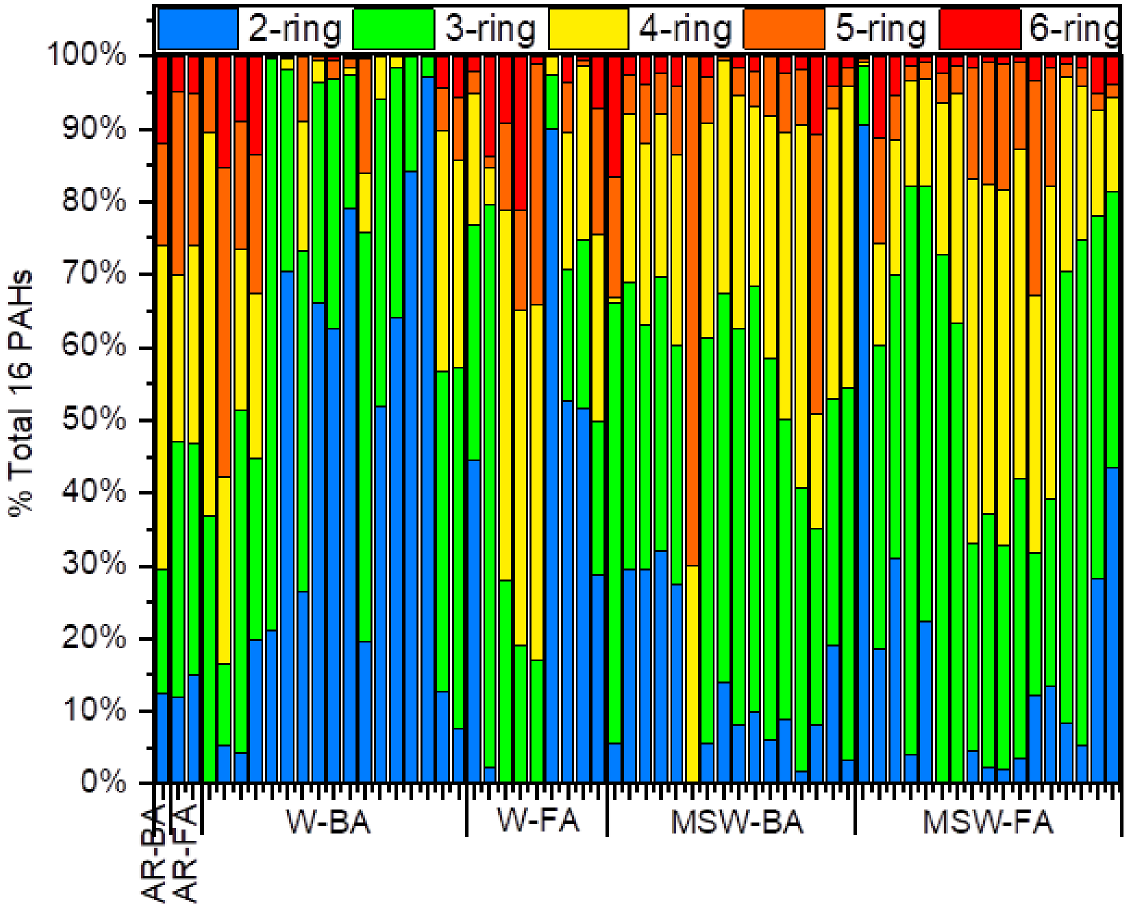

Figure 6.3. PAHs profile in different biomass ashes based on the proportion of each ring number group of US EPA 16 PAHs.

6.3.3 PCDD/Fs content in biomass ash

The PCDD/Fs contents of the biomass ash vary over many orders of magnitude depending on the feedstock type and ash fraction, but typically are orders of magnitude higher in fly ash than in bottom/total ash (Figure 6.4). Statistical analysis indicates there are significant differences in PCDD/Fs content between the fly ash and bottom/total ash for wood (median 121 and 2.3 ng TEQ/kg) and MSW (645 and 11 ng TEQ/kg; Table 6.4). Differences between agricultural residue fly and bottom/total ash, and waste wood fly and bottom/total ash, are not statistically significant (the probability that the differences arise by chance is >5%), but this probably reflects the limited amount of data for these materials as there is one and two orders of magnitude difference in the median PCDD/Fs contents of the agricultural residue fly and bottom/total ash (63 and 5.5 ng TEQ/kg, respectively) and the waste wood fly and bottom/total ash (3,133 and 22 ng TEQ/kg, respectively). Overall, there is no statistically significant difference ($p < 0.05$) between the PCDD/Fs contents of any of the fly ashes, nor is there a significant difference between the bottom/total ashes.

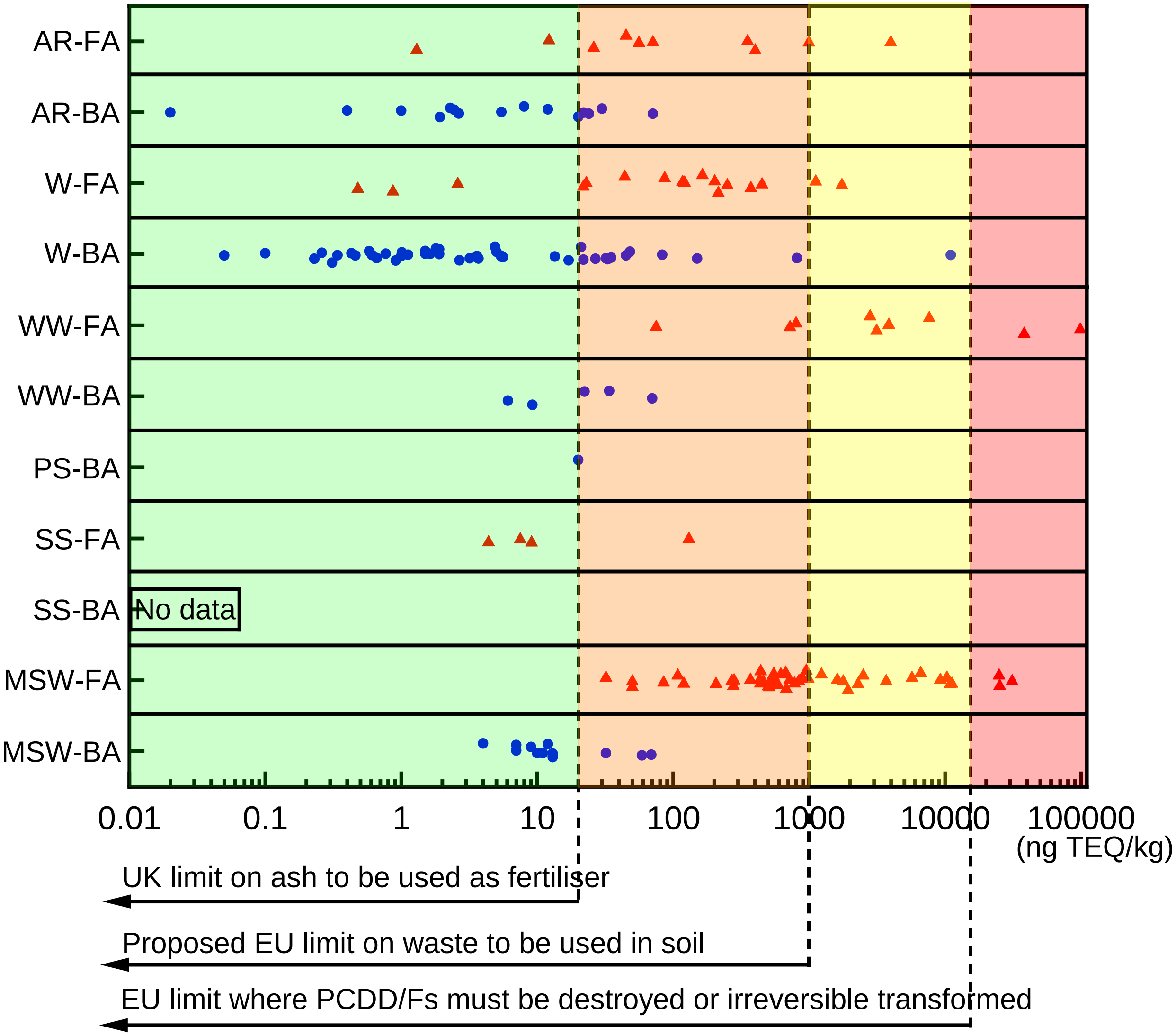

Figure 6.4. PCDD/Fs content distribution based on biomass ash categories and ash fractions.

6.3.4 PCBs content in biomass ash

Data reporting the PCBs contents of biomass ash is less abundant than that for other POPs (n≥5 only for agricultural residue, wood and MSW bottom/total ash, and MSW fly ash; Figure 6.5). The PCBs content of agricultural residue, wood and MSW bottom/total ash were similar (median PCBs contents were 0.18, 0.14 and 0.46 ng TEQ/kg, respectively), with no significant difference in PCBs content between any pair of these ashes (Table 6.4). However, there was a significant difference in the PCBs content between MSW fly ash (median value 22 ng TEQ/kg) and any of these three.

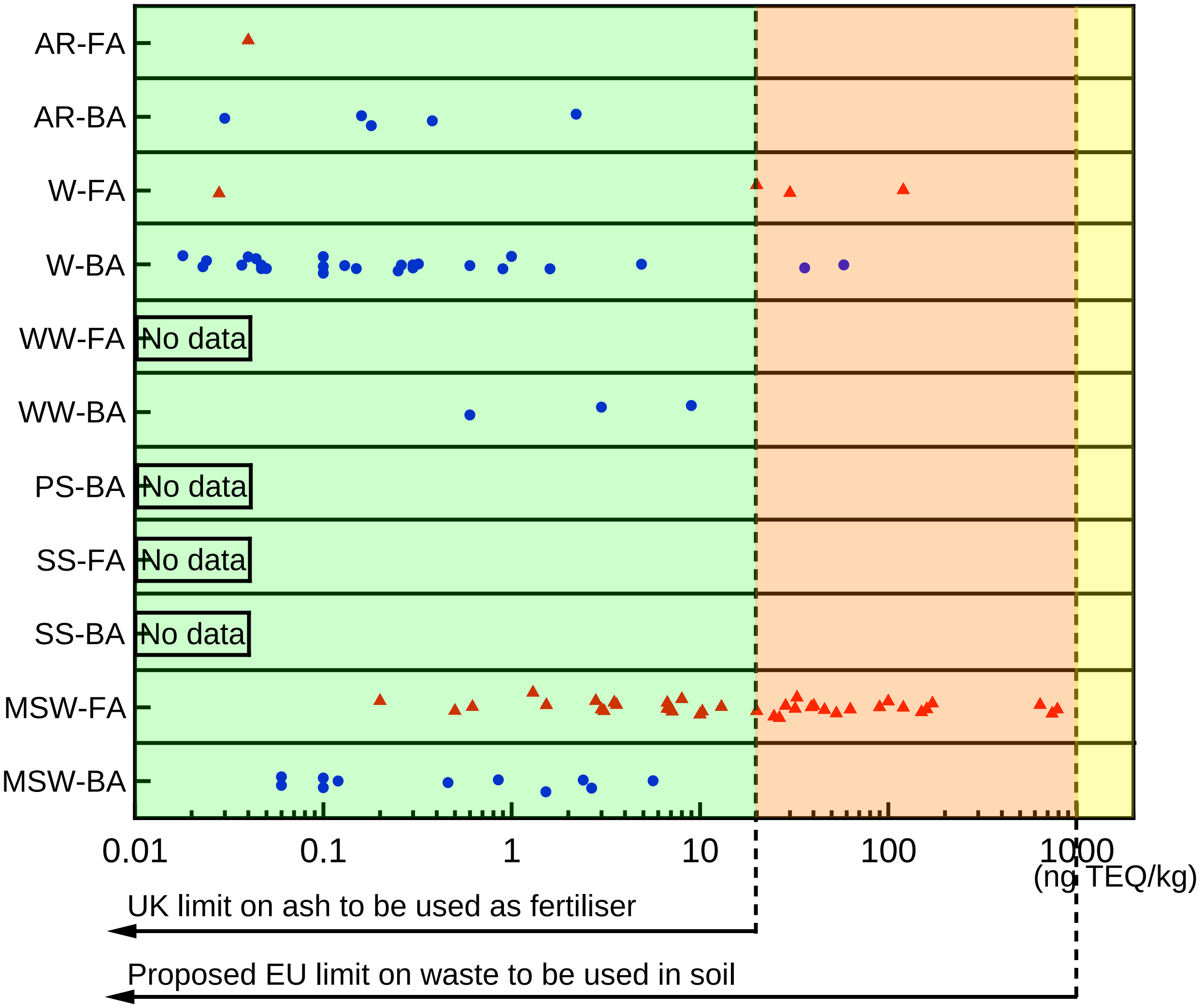

Figure 6.5. PCBs content distribution based on biomass ash categories and ash fractions.

6.3.5 Association analysis of PAHs, PCDD/Fs and PCBs in biomass ash

Pearson correlation analyses of the PAHs, PCBs and PCDD/Fs contents of biomass ash indicates a strong positive correlation between the PCB and PCDD/Fs contents (Table 6.5), that is significant at a 99.9% confidence level. This correlation suggests there is a linear relationship between the logarithm of the PCDD/Fs concentration and the logarithm of the PCBs concentration (Figure 6.6). No significant correlation was found between the PAHs and PCBs contents, or between the PAHs and PCDD/Fs contents.

