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Beneficial management of biomass combustion ashes

Jihua Zhai [a], Ian T Burke [b], Douglas I. Stewart [a, *]

[a] School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK

[b] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

[*] Corresponding Author: d.i.stewart@leeds.ac.uk

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Highlights

- Current global production of biomass ash is ~170 Mt/yr
- Production could be 1000 Mt/yr with greater use of agricultural residues and wastes
- Burning virgin biomass in a modern furnace gives ash suitable application to land
- Burning biomass waste gives ash with potentially problematic contaminant levels
- Pollutants in flue gases mean fly ash and similar residues need controlled disposal

Abstract: Use of biomass for energy production is increasing, so management of the resultant ash is important. This review compares current and future production, chemical composition, and reuse options for ash from common feedstocks (agricultural residues, energy crops, woody biomass, forest residues, recovered wood, paper sludge, sewage sludge and municipal solid waste). Global production is ~170 Mt/yr, but could increase to ~1000 Mt/yr if all available biomass were exploited. Current production is dominated wood and waste derived ashes, but there is capacity to greatly increase use of agricultural residues. Combustion of virgin biomass in modern furnaces can produce ash with negligible persistent organic pollutants and low contaminant metals concentrations, so application to land is possible. Agricultural residue ashes contain abundant potassium and useful phosphate, so could potentially be used as fertiliser. Forestry ashes are rich in CaO, but slightly higher contaminant metals levels may restrict their use to forestry soils. Recovery of potassium from these ashes, and their use in cementitious materials have also been demonstrated. Biomass containing waste ashes potentially contain more persistent organic pollutants and contaminant metals. However, municipal solid waste bottom ash is routinely used as a construction aggregate for prescribed applications. Paper sludge ash is suitable for restricted use as a soil conditioner and possibly as a secondary pozzolan. However, controlled disposal may be required for recovered wood ash and sewage sludge incineration ash. As persistent organic pollutants tend to partition to the flue gases, fly ash and air-pollution control residues are likely to require controlled disposal.

Keywords: biomass ash; ash quantity; ash composition; classification; ash management

Word count: 10,283 (excluding title, author names and affiliations, keywords, abbreviations, table/figure captions, acknowledgments and references)

List of abbreviations

APC	Air pollution control
EJ	Exajoule (=10^{18} J)
est.	estimated
EU	European Union
EU-27	The European Union member countries
GJ	Gigajoule (=10^{9} J)
Gt/yr	Gigatonnes per year (=10^{9} t/yr)
kg	kilogram
kt	kilotonne (=10^{3} t)
MSW	Municipal solid waste
Mt/yr	Megatonnes per year (=10^{6} t/yr)
Myr	Million years
ng	nanogram (=10^{-9} g)
NCV	Net calorific value
PAHs	Polyaromatic hydrocarbons
PCDD/Fs	Polychlorinated dibenzodioxins/dibenzofurans
Pg C y^{-1}	Petagrams of carbon per year (=10^{15} g C y^{-1})
POPs	Persistent organic pollutants

SSIA	Sewage sludge incineration ash
t	tonne (= 10^3 kg)
TEFs	Toxic equivalency factors
TEQs	Toxic equivalents units
UN	United Nations
wt.%	percentage by weight

1. Introduction

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 [1, 2]. The balance in global energy consumption has been supplied by nuclear energy (~2%) and renewable energy sources (~18%) [3]. 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 [3]. 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 [3].

There are different definitions of biomass [3-7]. The word is widely used to describe "all organic material that stems from plants (including algae, trees and crops)" [4]. 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” [5], 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, sewage sludge, demolition wood, paper sludge, etc.), and biomass mixtures.

Electricity generation, accounts for about 15% of biomass consumption [3]. Commonly, the biomass is burned in a fixed, fluidised or pulverised bed boiler to produce high-pressure steam, which then drives a turbine to generate electricity [8]. Generation is undertaken in both electricity only and combined heat and power plants (the former is ~30% energy efficient, whereas the latter can have an overall efficiency of ~80% [9]). At present, the types of biomass used for heat/electricity generation are commonly from agriculture/forestry residues, dedicated energy crops, wood fuel/charcoal/chips/pellets, municipal solid waste, sewage sludge, and paper sludge [3, 5, 10]. The net calorific value (NCV) of dry biomass varies with feedstock. It is between 16 -19 MJ/kg for hard wood, softwood cereal crop straw, rape straw and sunflower straw [4, 11]. Rice straw and sugarcane stalks have lower NCVs than other agricultural residues (12 and 8 MJ/kg, respectively [11]). The NCV of municipal solid waste (MSW) varies between 4-17 MJ/kg depending on the waste composition [12, 13] and for dried paper sludge it is 6 MJ/kg [14]. 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 [3, 15]. Also, with the increasing population growth and urbanization, more energy extraction by combustion of MSW and sewage sludge can be expected in coming decades [16, 17]. Therefore, it is anticipated that bioenergy from a variety of different alternative fuels will make an important contribution to meeting future energy demands.