Table 6.5. Pearson correlation test results of PAHs, PCBs and PCDD/Fs in biomass ash (shown as "Pearson correlation coefficient (p value)"; value with ** superscript indicates a significant correlation at 99.9% confidence level).

Pearson correlation coefficient	PAHs	PCDD/Fs	PCBs
PAHs	1	-0.150 (0.438)	-0.083 (0.737)
PCDD/Fs		1	**0.886 (< 0.001)** **
PCBs			1

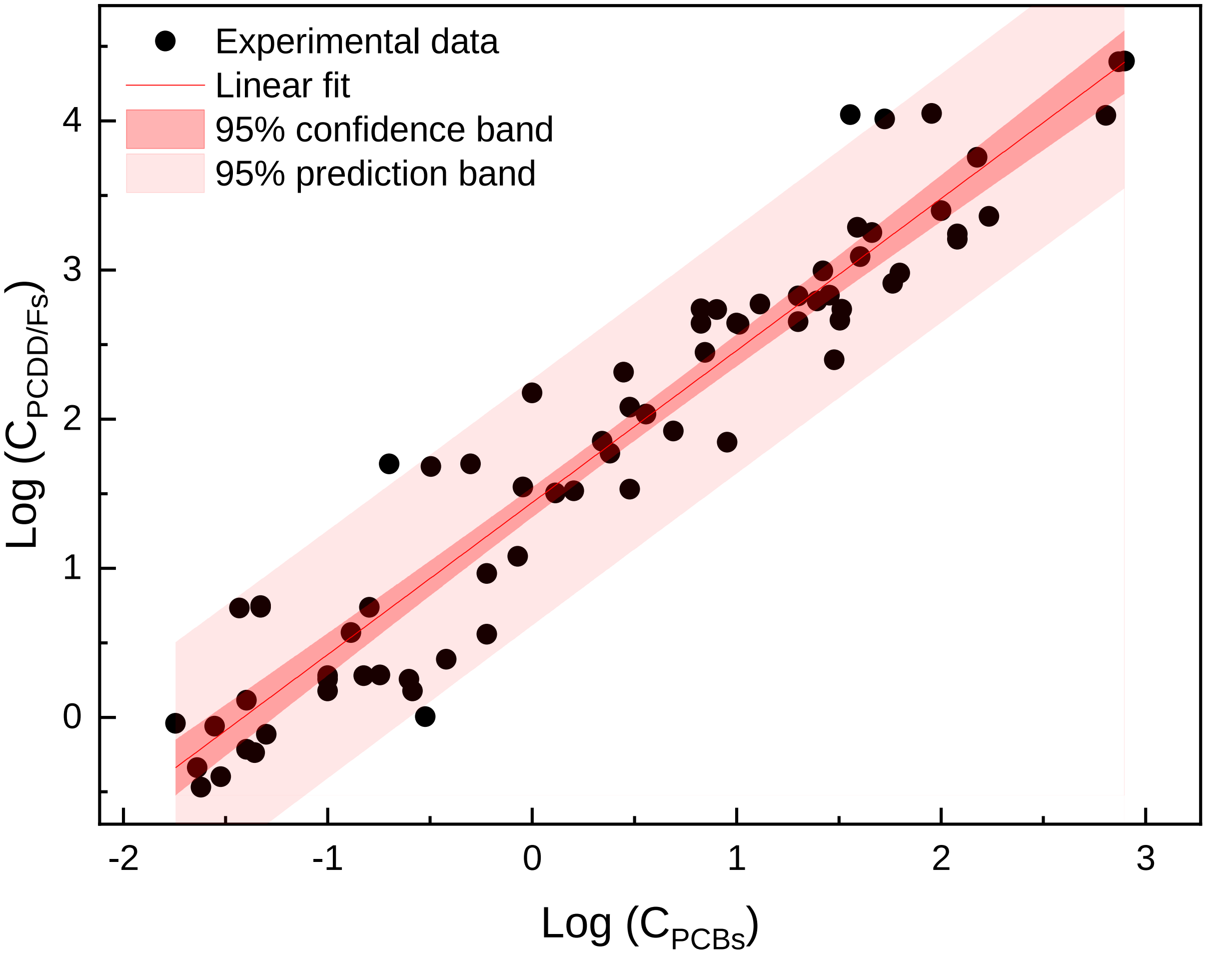

Figure 6.6. Linear fit results of Log (PCBs concentration) versus Log (PCDD/Fs concentration) (unit: ng TEQ/kg).

6.4 Discussion

6.4.1 Comparison of POPs in biomass ash with regulations

The UN Stockholm Convention on Persistent Organic Pollutants requires member nations to restrict the creation of unintentionally produced POPs (UNEP, 2001), but the maximum concentrations that are permitted in ash are dependent on the country in which it is produced and the intended end use or disposal method for the ash. For example, the EU has placed upper limits on PCDD/Fs and PCBs contents for disposal to landfill (above which the POPs must be destroyed or irreversible transformed before disposal (European Parliament, 2019)), and there is a recommendation that the EU sets lower limits on these POPs in ash that is to be put directly onto or mixed with soil (e.g. road sub-bases, engineering fills, etc. (BiPRO, 2005)). The UK has set very stringent limits on the PCDD/Fs and PCBs contents in its end of waste criteria for poultry litter incineration ash to be use as a fertilizer (EA-UK, 2012). The Stockholm Convention does not cover PAHs, but the EU and various nations are proposing limits on the PAHs content of ash to be mixed with soil or used as fertiliser (Huygens et al., 2019; Košnář et al., 2019; Swedish National Board of Forestry, 2002).

6.4.1.1 PAHs

The Czech Republic limits the PAHs content of ash to be used as soil organic amendment or fertiliser to 20 mg/kg (Košnář et al., 2019). In comparison, the proposed EU limit for ash to be used as fertiliser is 6 mg/kg (Huygens et al., 2019), and the proposed Swedish limit for wood ash to be recycled to forest soil is 2 mg/kg (Swedish National Board of Forestry, 2002). All the PAHs data collected for bottom/total ash are below the higher Czech limit, and most of the data for agricultural residue and wood bottom/total ashes are also below the Swedish limit (Figure 6.1). In contrast, more than half the PAHs data collected for MSW bottom/total ash falls between the Swedish and Czech limits. For fly ash, half (or more) of the PAHs data falls above the lower Swedish limit, and all the fly ashes for which data is available occasionally exceed the higher Czech limit.

6.4.1.2 PCDD/Fs

The EU limit on the PCDD/Fs content of ash to be disposed of to landfill is 15000 ng TEQ/kg (European Parliament, 2019), and proposed EU limit for ash to be used in contact with soil (e.g. road sub-bases, engineering fills, etc.) is 1000 ng TEQ/kg (BiPRO, 2005). The UK limit for poultry litter incineration ash to be use as a fertilizer is 20 ng TEQ/kg (EA-UK, 2012). All the PCDD/Fs data collected for bottom/total ash are below the limit for landfilling and, except for one point, all are below the EU limit for use in contact with soil (Figure 6.4). Further, for agricultural residue, wood and MSW bottom/total ash, >2/3rd of the data is below the UK use as a fertilizer. Generally, the fly ashes have a larger PCCD/Fs content than the bottom ashes, but most of fly ash data falls below the limit for disposal to landfill, although ~25% of the waste wood and ~5% of the MSW samples would require pre-treatment to destroy the PCCD/Fs content before landfill disposal. Interestingly, 90%, 88% and 68% of the agricultural residue, wood and MSW fly ash data are below the EU limit for use in contact with soil, although the physical characteristics of fly ash probably make it unsuitable for use as an engineering fill.

6.4.1.3 PCBs

The PCBs data in biomass ash are generally reported as their TEQ values, which are based on those dioxin-like PCB congeners. The two dioxins regulatory limits are reported as TEQ values so can be used for comparison with the PCB content (Figure 6.5): UK limit at 20 ng TEQ/kg for ash to be used as fertiliser (EA-UK, 2012), and proposed EU limit at 1000 ng TEQ/kg for ash to be used in contact with soil (BiPRO, 2005). All the PCBs data collected are below the EU limit for ash use in soil as road sub-bases, engineering fills, etc. (Figure 6.5), and moreover, all the PCBs data collected for bottom/total ash, except two points for wood, are below the UK limit on ash use as fertiliser. However, the available dataset for wood and MSW fly ashes shows that only 50% of these ashes are below the UK limit.

6.4.2 Correlation between PCDD/Fs and PCBs in biomass ash

There is a strong correlation in PCDD/Fs and PCBs content of the biomass ashes used in this study (Figure 6.6). This likely reflects a common mode of formation during combustion (Lemieux et al., 2001; Schoonenboom et al., 1995). However, the relationship between PCDD/Fs and PCBs is such that PCBs typically contribute just 4% (95% prediction bands = 0.5-25%) of the TEQ concentration compared to that produced by PCDD/Fs. PCB content is not routinely measured for ash management, which has resulted in a lack of published biomass ash PCBs data. However, the correlation presented in Figure 6.6 suggests ash risk assessment could be performed using the PCDD/Fs concentrations alone without significant error. Better still, the PCDD/Fs concentrations could be factored upwards to account for the likely PCBs content (the upper prediction band indicates that 1.25 would be a conservative factor). Such an approach would avoid the need to routinely measure PCBs concentrations for ash management.

6.4.3 Ash fractionation effect on POPs distribution

Volatile chemical elements, such as K, Cl, Zn, Pb, Cd and Hg, that enter biomass furnaces in the fuel tend to have higher concentrations in fly ash than bottom ash (Belevi and Moench, 2000; Yin et al., 2008; Zhang et al., 2008). This fractionation effect occurs because the volatile elements condense onto ash surfaces as the flue gases cool post-combustion, and fly ash has a far higher specific surface area than bottom ash. Also, the bottom ash is separated from the flue gases within the furnace while the temperature is still high, whereas the fly ash leaves the furnace suspended in the flue gases. These differences between bottom and fly ash can also result in fractionation of POPs. Unintentionally produced POPs in biomass ash either form during combustion or, in many cases, as the combustion gases cool as they leave the combustion zone from precursor molecules that survive transit through the furnace. For example, PCDD/Fs can form as the combustion gases cool by a homogeneous pathway at 400-800℃ and by two heterogeneous pathways at 200-400℃ (Altarawneh et al., 2009; Gullett et al., 1992; Huang and Buekens, 1995; Launhardt and Thoma, 2000; Stanmore, 2004). Fractionation leads to far higher PCDD/Fs concentrations in fly ash than bottom ash for the same fuel (Zhang et al., 2017). Significant fractionation of PCDD/Fs towards the fly ash is observed with wood ash and MSW ash, and of PCBs in MSW ash ($p < 0.05$; Table 6.4). There is also evidence for fractionation of PAHs in wood ash and PCDD/Fs in waste wood ash ($p < 0.1$; see Appendix D for raw Kruskal-Wallis test results used to make Table 6.4). Fractionation of PCDD/Fs is not clearly demonstrated for agricultural residue ash (pairwise comparison using the Mann-Whitney U test in Table 6.6 indicated a significant difference, $p < 0.01$, but the Dunn's post-hoc test with Bonferroni correction for multiple tests indicates a 43% probability that difference arises by chance). This ambiguity probably arises due to modest size of the agricultural residue ash datasets (10 fly ash and 15 bottom/total ash datapoints for PCCDD/Fs), and the overlap between the various datasets considered in the Dunn's post-hoc test, so further data for the PCDD/Fs contents of agricultural residue ashes is needed to clarify the situation.

Table 6.6. Pairwise comparison results of POPs contents in fly ash and bottom/total ash from the same biomass (based on the Mann-Whitney U test for two independent samples where no less than 5 samples are available for comparison).

POP type	Sample 1-Sample 2	Mann-Whitney U	Z	Asymp. Sig. (2-tailed)
PAHs	W-BA – W-FA	108	-2.57	**0.01**
PAHs	MSW-BA – MSW-FA	129	-0.22	0.83
PCDD/Fs	AR-BA – AR-FA	22	-2.94	**0.003**
PCDD/Fs	W-BA – W-FA	145	-3.82	**<0.001**
PCDD/Fs	WW-BA – WW-FA	0	-3.00	**0.003**
PCDD/Fs	MSW-BA – MSW-FA	7	-5.41	**<0.001**
PCBs	MSW-BA – MSW-FA	28	-4.34	**<0.001**

Neither the Dunn's test nor the Mann-Whitney test indicated any significant difference in PAHs content between the fly ash and bottom/total ash from MSW incineration (Tables 4 and 6). This may indicate that regional differences in the composition of MSW, and that the type of incinerator and air-pollution control measured used in different countries have a bigger impact on the PAHs content than the fractionation effect, as some studies indicated the higher PAHs in fly ash than bottom ash (Peng et al., 2016; Zhou et al., 2005) whereas another does not (Shi et al., 2009).

In summary, for the four fuels for which there is sufficient data to compare the PCDD/Fs contents in the fly ash and bottom/total ash, three show a significant fractionation effect (wood, waste wood and MSW ash) while further agriculture residue ash data is required to determine the significance of the difference. For the two fuels for which there is sufficient data, one exhibits a fractionation in the PAHs content towards the fly ash (wood ash) and one does not (MSW ash). The only fuel for which there is sufficient data for comparison of the PCB contents (MSW) exhibits a fractionation towards the fly ash. However, it is noted that the PCBs content of biomass ash is strongly correlated with the PCDD/Fs content, so fractionation of PCBs towards the fly ash should be anticipated for other fuels.