When fuels derived from these renewable resources or waste materials are burnt to produce electricity/heat, ash will inevitably be produced, and that ash will differ in its physical and chemical properties from ash produced by more traditional fuels such as coal [18-20]. Thus, alternative reuse or, if necessary, disposal strategies are required [21]. Also, while the ash's weight/volume will be a fraction of that of the feedstock (for example, ash content for woody biomass is typically 1.5 – 2% [5, 22], and incineration reduces MSW by ~90% in volume and ~70%-80% in mass [23, 24]), the total amount of ash produced globally is still considerable, and is likely to increase as bioenergy utilization increases. Better understanding of the ash produced from above-mentioned alternative fuels 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 [25, 26].

When a renewable fuel feedstock is burnt to generate electricity/heat, there are many factors that can determine the resultant 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 feedstock composition [25, 27-29], 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 [6, 30-33]. Biomass ashes are usually rich in elements such as Si, K, Ca, P, Mg, etc. [34-37], 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 [38-40]). 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 [41-43]. 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 [44-47]), and MSW incineration ashes contain a variety of ferrous and non-ferrous metals that can be recovered [48-50].

This paper provides a comprehensive review of the current production of biomass ash derived from common feedstocks used for energy generation. It estimates potential future ash arisings based on authoritative data on the production of the feedstocks and their different ash contents and predicts likely changes in biomass ash production rates. Finally, it reviews the reuse options for the major biomass ash types being produced now and in the future. Ash from combustion of agricultural residues, energy crops, woody biomass, forest residues, recovered wood, paper sludge, sewage sludge, and municipal solid waste are considered. Increased future use of biomass to provide energy is seen by many as essential in the transition to a low carbon future, particularly if it can be combined with carbon capture and storage [51, 52], and can help nations achieve emissions targets as established by the United Nations Framework Convention on Climate Change. Therefore, the aim of this paper is to provide a comprehensive overview that supports their sustainable management, and thus informs rational decision-making about energy generation from biomass feedstocks. Specifically: (1) the amount of biomass from different sources that is burnt globally as bioenergy and resulting ash production are quantified, and the potential for future changes in these quantities are estimated, (2) the typical major element compositions, and the potential trace metal and toxin contents of ash from different feedstocks are reported, (3) biomass ash classification systems that inform ash management are discussed, and (4) options from beneficial reuse, value recovery from, or sustainable management of ash from different feedstocks are reviewed.

2. Global ash-products distribution

Currently, national biomass ash production figures are not routinely published, and annual production is changing rapidly as many nations are attempting to transition to a low-carbon economy [53-55]. Therefore, it is difficult to directly estimate the worldwide production of ash from sustainable fuels. This is further complicated by national differences in how data is reported (e.g. biomass ash figures from some countries include partial coal co-combustion with biomass) [56]. However, ash production can be estimated from biomass production data, which is better recorded in most regions.

Estimates of the sustainable amount of biomass that is available for energy production can be compared to the amount of carbon that is captured annually by terrestrial photosynthesis. A review in 2015 estimated terrestrial photosynthesis to be between 119 and 169 Pg C y^{-1} [57]. Similarly, a best-estimate of 147 Pg C y^{-1} (range 131-163 Pg C y^{-1}) has been obtained from remote sensing of the near-infrared reflectance of vegetation [58]. This estimate of global net primary production corresponds very approximately to about 300 Gt/yr of organic matter [59]. However only a small fraction of this organic matter can be harvested, 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.

It was estimated in 2013 that approximately 7 billion tonnes (Gt) of biomass were burned annually for energy production [25]. This widely cited figure represents about 2% of the organic matter created annually by photosynthesis. 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 [60]. Three separate sources were used to estimate the range for agricultural residues (between 1.1 and 3.1 Gt/yr [60-62]) however a high-end figure is incorporated into the total. Typical ash production rates [5] were used to estimate that this biomass would have produced about 480 million tonnes of ash. Separately, it has been estimated that, globally, 43.5 – 56.5 EJ of energy was produced from biomass fuels in 2016 [3, 63]. 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. This more modest figure represents about 1% of the organic matter created annually by photosynthesis.

As the estimates of biomass burned for energy production reported in the literature are based on data >10 yrs old, a new estimate of biomass fuel usage has been made (Table 1). 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 [3] and average crop to residue ratios [64]. Worldwide, agricultural residues contribute less than 3% to the total bioenergy production of 55.6 EJ in 2017 [3], which corresponds to usage of about 93 Mt/yr (an energy yield from agricultural residues by combustion of 18 GJ/t is assumed [60, 65, 66]). 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 utilization rate can be obtained (the maximum sustainable utilisation was assumed to be 50% as the remainder must be returned to the land for soil health [3]). Combustion of agricultural residues produces 6 wt.% ash [5, 65, 67], so currently about 6 Mt/yr of ash is produced from agricultural residues.