6.4.4 Implications for biomass ash management

The ash size fraction (fly ash or bottom/total ash) is the biggest determinant of the POPs contents of biomass ash, and thus this should be the primary consideration for ash management. Furthermore, waste fuels tend to produce ash with higher PCDD/Fs contents than non-waste fuels (particularly waste wood fly ash and MSW fly ash). As waste biomass fuels also produce ash with contaminant trace metal concentrations that often exceed regulatory limits for reuse as a forest fertiliser, whereas ash from virgin biomass is usually below those limits (Zhai et al., 2021a; Zhai et al., 2021b), different ash management strategies may be required for virgin biomass bottom ash, virgin biomass fly ash, waste biomass bottom ash, and waste biomass fly ash.

In the dataset presented, >90% of virgin biomass bottom ash contains PAHs and PCBs contents that are respectively below proposed EU limit (Huygens et al., 2019) and the UK limit for ash to be used as fertiliser (Figures. 6.1 and 6.5: the UK limit for PCDD/Fs is expressed as a toxic equivalency (EA-UK, 2012) so it can also be used as the comparator for PCBs). In comparison, ~75% of virgin biomass bottom ash has PCDD/Fs concentrations that are below the UK limit for ash to be used as fertiliser (Figure 6.4). Interestingly, all the samples that were compliant with UK limit on PCDD/Fs in ash to be used as fertiliser, were still below that limit when the PCDD/Fs and PCBs content were summed (PCDD/Fs content was measured in >95% of the samples where PCBs content was measured). PAHs are rarely reported for the same virgin biomass bottom ash samples as the PCDD/Fs and PCBs contents, so while the exact proportion is not known, it is nonetheless clear that the majority of virgin biomass bottom ash is compliant with the limits on POPs for use as fertiliser. Thus, agricultural residue ashes, which contain abundant potassium, modest amounts of phosphate, and typically very low contaminant metal concentrations (Zhai et al., 2021b), could potentially be used directly as a fertiliser additive. While wood ashes, which are rich in CaO, contain modest amounts of potassium and phosphate, but typically low contaminant metal concentrations can continue to be used as a forestry fertiliser (Dahl et al., 2010; Swedish National Board of Forestry, 2002). Further, fuel quality (which affects combustion temperature), furnace technology (particularly the bottom ash cooling regime), and ash management practices (such as combining the ash fractions), are major determinants of whether ash complies with the regulatory limits on POPs (Chagger et al., 1998; Khan et al., 2009; Peng et al., 2016). Thus, better furnace technology and/or management could increase the proportion of virgin biomass bottom ash that is compliant with regulatory limits for POPs.

It has been suggested above that routine determination of ash PCBs content is probably unnecessary as, for ash management purposes, the PCBs content can be estimated from the PCDD/Fs content. Therefore, it is interesting to note that factoring the PCDD/Fs content upwards by the conservative factor of 1.25 as a nominal allowance for PCBs resulted just one sample of virgin biomass bottom ash where the sum of the measured PCDD/Fs and PCBs contents was below the UK limit for fertiliser to appear to marginally exceed that limit.

Like virgin biomass bottom ash, waste biomass bottom ash has low PAHs and PCBs contents (~90% has a PAHs content below proposed EU limit for fertiliser use, and all has a PCBs below the UK limit for ash for fertiliser use). Further, about two-thirds of the waste biomass bottom ash samples have PCDD/Fs concentrations that are below the UK limit for ash to be used as fertiliser. So, like virgin biomass bottom ash, the PCDD/Fs content is the limiting POP for waste biomass bottom ash reuse, and while about a third of waste biomass bottom ash exceeds the limit for fertiliser use, better furnace technology/management could improve that situation. Thus, beneficial reuse of waste biomass bottom ash is likely in future to be determined by its contaminant metals content. Currently, MSW bottom ash, which represents ~95% of waste biomass bottom ash currently produced (Zhai et al., 2021b), is routinely used as a construction aggregate for prescribed applications (e.g., in road bases), and this work supports its continued use for such applications.

In the dataset presented, only about half of virgin biomass fly ash has a PAHs content below proposed EU limit on ash to be used as fertiliser, and only ~40% has a PCBs below the UK limit for ash to be used as fertiliser (although the dataset for PCBs is small). However, all the virgin biomass fly ash samples have PCBs contents below proposed EU limit on waste to be used in soil (BiPRO, 2005). Similarly, only ~20% of the virgin biomass fly ash samples have PCDD/Fs contents below UK limit for ash to be used as fertiliser, but ~90% have PCDD/Fs contents below proposed EU limit on waste to be used in soil. There is less pressure to find beneficial uses for fly ash, as it is usually only a small proportion of the ash produced (typically 10~30% (Obernberger and Supancic, 2009; Wiles, 1996)). However, its POP concentration will restrict its use for fertiliser applications, while its size and other engineering properties will limit its use as a construction aggregate or bulk fill (typical uses of waste in soil). Thus, unless the POPs content of virgin biomass fly ash can be limited by better combustion technology, it is likely that this ash will require landfill disposal.

Whilst ~75% of waste biomass fly ash has a PAHs content below proposed EU limit on ash to be used as fertiliser (although no data is available for waste wood fly ash), only about half has a PCBs below the UK limit for ash to be used as fertiliser (data is only available for MSW fly ash), although all has a PCBs content below proposed EU limit on waste to be used in soil (BiPRO, 2005). However, the challenging POPs in waste biomass fly ash are PCDD/Fs. Only ~5% of the waste biomass fly ash samples have PCDD/Fs contents below UK limit for ash to be used as fertiliser, although cumulatively nearly two-thirds have PCDD/Fs contents below proposed EU limit on waste to be used in soil. Problematically, >5% of waste biomass fly ash samples have PCDD/Fs contents that exceed the limit stipulated in United Nations held the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001), and the PCDD/Fs content must be destroyed or irreversibly transformed before disposal according to EU waste legislation (European Parliament, 2019).

6.5 Conclusions

Biomass combustion ash can be sub-divided into four categories when considering the impact of their POPs content on potential reuse or disposal options:

- Virgin biomass bottom ash usually has a low POPs content, and the most is compliant with regulatory limits for use as fertiliser.
- Waste biomass bottom ash typically has a relatively low POPs content, and its reuse is usually limited by other factors (such as slightly elevated contaminant trace metals). However, data on the POPs content supports its continued use as a construction aggregate for prescribed applications.
- Virgin biomass fly ash usually has a POPs content that is incompatible with its use as fertiliser, but is compatible with use in soil for prescribed applications although the physical characteristics of fly ash make such use difficult.
- Waste biomass fly ash can have a wide range of POPs contents, so while much is below regulatory limits for use in soil for prescribed applications, >5% has PCDD/Fs contents that must be destroyed or irreversibly transformed before disposal.

For biomass ash there is still a paucity of published POPs data, particularly the PCBs content. The strong correlation in PCDD/Fs and PCBs content of the biomass ashes, however, can be used to conservatively estimate the PCBs content of biomass ash for routine ash management. It is also clear that there is a wide variation in POPs composition within every class of biomass ash studied. Therefore, it is clear that better furnace technology that ensures optimum combustion temperature such that POPs contents are minimised, is important to maximise the reuse potential and minimize the amount of waste biomass fly ash requiring further treatment before disposal. Finally, POPs data cannot be used in isolation to consign ash reuse, and consideration of other physical properties and trace metal content must be considered to produce robust assessments of biomass ash reuse potential.

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Chapter 7: Summary and recommendations for future work

7.1 Summary

Biomass ash is the ubiquitous by-product of solid biomass combustion (the primary bioenergy utilisation pattern), and thereof, resource recovery, beneficial reuse or safe disposal of biomass ash must be explored to promote a circular material economy. This project aims to address the following four research questions that can assist with biomass ash management:

1. Question 1: How much biomass ash is produced globally, and what is the distribution pattern of biomass ash across the globe as affected by biomass types?
2. Question 2: How should biomass ash be scientifically categorised?
3. Question 3: How will the biomass feedstock influence the ash characteristics and what are the resulting implications for biomass ash management?
4. Question 4: What is the level of persistent organic pollutants (POPs) in biomass ash and to what extent will POPs affect ash management?

Delivering research question 1: Chapter 3 of this thesis presents an up-to-date estimate of global biomass ash production and their distribution. Two determinant factors are considered: varying ash contents of different biomass types and the available biomass amounts that can be used for bioenergy production for five continents (Africa, Americas, Asia, Europe and Oceania). Around 170 Mt biomass ash is being generated per year with about 2-3 Gt/yr of biomass used globally for energy production. In future, the ash amounts may increase to about 1000 Mt/yr if all currently available biomass is exploited. Municipal solid waste ash and wood ash are now the two major ash types. However, agriculture residue has great potential to be utilised in future bioenergy supply and more agriculture residue ash is projected to be generated. Similarly there is scope for increased recovery of energy from MSW, and thus, future biomass ash production is likely to be dominated by municipal solid waste and agricultural residue ash. Additionally, sewage sludge ash amount is also expected to increase by more than 4 times than current level so its proper treatment should be explored.

Delivering research question 2: A good understanding of ash physiochemical properties is the basis for biomass ash management, along with a viable ash classification system to support it. It has been shown in Chapter 4 that virgin biomass ash characteristics depend on the taxonomy of the feedstock, and a ternary diagram using K_2O, SiO_2 and CaO (three most abundant elemental compositions for most biomass ashes) as three end members is used for ash classification. Ash derived from virgin biomass has been classified as hardwood ash, softwood ash, eudicot straw ash and grass straw ash. Ash chemical composition (nominal oxides) shows that CaO, K_2O and P_2O_5 are abundant (> 5%) in hardwood ash, whereas CaO, SiO_2 and K_2O are abundant in softwood ash. As for eudicot straw ash, K_2O, CaO, P_2O_5 and Cl_2O are four abundant components and SiO_2, K_2O and CaO are abundant in grass straw ash. Generally, Herbaceous feedstocks produce significantly more ash (eudicot straw and grass straw; typically 5–9%) than woody feedstocks (hardwood and softwood; typically 1–2%) but, possibly as a result, the ashes generally contain lower concentrations of contaminant trace metals. SO_3 and Cl_2O compositions are important for high temperature corrosion effects in furnaces and environmental emission control. Significantly higher Cl_2O content in eudicot and grass straw ash than softwood and hardwood ash is found, but SO_3 content is not significantly different between ash categories. It is also shown in this chapter that the initial deformation temperature of ash from herbaceous feedstocks (typically 860-910 ℃) is significantly lower than that of woody feedstocks (typically 1196-1363 ℃). This indicates a higher potential for herbaceous biomass to form slag and foul the biomass furnace.

Delivering research question 3: Detailed characterisation work has been conducted on 11 biomass ash samples and the implications for ash management are discussed in Chapter 5. It is shown that biomass type and ash generation procedure have significant influence on ash major chemical composition and minerology. Most of the 11 ash samples are situated in reasonable locations on the K_2O-SiO_2-CaO ternary diagram, and are comparable with previously published data. The 11 biomass ash samples are all alkaline (liming effects) in nature and their leachate pH from water leaching tests at L/S of 100 falls within the range ~9-12. Biomass selection can influence ash amounts to be generated, for example, *Cedrus* spp. (ash content of ~5%) as the feedstock will produce about 5 times as much ash as *Alnus* spp./*Crataegus* spp./*Fraxinus* spp./*Salix* spp. (~1%). Ash recirculation to soil as fertiliser materials or soil amendment should not only take total contents (bulk composition) of trace toxic elements into consideration, but also consider trace toxic element leaching behaviour as some trace toxic elements (e.g. Cr and Mo) may be present in easily solubilised forms. Potassium in most ash samples is extractable by water leaching and therefore potassium recovery from potassium rich biomass ash (e.g. *Cedrus* spp. ash and *Fraxinus* spp. ash) is attractive and viable. Referring to EU waste acceptance criteria, industrial wood ash creates more challenges for landfill disposal than laboratory wood ash as the former tend to contain more trace toxic elements. Therefore, controlling trace toxic elements entrainment (especially for Cr and Mo from this research) during biomass processing, ash production and its initial storage may be helpful in reducing ash management costs.

Delivering research question 4: Persistent organic pollutants (POPs) in biomass ash can also influence ash management options but has yet received systematic studies (e.g. POPs difference with ash type and ash fraction; and implications POPs have for ash management). Chapter 6 focuses on the study of POPs (PAHs, PCDD/Fs and PCBs) content of different ash types and size fractions and discusses POPs influence on ash management. It is found that ash POPs content generally varies with biomass type and ash size fraction. The available data indicates POPs are more concentrated in fly ash than associated bottom/total ash for all biomass ash types. A strong positive correlation between PCBs and PCDD/Fs in ash is identified, which can offset the limited PCBs data collected and allow PCBs + PCCD/Fs content to be estimated conservatively as 1.25 x PCCD/Fs content to guide ash management. By comparing the available POPs dataset with current regulatory limits and guidelines, biomass combustion ash can be sub-divided into four categories: (1) virgin biomass (e.g. agriculture residues and woods) bottom/total ash usually has a low POPs content, and the most is compliant with regulatory limits for use as fertiliser; (2) waste biomass (e.g. sewage sludge and municipal solid waste) bottom/total ash usually contains low POPs content and this supports its continued use as a construction aggregate for prescribed applications; (3) virgin biomass fly ash usually has a POPs content that constrain its use as fertiliser but supports its controlled use in contact with soil for prescribed applications; and (4) waste biomass fly ash contains POPs in a wide concentration range and the most challenging POPs restricting ash use are PCDD/Fs; and moreover, > 5% of waste biomass fly ash samples have problematically high PCDD/Fs contents that must be destroyed or irreversibly transformed before ash disposal.

7.2 Recommendations

The project has addressed some research gaps (from Chapter 3 to Chapter 6) for a better understanding and management of biomass ash, but due to time constrains, some other interesting respects on biomass ash management are out of scope of this project. Herein, some research points are recommended for future biomass ash studies:

1. Element speciation identification. While ash minerology characterised by XRD indicates the form of major elements in ash, some trace toxic elements in some cases needs to be clarified, especially when evaluating their environmental risks and bioavailability. For example, hazardous property of seven sewage sludge ash samples in UK is ultimately determined by the Zn speciation (ZnO, $Zn_3(PO_4)_2$ or Zn_2SiO_4) (Donatello et al., 2010). Also, the speciation of leachable elements in water leachate can be further explored, so as to get more details on their environmental behaviours to guide ash management. PHREEQC can be used to conduct the theoretical calculation of the relative content of element species with the basic information of the water leachate (pH, element concentration, temperature, etc.) (Bogush et al., 2018).
2. Carbon capture and storage potential of biomass ash. Most biomass ashes are alkaline solid waste and contain abundant alkaline-earth and alkaline oxides/carbonates/oxyhydroxides that can capture and store atmospheric CO_2 by formation of carbonates and/or bicarbonates by exposure to air. Meanwhile, CO_2 sequestration also occurs with biomass ash reutilisation as fertiliser (López et al., 2018). More detailed studies on capacity of CO_2 capture and storage by biomass ash will also support the life cycle assessment of bioenergy utilisation. However, ash mineral phase compositions will change after carbon capture and storage and this may influence ash value recovery and leaching behaviour of trace toxic elements, which should be studied as well.
3. Mild technology for value recovery from biomass ash. Current value recovery from waste biomass ash is usually based on traditional methods, e.g., aggressive wet chemical leaching and high energy-demand thermal treatment (Donatello and Cheeseman, 2013; Fang et al., 2018; Kuboňová et al., 2013; Zucha et al., 2020), which may leave waste solutions and residues that are probably more problematic than the original ash). Therefore, there are major opportunities to recover valuable elements from biomass ash for return to the circular economy, but work is needed to make recovery economically beneficial and eliminate secondary wastes from the recovery processes. Mild methods, such as the bioleaching with acclimated microorganism and development of environmentally friendly extractant, may be explored for value extraction from biomass ash.

4. Biomass ash comprehensive reutilisation. Except for the ideal recirculation of biomass ash to soil as ameliorator, value recovery from biomass ash is attractive before end disposal, such as K and P recovery from straw ash and sewage sludge ash, respectively. However, most research to date focus on specific component recovery, which could produce large amounts of waste brines or problematic residues to be disposed of. Biomass ash reuse as partial raw construction material may cause the losing of valuable components in ash, and therefore, value recovery by mild treatment followed by the residue reuse in construction will be favourable. By all possible means, recovery of multiple valuable components in a sequence of compatible recovery steps should be explored, which would maximise economic return while minimise secondary wastes, but more research is required.
5. Long-term durability of biomass ash participated construction products. Various biomass ashes have been tried in construction materials production and the engineering properties of as-obtained products show ash's possibility in this application. However, the long-term durability of these products, as well as their environmental impacts, should be traced and studied.

7.3 References

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Appendix A: Appendices for Chapter 2

Raw data and associated references can be found and downloaded online at https://doi.org/10.1016/j.rser.2021.111555.

Appendix B: Appendices for Chapter 4

B.1 Raw data collated

Table AB.1. Chemical composition (wt. %) dataset of four different ash categories (black font for hardwood ash; red font for softwood ash; blue font for eudicot straw ash; green font for grass straw ash).

ID-number	CaO	MgO	MnO	K_2O	P_2O_5	SO_3	Cl_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2
#2142	26.1	9.2		23.5				20	7	1.4	1.8	
#77	45	10.8		11.4	17	2.2		2.8	1.4	0.7	1.3	0.1
#91	65	8.3		9.9	7.5	2.2		2.3	0.9	0.5	0.8	0.1
#92	40.02	0.13	0.1	4.64					0.58	0.22	0.47	
#803	10.9	4.15		22.4	1.33	2.69		20.97	2.99	2.94	1.4	0.27
#2894	15.76	11.96		14.46				2.5	11.14	1.25	0.65	
#288	29.24	0.12	0.1	10.72					0.51	0.31	0.4	
#700	47.28	11.58		24.37	14.81			9.22	3.26		0.1	
#845	44.4	4.32		20.08	0.15	3.95		0.88	0.31	0.57	0.23	0.16
#806	49.92	18.4		9.64	1.34	2.04		5.9	0.84	1.4	0.13	0.3
#1998	38.5	3.6		15.2	9.3			22.7	0.6	0.4	0.8	0.1
#719	45.62	1.16		13.2	10.04	1.15		8.08	1.39	0.84	2.47	0.06
#947	32	3		17	9.3	1.5	0.14	15	1.6	0.92	2.6	
#1305	37.2	4.8		12.1	10.2	3.2	0.92	2.3	0.35	0.33	2.8	0.03
#1306	25.1	4.1		10.1	7.3	2.6	0.49	27.4	2.6	1.4	2.5	0.15
#1307	37.5	5.1		12.8	10.8	3.6	0.86	2	0.3	0.2	2.9	0.02
#851	34.86	2.46		12.2	10.36	1.7		16.76	3.01	0.85	3.05	0.07
#852	36.51	1.54		19.9	12.9	1.94		2.83	0.12	0.42	1.97	0.06
#867	40.48	3.04		13.9	8.16	1.7		1.11	0.09	0.21	0.77	0
#868	32	7.67		22.1	11.68	3.09		1.89	0.16	0.3	0.65	0.04
#869	41.2	2.47		15	7.4	1.83		2.35	1.41	0.73	0.94	0.05
#870	44.68	2.16		15.3	7.18	2.33		1.82	1.48	0.49	0.86	0.05
#3159	30.78	5.14		26.5	11.46	3		0.43	0.3	0.19	0.24	0.02
#720	34.18	2.98		18.4	7.1	2.92		2.05	1.97	0.35	2.67	0.03
#1267	42	11.8		12.3				8.3	2.1	1.9	0.24	0.12
#3160	41.84	11.81		12.29	5.25	1.95		8.34	2	1.84	0.24	0.12
#765	37.08	5.86		17	1.86	11.2	0.01	12.26	2.83	4.24	3.16	0.08
#3154	33.58	5.14		12.05	4.81	1.62		23.53	5.1	2.14	0.19	0.06
#122	32.9	1.55	1.2	6.75					2.52	2	0.94	
#123	32	1.02	0.8	6.57					1.76	2.07	0.74	
#151	25.5	6.5		6				39	14	3	1.3	
#1786	29.05	4.73		13.06	5.27			46.06	10.91	4.48	0.62	0.17
#1996	12.3	0.6		1	0.1						0.2	
#1808	49.27	13.53		10.03	2.82	13.46		6.15	0.92	1.53	1.28	1.2
#163	42.2	2.4		7.3	2.84	1.29	0.21	8.5	1.03	0.78	0.23	
#166	31.9	3.55		10.3	3.39	1.46	0.16	21.9	0.56	0.83	0.24	
#167	32	3.94		13.5	4.22	0.97	0.06	18.2	0.42	0.74	0.28	
#177	39.6	5		6.8	2.2			25.3	4	2.8	0.8	
#2134	37.08	5.86		17	1.86	11.2		12.26	2.83	4.24	3.16	
#3155	15.39	3.98		8.31	3.21	1.62		38.51	4.72	3.72	0.31	0.5

Continued from Table AB.1

ID-number	CaO	MgO	MnO	K_2O	P_2O_5	SO_3	Cl_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2
#3156	11.89	1.82		4.1	1.76	1.35		27.81	5.67	2	1.44	0.35
#2801	48.05	7.39		16.06	4.69			14.01	4.68	1.71	0.58	0.19
#804	11.9	4.59		7	2.87	2.93		15.17	3.96	6.58	23.5	0.27
#880	51.6	5.5		4.1				16	6.3	5		
#2895	48.05	7.39		16.06	4.69			14.01	4.68	1.71	0.58	0.19
#2770	8.75	3.35		4.94	1.44	0.05		57.2	13.4	5.94	1.38	1.16
#2912	21.09	5.69	0.16		6.24				9.38	7.49		
#299	32	4.4		8.5	4.8	1.7		36.3	4.7	1.5	2.3	0.3
#1995	28.6	6.7		23.9	11.6			2.77	0.7	0.4	0.9	0.1
#2929	23	4.9		7.5	0.9	1.8		37.2	8.7	6.2	6.3	0.3
#847	9.5	2.52		7.86	2.4	11.36		38.89	14.74	9.3	0.53	0.36
#2030	39.95	4.84		9.81	2.06	1.86		23.7	4.1	1.65	2.25	0.36
#408	8.88	2.58		13.1	8.92	4.05	3	1.4	0.06	0.12	2.6	
#409	24.9	3.14		25.4	7.86	14	7.3	4.1	0.28	0.75	1.37	
#410	14.5	16		24.1	40.9			1.3	0.2	0.6	0.1	
#538	22.9	2.5		21.6	5.1	12.7	11.27	7.8	1.57	0.78	6.8	
#539	39.97	5.41		16.86	3.76	2.65		8.49	0.09	0.56	2.7	0.1
#540	46.63	4.51		7.95	5.93	3.37		12.49	2.8	4.43	0.96	0.68
#541	66	1.9		13.6	3.2	9.3		0.9	0.2	0.2	2.6	0.01
#542	50.3	2.5		21	5.9	10.9		1.3	0.4	0.2	3.8	0.02
#543	33.1	1.4		16.4	4.8	5.4		30.5	3.8	2.2	0.8	0.23
#544	26.5	1		30.7	3	6.6	6.50	0.3	0.1	0.1	5.6	0.01
#3162	29.38	0.63		16.86	8.94	10.74		3.21	0.47	0.94	0.35	0.07
#419	6.6	4.27		27.5	18.5	3.22	1.53	3.1	0.11	0.18	0.04	
#420	10.6	5.25		33.5	13.1	3.77	1.73	8.1	0.29	0.28	0.08	
#553	14.9	1.85		43.7	2.7	2.55	7.9	4.5	0.12	1.02	0.03	
#554	8.82	1.17		19.5	3.36	1.81	4.83	4.4	0.1	0.05	0.1	
#555	13.1	1.82		13.9	0.89	0.81	4.23	6.4	0.28	0.12	0.32	
#556	13.2	2.76		40.6	0.66	1.12	8.08	3.9	0.34	0.24	0.35	
#624	14	2.21		44.2	8.79	3.59	5.86	6.2	0.45	0.36	0.2	
#625	22	2.23		38	5.27	6.3	5.77	13.1	1.11	0.41	0.35	
#626	18.2	2.5		36.7	5.13	2.8	4.17	2.1	0.21	0.17	0.19	
#627	15.6	1.96		41.1	5	2.87	3.30	2.3	0.24	0.19	0.2	
#628	22.6	2.65		35.6	7.01	3.88	3.47	4.5	0.32	0.24	0.14	
#629	17	3.42		40.6	6.99	4.2	6.32	4.3	0.3	0.25	0.24	
#630	11.2	2.87		33.97	10.46	4.64		7.96		51	3.64	
#1902	27.7	3.1		28.4	8.2	1.9	5.39	3.3	0.3	0.3	0.7	
#1993	27.7	3.1		28.4	7.6			3.3	0.3	0.3	0.7	
#432	5.1	0.77		5.6	1.22	0.91	2.76	59.4	0.38	0.22	0.26	
#433	8.3	2.22		26.1	2.73	4.43	14.58	33.8	0.28	0.28	4.11	
#434	5.6	1.81		14.54	1.88	2.57		67.93	0.09	0.16	0.38	0.1
#435	11.6	1.79		14.5	4.06	2.9		50.92	0.09	0.4	1.01	0.1
#436	8	1.1		33	4.2	3.1	16.17	35.4	0.1	0.1	1.5	0.01
#437	8	1.6		21.6	2.6	2.4		59.3	0.2	2	2.3	0.02
#438	3.22	4.84		8.01	11.56	1.8		44.7		2.6	5.25	
#439	14.7	2		24.4	4.1	4.8		47.1	0.2	0.1	1.5	0.01

Continued from Table AB.1

ID-number	CaO	MgO	MnO	K_2O	P_2O_5	SO_3	Cl_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2
#440	5.2	1.6		8.8	3.4	2		69.8	2.1	6.3	0.3	0.17
#441	8.1	1.6		26	5	2.8	3.92	47.6	0.3	0.2	1	0.02
#946	18	2.1		41	4.9	4.3	5.52	22	0.64	0.67	1.9	
#3169	4.48	2.16		19.27	2.52	1.42		62.04	0.19	0.17	0.44	0.02
#517	0.46	2.7		10.28	0.66	2.2		71.7		7.1	0.33	
#518	3.9	3.08		10.3	10	11.08		50.7		3.14	0.53	
#519	0.56	4.78		8.37	2.06	7.2		63.3		4.72	0.47	
#704	8.66	6.11		20.67	8.68			54.04	1.99		0.15	
#401	4	0.59		18.5	4.7	1.3	13.97	61.7	0.72	0.17	0.23	
#533	3.5	3		38.7	9.2	1.8	4.54	31.2	0.38	0.56	0.73	
#534	9.9	4.25		21.8	2.18	2.03	5.36	36.4	0.51	0.59	0.08	
#516	1.05	3.32		9.59	2.98	3.48		55.3		2.4	0.73	
#444	1.9	1.8		13.5	1.4	0.7		73	1.4	0.6	0.4	
#448	0.72	0.83		11.9	8.87	1.51		75.2		0.58	0.28	
#449	0.88	2		14.5	0.9	1.83		78.6		0.44	0.44	
#450	0.7	2		13	0.8	1.69		78.3		0.36	0.43	
#451	1.1	2.5		15.85	1.1	1		75		0.47	0.54	
#702	1.97	2.05		5.72	1.67			80.68	1.49	0.88	0.74	
#994	3.01	1.75		12.3	1.41	1.24		74.67	1.04	0.85	0.96	0.09
#2001				16.6				72.2	0.1		0.4	
#2802	1.74	1.79		13.02	0.66			82.13	0.1	0.11	0.15	0.01
#2896	1.74	1.79		13.02	0.66			82.13	0.1	0.11	0.15	0.01
#2002				2				82.2	4.4		0.6	
#737	2.09	1.32		2.21	0.63	0.36		91.6	0.82	0.5	0.19	0.02
#736	2.12	0.86		2.03	0.39	0.32		93.13	0.98	0.46	0.18	0.05
#735	2.36	2.17		7.45	1.68	0.86		81.3	0.59	0.74	1.57	0.07
#766	1.61	1.89		11.3	2.65	0.84		74.31	1.4	0.73	1.85	0.02
#547	9.7	1.87		28.9	4.85	4.19	8.76	23.2	0.23	0.22	0.12	
#548	2.96	1		2.1	0.64	0.55	0.16	67.9	0.26	0.18	0.04	
#558	9.9	3.36		33.6	7.8	2.93	6.25	30.1	0.86	0.41	0.22	
#559	26.5	3.42		11.4	0.89	1.23	2.71	44.3	3.42	2.03	0.51	
#560	11.8	3.69		18.2	5.2	3.64	2.15	43	1.83	1.5	0.17	
#561	8.8	3.6		24	6.5	3.4	2.33	45.1	1.19	0.71	0.45	
#562	8.1	4		28.6	6.2	3.6	2.70	46	0.53	0.39	0.48	
#563	23.8	4.43		20.4	4.19	1.04	4.91	16.2	0.52	0.34	0.12	
#564	8	2.87		13.5	4.59	4.29	2.05	52.7	3.51	1.82	0.32	
#3166	8.95	2.65		8.19	2.98	3		57.76	0.66	0.53	1.31	0.05
#424	4.1	1.96		11.2	6.42	1.12	2.4	35.3	0.35	0.25	0.08	
#425	2.7	1.56		12.2	5.68	1.15	3.05	38.6	0.26	0.19	0.06	
#426	4.1	1.04		17.4	2.16	1.56	4.71	61.5	0.57	0.28	0.1	
#427	4.3	2.65		15.1	7.86	1.49	3.52	45.5	0.33	0.22	0.15	
#454	4.03	0.75		5.9	2.75	0.83	0.21	62.5	0.48	0.29	0.21	
#455	8.7	2.27		26.2	2.18	4.56	7.81	39.2	0.2	0.19	0.16	
#456	5.1	2.22		23.9	2.05	1.47	8.86	59.3	0.16	0.11	0.11	
#457	4.4	0.81		20.1	2.74	1.55	5.07	66	0.17	0.09	0.14	
#459	12.03	3.7		24.1	3.02	6.02		42.79	0.09	0.39	1.54	0.1

Continued from Table AB.1

ID-number	CaO	MgO	MnO	K_2O	P_2O_5	SO_3	Cl_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2
#460	9.18	1.92		12.3	3.07	2.55		69.41	0.09	0.4	0.3	0.1
#462	4	1.2		16.3	2	2.5		72.5	0.2	0.1	0.1	0.02
#463	7.6	1.3		22	2.9	3.5		61.1	0.3	0.2	0.3	0.01
#464	3.7	1.4		16.8	3.6	2.1		71.1	0.5	0.2	0.2	0.02
#465	5.9	1.3		16.7	1.9	2.4		70.8	0.1	0.1	0.2	0.01
#466	17	2.6		22	7.4	6.6		42.6	0.4	0.2	0.4	0.02
#467	7.3	1.8		19.1	3.4	3.9		63	0.2	0.3	0.5	0.02
#468	11.4	1.2		16.3	2.6	3.2		60.6	1.5	2.2	0.3	0.11
#470	10	2.1		21.4	2.8	6.4		55.4	0.3	0.3	0.6	0.02
#472	5.97	2.53		19.3	1.72	4.43		40.58	2.66	0.98	9.77	0.12
#475	2.6	2.4		22.8	1.2	1.7		55.7	1.8	0.7	0.9	
#476	4.91	2.55		21.7	2.04	4.44		37.06	2.23	0.84	9.74	0.17
#703	2.79	2.62		11.4	1.35			65.49	1.94	1.03	1.85	
#712	9.33	1.58		7.96	3.49			63.15	2.16	1.36	0.91	
#713	12.2	2.58		9.63	4.28			54.64	0.59	0.89	1.49	
#760	10.79	4.19		36.15	6.5	2.47		27.26	0.73	0.76	0.97	
#945	8.1	1.8		14	2.4	2.6	0.68	62	1.7	2	0.36	
#990	12.27	2.48		12.9	4.3	2.49		55.32	0.84	1.05	1.51	0.22
#991	9.95	2.45		25.2	3.32	4.92		46.07	1.69	1.85	1.18	0.09
#992	6.14	1.06		25.6	1.26	4.4		55.32	1.88	0.73	1.71	0.08
#1271	8.1	2		20.2				58.2	0.8	0.7	0.5	0.03
#1903	7.9	2.4		25.3	4.7	4	4.54	30.6	0.5	0.4	0.7	
#1965	14.4	4.3		14.06		5.27	3.35	39.2	3.85		4.3	
#2141	10.2	2.5		36.7				36.6	0.8	0.6	2.3	
#3161	7.28	1.82		16.86	2.27	1.1		59.9	0.81	0.54	0.42	0.04
#1302	6.3	2		21.3	2.3	3.5	4.29	54	0.12	0.06	0.23	0.01
#1308	6.5	2		19	2.6	3.9	3.56	55	0.1	0.9	0.2	0.01
#1310	6.4	2		22	2.4	5.6	2.94	54	0.14	0.08	0.4	0.01
#1303	14	2.6		21	4.2	5	0.80	42	0.4	0.2	0.3	0.02
#1309	15	3		24	4	5.4	0.86	43	0.4	0.2	0.4	0.02
#1311	14	2.6		22	4	5	0.98	38	0.4	0.2	0.3	0.02
#2804	9.2	1.8		21.9	3.2	4	6.86	52	0.6	1.1	0.3	
#714	7.62	1.67		11.73	2.77			57.79	0.38	0.58	0.72	
#1966	4.43	0.92		13.12		5.9	3.65	38.5	1.73		3.3	
#739	5.84	2.37		5.81	3.35	1.68		61.79	2.85	1.62	3.48	0.04
#767	4.66	2.51		18.4	1.47	5.46	18.01	35.84	2.46	0.97	10.5	0.15

Table AB.2. Ash fusion behaviour (IDT, SOT, HT and FT; °C for all) dataset of four different ash categories (black font for hardwood ash; red font for softwood ash; blue font for eudicot straw ash; green font for grass straw ash).

ID-number	IDT	SOT	HT	FT
#77	1365			1380
#91	1360			1380
#947	1110		1470	1500
#3159	1490			
#3160	1150	1180	1200	1225
#3154	1210	1225	1250	1275
#151	1193		1277	1266
#1786	1198	1219	1228	1235
#1808	1343	1354	1360	1377
#163	1110	1640	1700	1750
#166	1140	1580	1630	1660
#167	1340	1410	1750	1800
#177	1340	1410	1700	1700
#3155	1175	1205	1230	1250
#3156	1180	1190	1205	1235
#2801	1236	1244	1246	1249
#880	1343		1400	1400
#299	1170		1180	1200
#408	1380	1590	1640	1660
#409	900	1420	1660	1750
#410	1000	1120	1140	1140
#538	920	1380	1460	1530
#539	1380		1400	1420
#3162	1500			1600
#419	1100	1180	1300	1340
#420	1020	1100	1750	1800
#553	600	620	650	680
#554	820	920	1640	1650
#555	700	780	1750	1800
#556	620	630	670	700
#624	820	840	1560	1590
#625	1130	1500	1650	1670
#626	650	680	760	1680
#627	660	680	710	710
#628	650	680	1620	1750
#629	800	820	1640	1650
#630	700			1550
#1902	1550	1580		
#432	900	1000	1110	1180
#433	720	760	1010	1080
#435	1120		1180	1230
#438	925			1100
#946	1160		1230	1250
#3169	750			1050

Continued from Table AB.2

ID-number	IDT	SOT	HT	FT
#517	980			1140
#518	820			1091
#519	1120			1235
#401	920	1040	1140	1200
#533	830	960	1050	1130
#534	930	1050	1120	1140
#516	1010			1180
#448	823			1190
#449	850			1280
#450	1060			1250
#451	985			1200
#2802	1240	1378	1429	1470
#547	840	850	1030	1100
#548	880	1120	1270	1320
#558	920	950	1040	1040
#559	1140	1220	1250	1250
#560	850	1060	1120	1140
#561	900	1000	1080	1130
#562	950	1050	1070	1130
#563	1260	1350	1440	1490
#564	1120	1150	1200	1250
#3166	975	1090	1257	1340
#424	970	1020	1120	1180
#425	980	1020	1130	1190
#426	780	800	1140	1260
#427	1010	1020	1170	1220
#454	900	1110	1270	1330
#455	860	900	1040	1080
#456	820	880	1050	1210
#457	800	860	1130	1220
#459	1080		1280	1500
#945	790		1120	1320
#1903	900	1040	1170	1190
#3161	860	1030	1045	1365
#1302	850		1090	1200
#1303	870		1050	1240

Table AB.3. Proximate and ultimate analysis (wt. % of biomass) dataset of four different biomass categories (black font for hardwood; red font for softwood; blue font for eudicot straw; green font for grass straw).

ID-number	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Ash content	Volatile matter	Fixed carbon
#2142	49.8	6.3	0.1	0.1	43.7	0.6	84	15.4
#803	50.12	5.94	0.03	0.01	43.9	0.31	86.22	13.47
#2894	51.01	8.12	0.58	0.02	40.26	3.71	83.64	12.65
#700	50.03	6.07	0.23	0.05	43.6	1.22	85.07	13.71
#845	51.65	5.99	0.6	0.02	41.71	1.6	86.14	12.26
#806	51.57	6.23	0.62	0.02	41.55	2.7	84.81	12.49
#1998	49.54	6.32	0.51	0	44.14	1.9	82.6	15.5
#719	49.56	5.95	0.36	0.03	44.1	0.95	85.24	13.81
#947	50.36	6.74	1.12	0.1	41.64	2.1	78.6	19.3
#1305						4.59		
#1306						4.01		
#851	48.47	5.9	0.64	0.06	44.91	1.1	84.91	13.99
#852	50.9	6.08	0.51	0.07	42.43	1.2	83.05	15.75
#867	49.69	6.14	0.72	0.06	43.37	1.7	82.16	16.14
#868	50.51	6.09	0.66	0.09	42.64	1.5	81.83	16.67
#869	50.77	6	0.62	0.07	42.53	1.71	82.22	16.07
#870	49.47	6.11	0.36	0.04	44	1.06	84.13	14.81
#3159	50.29	6.17	0.4	0.03	43.1	1.18	79.9	18.92
#720	50.61	6.04	0.98	0.13	42.24	2.34	79.66	18
#1267	51.05	6.01	0.1		42.83	0.1	83.1	16.8
#3160	51.04	5.99	0.08	0	42.85	0.08	83.1	16.82
#3154	52.11	6.14	0.3	0.01	41.44	0.6	80	19.4
#151	55	5.8	0.1	0.1	39	3	73	24
#1786	52.88	4.84	0.53	0.15	41.6	3.03	75.56	21.41
#1996	52.77	5.85	0.2		41.27	0.9	81.9	17.2
#1808	51.31	6.36	0.25	0.01	42.07	0.22	83.15	16.63
#163	51.59	5.59	0.12	0.01	42.68	0.96		
#166	50.74	5.7	0.11	0.01	43.43	0.28		
#167	50.81	5.68	0.11	0.01	43.38	0.32		
#177	50.85	5.68	0.11	0.01	43.34	0.3		
#2134	50.97	6.02	0.3		42.7	0.5	83.69	15.81
#3155	51.99	6.18	0.41	0.02	41.4	1.33	79.3	19.37
#3156	53.15	6.04	0.94	0.04	39.82	4.05	74.1	21.85
#2801	54.83	5.9	0.08	0.02	41.29	1.2		
#804	51.44	6	0.06	0.03	42.27	0.41	82.11	17.48
#880	53.4	5.9	0.1		40.6	2.17	74.33	23.5
#2895	53.64	5.77	0.1	0	40.49	1.2		
#2770	49.15	6.41	0.2	0.2	44.04	0.1	84.7	15.2
#2912	49	6.4	0.14	0.01	44.45	1.59	87.5	10.91
#1995	48.79	6.07	0.71		45.14	1.2	75.9	22.9
#2929	53.3	6.2	0.1	0.01	40.4	1.03	81.85	17.12
#847	54.43	5.89	0.55	0.42	38.72	5.21	73.99	20.8
#2030	49.8	6	0.4	0.02	43.76	1.06	84.57	14.37

Continued from Table AB.3

ID-number	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Ash content	Volatile matter	Fixed carbon
#408	54.07	6.82	2.43	0.42	35.98	5.54		
#409	53.97	6.57	1.99	0.71	36.06	7.66		
#410	53.58	7.32	5.39	0.82	32.86	6.3		
#538	49.47	5.68	1.55	0.33	41.87	9.73		
#539	43.22	5.27	0.87		50.59	3.85	76.5	19.65
#540	40.39	4.61	0.8		54.12	3.8	78.8	17.4
#3162	49.52	6.07	0.08	0.22		2.86	79.2	17.94
#419	62.52	7.39	2.07	0.12	27.77	3.51		
#420	56.45	6.01	1.34	0.13	35.99	2.95		
#553	49.87	5.56	1.38	0.11	42.04	12.9		
#554	53.12	6.26	2.15	0.24	37.65	11.95		
#555	48.1	5.66	1.11	0.12	44.13	11.14		
#556	49.91	5.52	0.34	0.03	43.45	8.82		
#624	50.26	5.54	3.68	0.18	39.69	10.28		
#625	50.95	5.77	3.68	0.34	38.66	10.71		
#626	49.77	5.68	1.86	0.13	42.23	6.92		
#627	50.3	5.72	3.24	0.26	40.14	10.1		
#628	51.03	5.91	3.18	0.29	39.25	9.17		
#629	51.74	5.73	2.33	0.16	39.5	10.71		
#1902	51.04	6.45	3.39	0.17	38.91	8.5		
#1993	49.67	6.62	2.76	2.21	40.73	9.4	73.9	16.7
#432	49.18	5.81	0.43	0.06	44.08	4.86		
#433	49.79	5.64	0.78	0.13	42.63	5.88		
#434	47.9	6.18	0.45	0.21	44.89	4.26	76.8	18.94
#435	49.25	6.34	0.83	0.36	42.81	6.4	75.4	18.2
#946	48.54	6.32	0.82	0.15	43.87	2.73	79.9	17.37
#3169	49.09	6.06	0.64	0.08	44.14	5.88	76.1	18.02
#704	49.31	6.04	0.7	0.11	43.56	5.06	80.86	14.08
#401	48.77	5.87	0.45	0.05	43.25	8.5		
#533	49.57	5.65	0.8	0.04	43.58	2.69		
#534	48.13	5.73	0.36	0.04	45.57	5.29		
#444	48.09	5.86	1.69	0.14	43.64	19.09		
#702	49.15	6.23	1.59	0.13	42.13	20.15	65.62	14.23
#994	47.02	6.39	1.07	0.22	44.58	18.67	65.47	15.86
#2001	48.47	5.63	0.86	0.13	44.55	18.3		
#2802	53.43	4.94	0.76	0.08	50.38	22.1		
#2896	49.42	4.62	0.77	0.13	44.42	22.1		
#2002	48.72	6.03	0.77	0.15	44.36	22		
#737	48.14	6.27	0.73	0.07	44.72	17.84		
#736	48.32	6.27	0.58	0.07	44.68	17.1		
#735	47.87	6.2	0.57	0.08	44.81	17.59		
#766	46.64	5.9	0.64	0.11	45.8	18.63		
#547	49.76	5.54	0.48	0.06	43.73	4.57		
#548	49.64	5.85	0.25	0.04	44.16	3.98		
#558	50.19	5.17	1.45	0.08	42.7	6.79		
#559	49.45	4.85	0.36	0.02	44.97	7.34		

Continued from Table AB.3

ID-number	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Ash content	Volatile matter	Fixed carbon
#560	48.52	6	0.8	0.05	44.49	6.96		
#561	48.78	5.87	1.17	0.08	43.81	5.48		
#562	49.08	5.9	1.18	0.07	43.38	5.42		
#563	47.7	6.1	1.34	0.06	44.37	7.44		
#564	51.46	5.71	1.01	0.08	41.42	10.18		
#3166	49.65	6.09	0.42	0.09	43.74	4.74	77.2	18.06
#424	48.46	5.79	1.74	0.11	43.64	5.04		
#425	48.83	5.7	1.32	0.09	43.67	4.58		
#426	52.12	5.48	0.51	0.08	41.36	7.36		
#427	48.46	5.8	1.62	0.12	43.73	5.16		
#454	49.71	5.83	0.29	0.03	44.09	3.22		
#455	49.99	5.53	0.49	0.08	43.48	4.35		
#456	50.34	5.57	0.4	0.06	42.94	7.17		
#457	49.74	5.61	0.55	0.06	43.53	6.63		
#459	48.24	6.07	0.8	0.25	44.36	8.95	73.4	17.65
#460	49.74	6.33	1.06	0.17	42.55	7	75.8	17.2
#472	47.42	5.76	0.63	0.39	43.56	9.44		
#475	48.84	5.83	0.96	0.21	43.92	7.35		
#476	47.43	5.65	0.59	0.32	43.74	9.55	71.11	19.34
#703	49.06	6.17	1	0.2	43.29	8.24	75.54	16.22
#712	49.63	6.08	0.75	0.12	43.15	5.82	78.72	15.47
#713	49.47	6.1	0.6	0.1	43.55	3.89	81.23	14.88
#760	47.59	5.98	0.57	0.12	45.71	3.41	78.8	17.79
#945	50.43	6.2	0.75	0.18	42.26	6.4	77.3	16.3
#990	49.47	6.1	0.61	0.09	43.54	3.89	81.24	14.87
#991	49.08	5.95	0.45	0.2	44.18	4.32	78.62	17.06
#992	48.31	5.87	0.47	0.17	44.92	7.02	75.27	17.71
#1271	49.09	5.96	0.53	0.09	44.01	6.1	75.8	18.1
#1903	47.61	6.06	0.85	0.1	45.27	5.9		
#1965	47.24	5.49	0.85	0.46	45.51	7.5	76	16.5
#2141	49.7	6.1	0.5	0.2	42.4	5.2	77.8	17
#3161	49.64	6.16	0.61	0.07	43.54	4.71	77.7	17.59
#1302	49.3	6.42	0.48	0.17	43.2	7.1	74.9	18
#1308	49.35	6.42	0.48	0.17	43.14	7.2	74.9	17.9
#1310	49.09	6.39	0.48	0.17	43.44	6.7	74.9	18.4
#1303						3.3		
#1309						2.94		
#1311						3.3		
#2804	49.33	6.63	0.57	0.14	43.33	7.79		
#714	49.32	6.02	0.73	0.1	43.36	5.89	78.93	15.18
#1966	50.34	6.34	0.66	0.26	42.07	5.04	77.23	17.73
#739	48.82	6.1	0.68	0.1	44.07	6.45		
#767	48.72	5.87	0.78	0.45	41.87	12.78		

Table AB.4. Heavy metal concentration (mg/kg) dataset of four different ash categories (black font for hardwood; red font for softwood; blue font for eudicot straw; green font for grass straw).

ID-number	Pb	Cd	Cu	Cr	Hg
#92	220	10	120		
#288	50	10	60		
#122	330	10	400		
#123	350	10	210		
#1786	22		115	70	
#163	29	1.7	148		1.8
#166	18	1.1	1290		1.7
#167	40	0.7	333		0.1
#177	13	0	324	127	
#2912			3879		
#408	3	0	33		0
#409	3	0.1	36		0
#410	0	0	75	7	
#538	27	0.1	82		0
#419	2	0.3	253		0
#420	13	0.1	340		0
#553	6	0	62		0
#554	5	0.1	84		0
#555	1	0	53		0
#556	1	0	38		0
#624	4	0	59		0
#625	9	0.1	98		0
#626	1	0.1	55		0
#627	1	0	89		0
#628	2	0	68		0
#629	4	0	81		0
#432	8	0	57		0
#433	2	0.2	36		0
#401	3	3	5.3		0
#533	255	0	270		0
#534	3	0.1	67		0
#547	3	0.1	34		0
#548	5	0	25		0
#558	25	0.4	138		0
#559	60	0.1	49		0
#560	22	0.3	84		0
#561	41	0.1	114		0
#562	33	0.4	95		0
#563	3	0.1	83		0
#564	40	0.1	57		0
#424	2	0.1	33		0
#425	2	0.2	37		0
#426	2	0	17		0
#427	4	0.2	46		0
#454	20	0	23		0
#455	3	0.1	28		0
#456	1	0	16		0
#457	2	0	13		0

B.2 Correlation of available trace metals concentration against ash CaO content

As for Cu, two samples with over 1000 mg/kg were excluded for the correlation analysis because both samples were obviously abnormal to others. The same applied to Pb (deleting three obviously higher values) during correlation analysis. The results are shown in Figure AB.1.

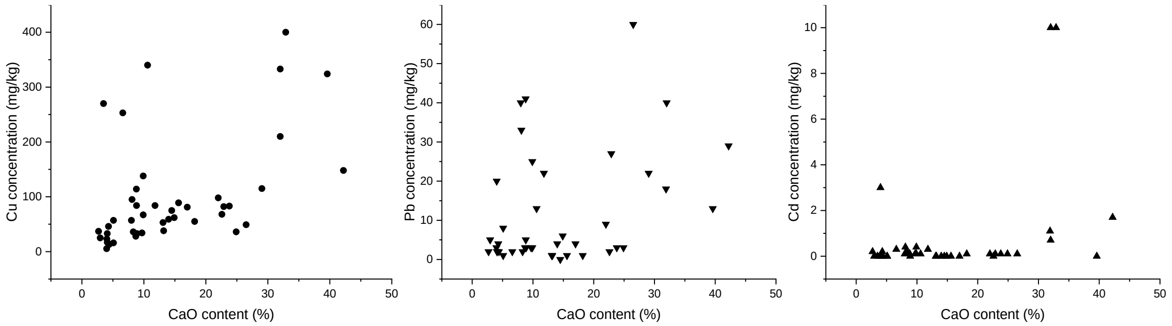

Figure AB.1. Scatterplots showing Cu, Pb and Cd concentration against CaO content.

Appendix C: Appendices for Chapter 5

C.1 Ash chemical composition determination via wet chemical digestion method

Solution A preparation:

Weigh 1.5gm of sodium hydroxide into a nickel crucible, cover with a nickel lid and heat to melt the sodium hydroxide over a burner*. Allow to cool before proceeding to the next step.

Weigh approximately 0.05g of the sample accurately to 4 decimal places and transfer to the cold sodium hydroxide melt. Heat the crucible and swirl gently to ensure that no particles of sample float on the surface of the melt. Continue fusing for about 5 minutes at a dull red heat, then remove the crucible from flame. Swirl the melt around sides and allow to cool.

Alternatively batch fusions can be carried out in a furnace at 650℃ for the same time. Add about 25ml of water and place on a steam bath for 30min. Pour the contents of the crucible into a 600ml beaker containing 400ml of water and 20ml of 1:1 HCl. With a rubber policeman remove any residue from the crucible and wash into the beaker. Do not allow the nickel crucible to come into contact with the acid. Transfer the solution to a 1000ml volumetric flask; dilute with distilled water to the mark, and mix. Store the solution in the plastic bottle marked A.

Solution B preparation:

Weigh approximately 0.4g of the sample accurately to 4 decimal places into the 60ml polypropylene beaker. Take it to the fume cupboard and add 2ml of distilled water, swirl then add 10ml. of Hydrofluoric acid. Place on a steam bath until all the HF has been evaporated.

To the dry residue add 10ml. of hydrochloric acid, replace the lid and place the poly beaker back on the steam bath for 10min. After which remove from the bath and pour approx. 30ml. of distilled water into the beaker and allow to cool. Transfer the contents of the beaker - washing out well - to a 400ml Pyrex beaker and place on a hot plate to evaporate to dryness. Remove the beaker from the hotplate and allow to cool then add 3ml of 1:1 H_2SO_4 and place back on the hotplate. The final stage of the solution B preparation requires care as the residue must not be allowed to dry. White sulphuric acid fumes must persist for at least 5 minutes. Remove the beaker and allow to cool; then carefully add approx. 200ml of distilled water and place back on the hotplate for 30 minutes. After cooling the solution is transferred to a 250ml volumetric flask and made up to volume and is finally stored in a plastic bottle.

Concentration determination:

Si is determined by colormetric method with solution A at 650nm; P is determined by colormetric method with solution B at 430nm; and the other elements are determined by AAS with solution B. The LOI is determined at 900 ℃ for 2 hours.

C.2 XRD spectra

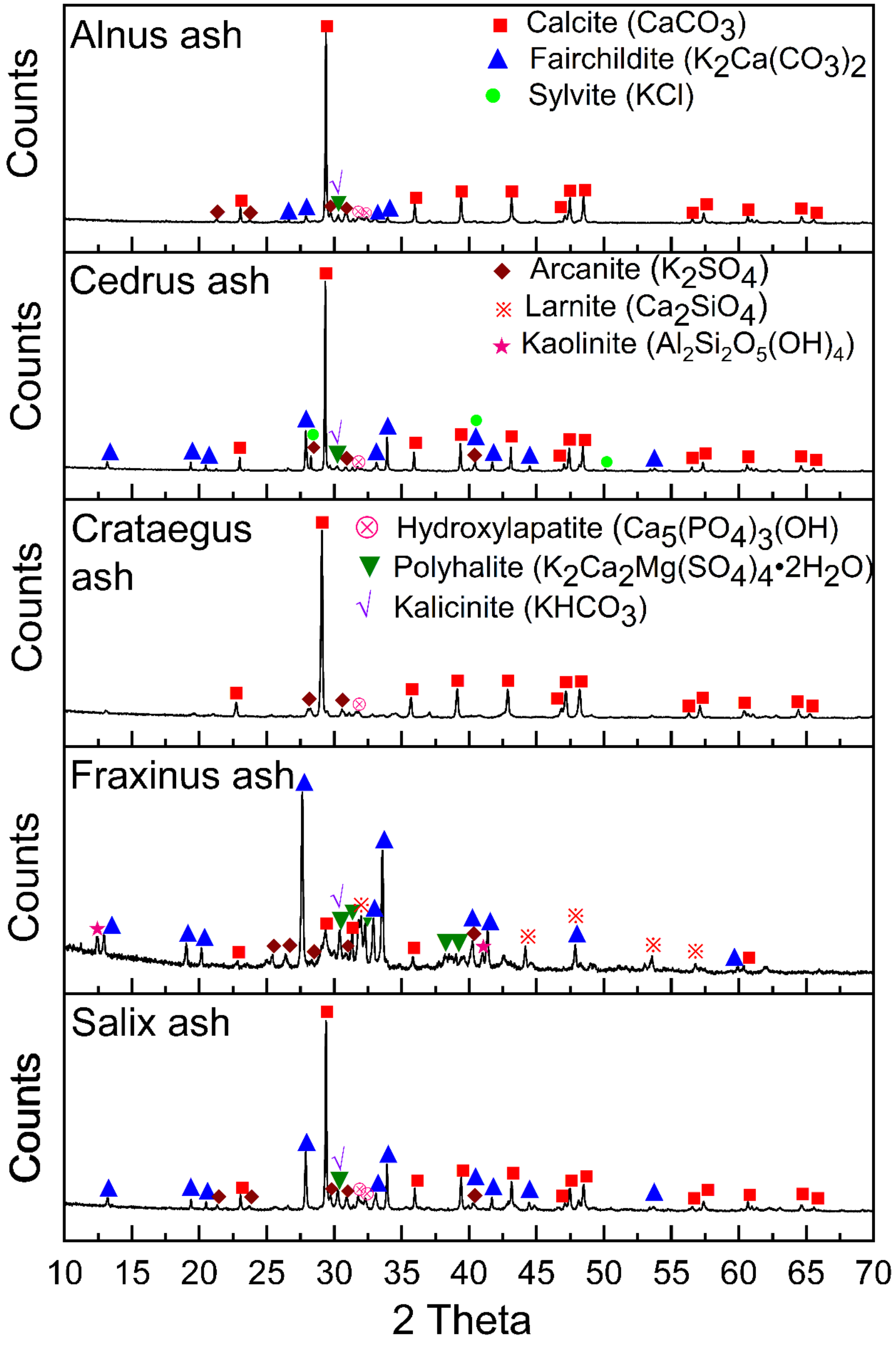
Alnus ash
Cedrus ash
Crataegus ash
Fraxinus ash
Salix ash
Counts
■ Calcite ($CaCO_3$)
▲ Fairchildite ($K_2Ca(CO_3)_2$)
● Sylvite (KCl)
◆ Arcanite (K_2SO_4)
※ Larnite (Ca_2SiO_4)
★ Kaolinite ($Al_2Si_2O_5(OH)_4$)
⊗ Hydroxylapatite ($Ca_5(PO_4)_3(OH)$)
▼ Polyhalite ($K_2Ca_2Mg(SO_4)_4•2H_2O$)
√ Kalicinite ($KHCO_3$)
10
15
20
25
30
35
40
45
50
55
60
65
70
2 Theta

Figure AC.1. XRD spectra of laboratory ash samples (mineral-phase symbols are uniform).

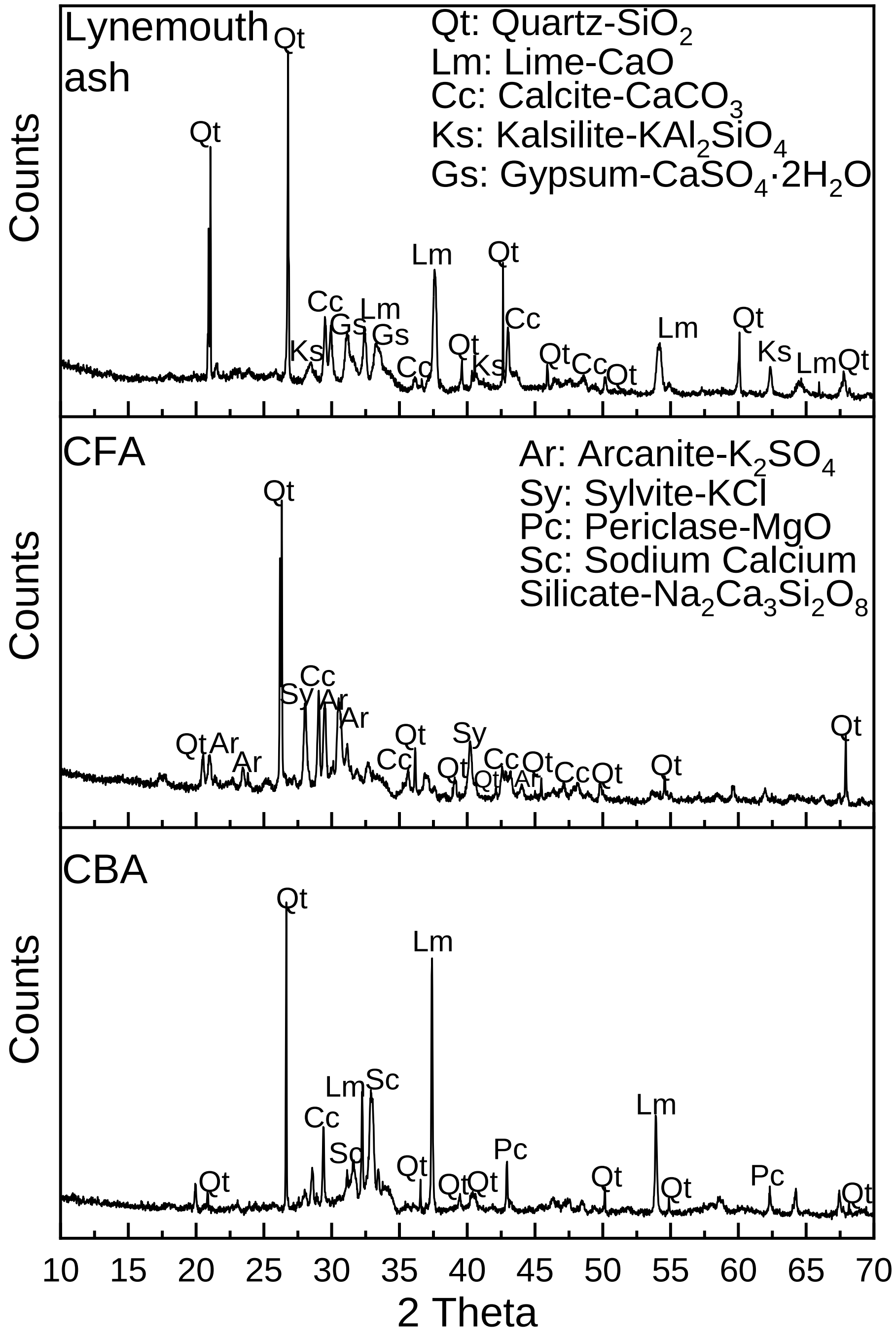

Figure AC.2. XRD pattern of Lynemouth ash, CFA and CBA.

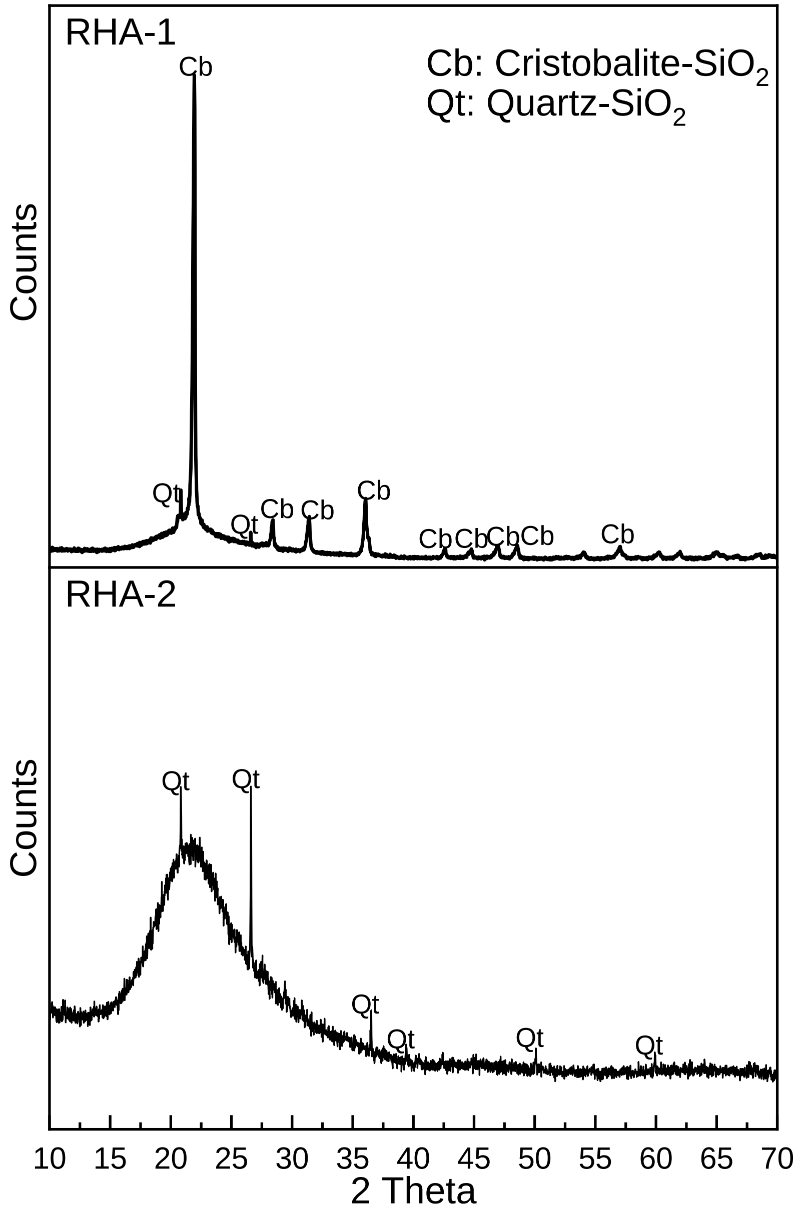

Figure AC.3. XRD pattern of two rice husk ash samples.

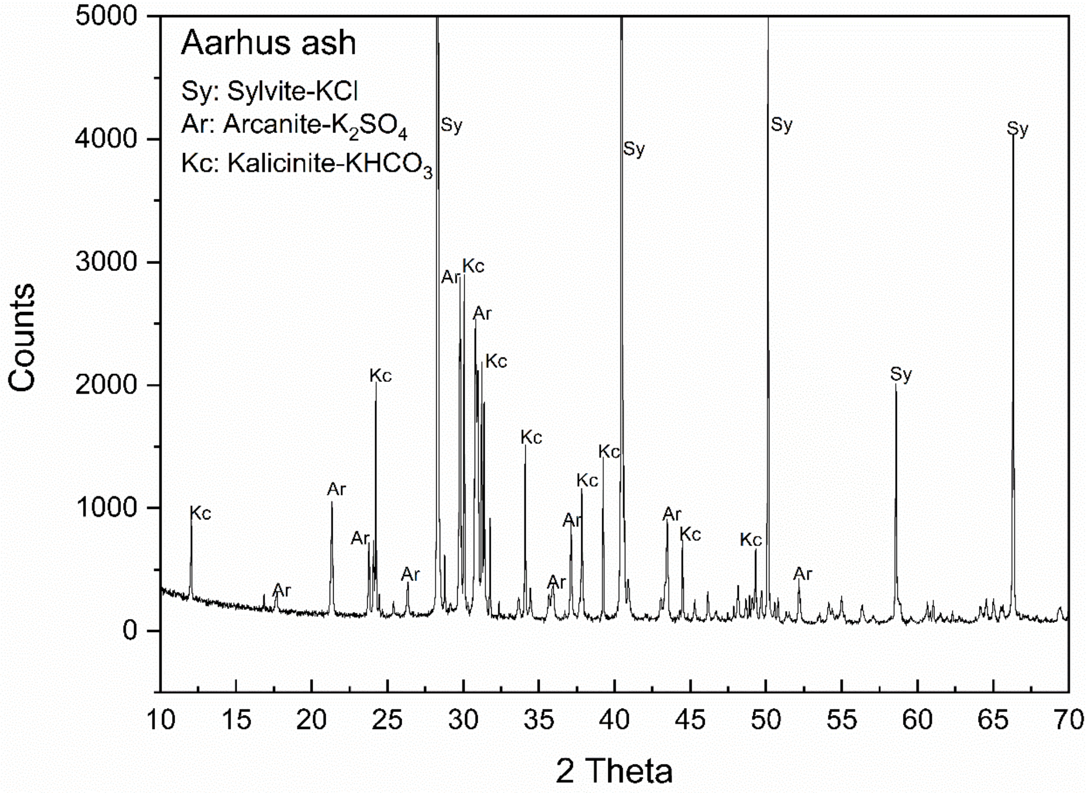

Figure AC.4. XRD pattern of straw ash.

C.3 FTIR spectra

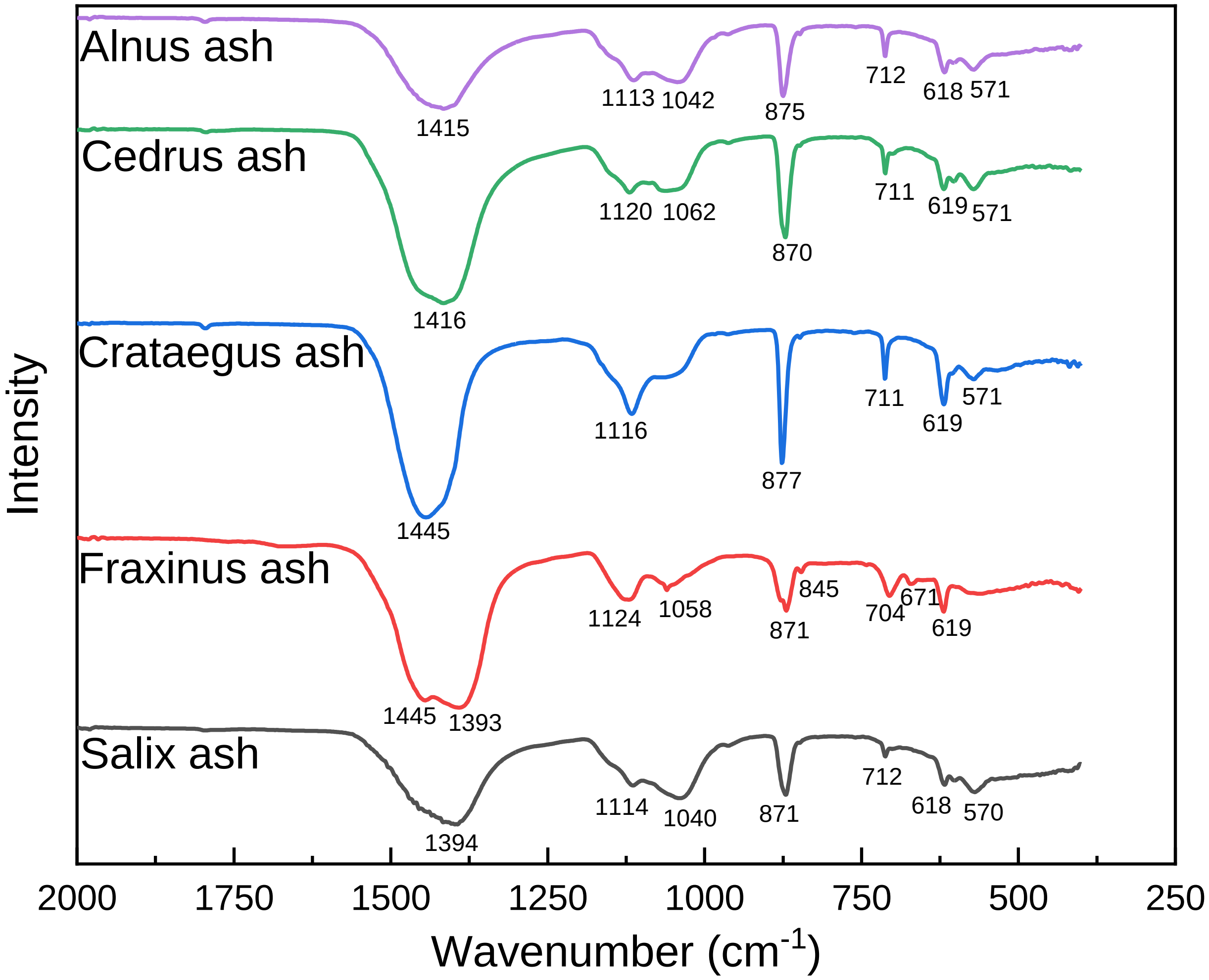

Figure AC.5. FTIR spectra of laboratory wood ash samples.

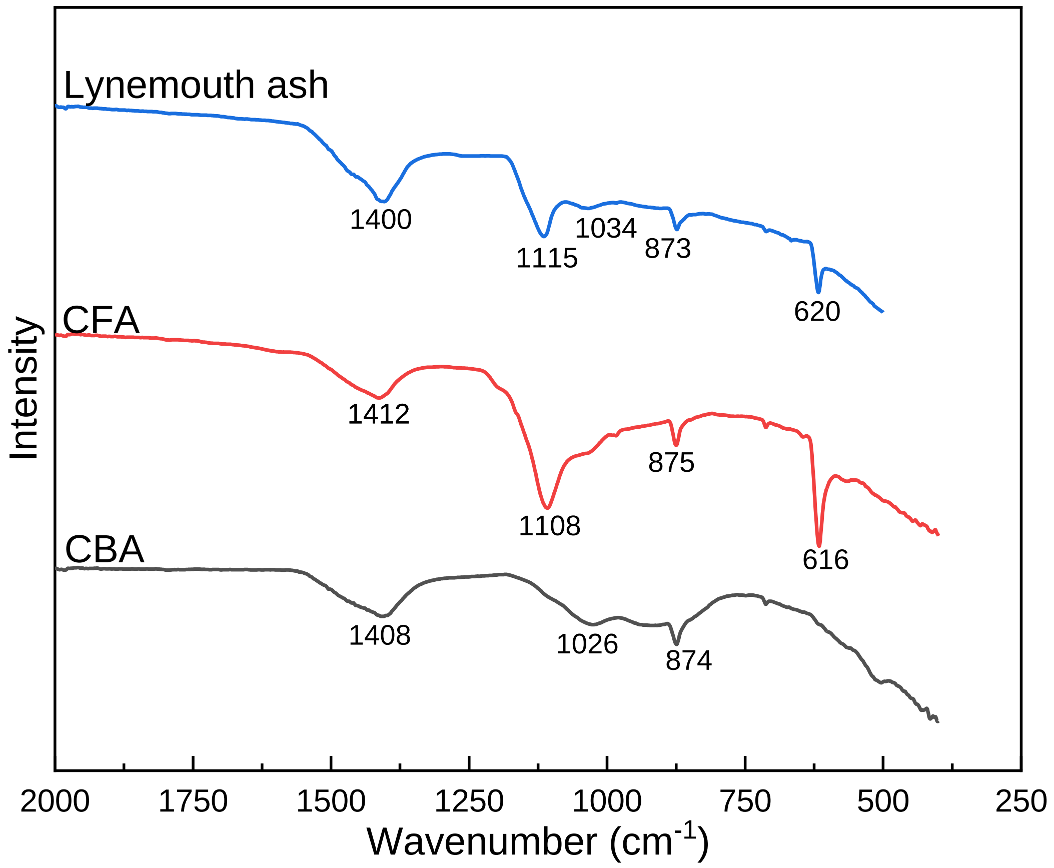

Figure AC.6. FTIR pattern of Lynemouth ash, CFA and CBA.

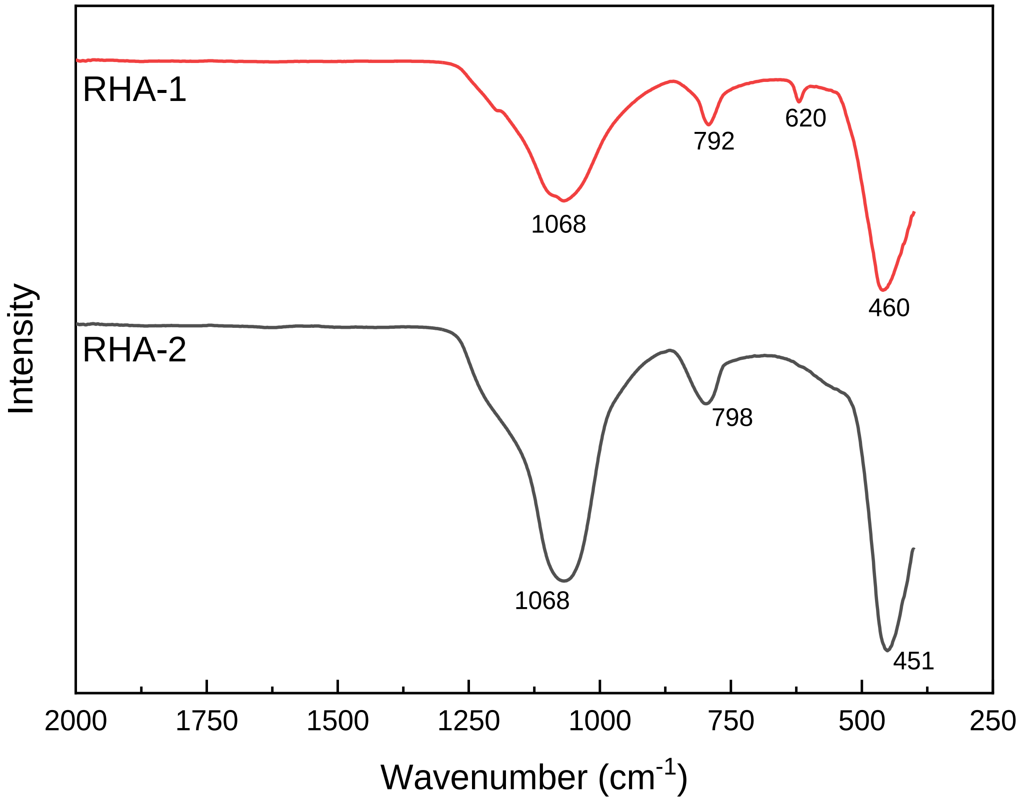

Figure AC.7. FTIR pattern of two rice husk ash samples.

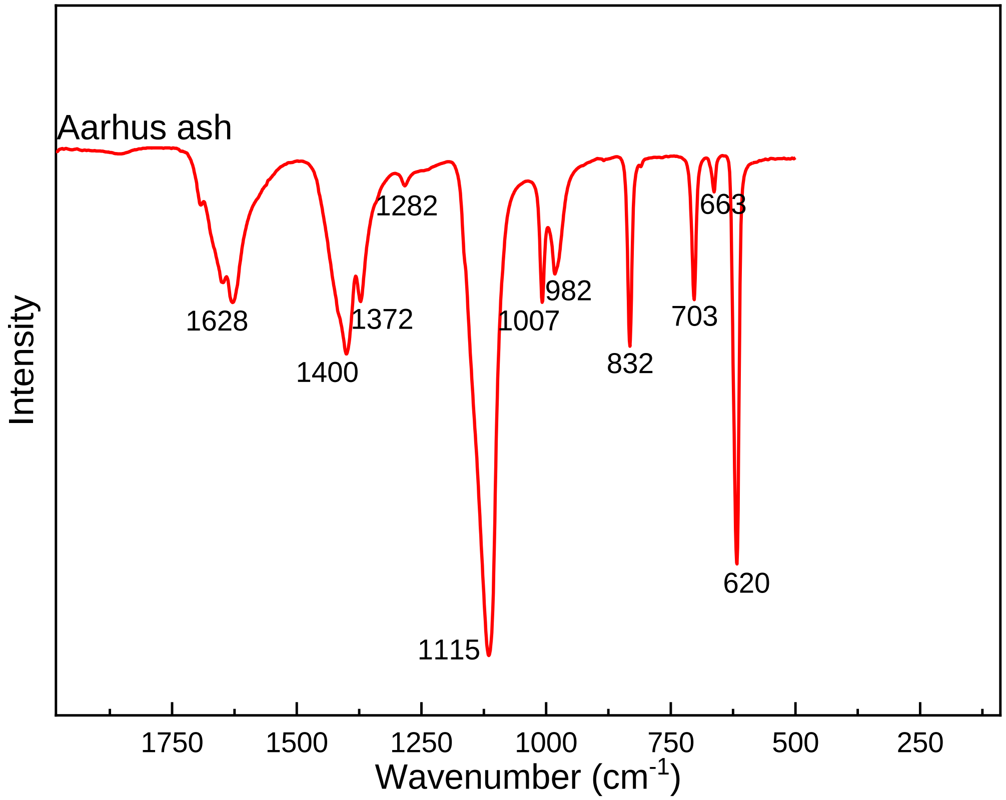

Figure AC.8. FTIR spectra of Aarhus straw ash.

C.4 WHO guideline values (World Health Organization, 2022) and USEPA limits (USEPA, 2022) for drinking water quality control

Table AC.1. WHO guideline values and USEPA limits for drinking water quality control (trace elements in ug/L).

Trace elements	WHO guideline values	USEPA limits
As	10	10
B	2400	
Ba	700	2000
Cd	3	5
Cr	50	100
Cu	2000	1300
Hg	6	2
Mo	70	
Ni	70	
Pb	10	15
Sb	20	6
Se	40	50

C.5 Finnish limit (Dahl et al., 2010) and Swedish limit (Swedish National Board of Forestry, 2002) on ash to be used as forestry fertiliser, and UK limit on poultry litter ash (PLA) to be used as a fertiliser (EA-UK, 2012)

Table AC.2. Finnish limit and Swedish limit on ash to be used as forestry fertiliser, and UK limit on poultry litter ash (PLA) to be used as a fertiliser (trace toxic elements in mg/kg).

Trace elements	Finnish limit	Swedish limit	UK PLA limit
As	30	30	17
B		500	
Ba			
Cd	17.5	30	3
Co			11
Cr	300	100	31
Cu	700	400	596
Hg	1	3	0.5
Ni	150	70	24
Pb	150	300	244
V		70	20
Zn	4500	7000	2063

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Appendix D: Appendices for Chapter 6

Raw data/results and associated references can be found and downloaded online at https://doi.org/10.1016/j.hazadv.2021.100038.