Table 1: Global estimate of biomass production rate, current incineration rate and ash production rate broken down by region.

Fuel Source		Africa	Americas	Asia	Europe	Oceania	Total
Agriculture							
Agriculture residues	Amount produced (Mt/yr) [3, 64]	624	3125	3244	998	67	8,058
	Utilization rate (%) [3, 60, 65, 66]	4.1%	0.6%	1.1%	1.3%	0.7%	1.1%
	Estimated ash production (Mt/yr)	1.54	1.08	2.16	0.75	0.03	5.56
Forestry							
Wood Fuel	Amount produced (Mt/yr) [64, 68]	298	145	305	74	4	826
	Utilization rate (%)	100%	100%	100%	100%	100%	100%
	Estimated ash production (Mt/yr)	4.46	2.17	4.58	1.11	0.06	12.34
Wood chips, particles and residues	Amount produced (Mt/yr) [64, 68]	1.0	49.8	54.1	57.8	5.7	168.4
	Utilization rate (%)	100%	100%	100%	100%	100%	100%
	Estimated ash production (Mt/yr)	0.02	0.75	0.81	0.87	0.08	2.53
Charcoal	Amount produced (Mt/yr) [64, 68]	34.2	9.2	9.0	0.7	0.04	53.2
	Utilization rate (%)	100%	100%	100%	100%	100%	100%
	Estimated ash production (Mt/yr)	2.05	0.55	0.54	0.04	0.00	3.19
Wastes and residues							
Recovered wood	Amount produced (Mt/yr) [64, 68]	-	-	0.8	26.4	-	27.2
	Utilization rate (%)	-	-	100%	100%	-	100%
	Estimated ash production (Mt/yr)	-	-	0.01	0.4	-	0.41
Sewage sludge	Amount produced (Mt/yr) [64, 69, 70]	5.9	11.2	21.0	16.8	0.9	55.7
	Utilization rate (%) [69-73]	0%	15%	25%	24%	0%	
	Estimated ash production (Mt/yr)	0	0.54	1.76	1.31	0	3.61
Municipal solid waste	Amount produced (Mt/yr) [64, 74]	302.7	550.4	1165.3	599.4	28.7	2,646.4
	Utilization rate (%) [75-81]	0%	7%	26.40%	25.80%	1.50%	
	Estimated ash production (Mt/yr)	0	10.07	83.37	41.91	0.12	135.46
Paper waste	Amount produced (Mt/yr) [82, 83]	0.2	4.7	8.6	4.7	0.2	18.3
	Utilization rate (%) [84]	54%	54%	54%	54%	54%	54%
	Estimated ash production (Mt/yr)	0.02	0.63	1.16	0.63	0.02	2.47

An estimate of the amount of wood fuel used by region was obtained from the UN forestry production figures for 2018 [64] by assuming a wood density of 425 kg/m^3 (air dry stacked log wood has a density of 350-500 kg/m^3 [68]). 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. The average ash content is assumed to be 1.5% (hardwood median 1.6%, softwood median 1.0% [22]). 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 [68]. 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 is burnt. An ash content of 1.5% was assumed for forestry residues, whereas loss of volatile wood components during charcoal production results in 75% mass loss [85], so a charcoal ash content of 6% is assumed.

Perennial bioenergy crops are widely seen as viable source of renewable energy that can contribute to climate change mitigation by substituting for fossil fuels [86, 87]. 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 [88]. 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 [15]. 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 [88]. However, there is also concern that widespread production will displace food crops [5, 87]. Global figures for perennial energy crop usage are not available, however 54 kt/yr were burnt in UK power stations in 2017/18 [89]. If the same per capital usage is assumed across Europe, it would represent ~0.2% of the amount of wood fuel burnt, and thus it surmised that the current contribution of perennial energy crops to global energy usage is small.

The quantities of post-consumer wood that are recovered in Europe and Asia are reported in the UN forestry production statistics [64]. The collection of such data implies either a market for such materials, or regulation of their disposal. In Table 1 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 recover wood and some will be used as fuel). The ash content of recovered wood is assumed to be 1.5 wt.% [22]. Overall, the estimated amount of recovered wood used as fuel is about 3% of the amount of wood fuel used, so the assumptions made to generate this estimate will have only a small impact on the ash generation figures.

The estimate of sewage sludge production around the world is based on the UN population data for 2018 [64]. 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 [69]. 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 [70]. 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 is based on data for Europe [69], U.S.A. [71], China mainland [70], Hong Kong [72] and Japan [73]. It is assumed that the ash content is 33 wt.% of dry solids [90-92]. The resulting world-wide estimate of SSIA production of 3.6 Mt/yr more than doubles the estimate published by Donatello and Cheeseman (2013) of 1.7 Mt/yr [44].

The estimate of MSW production around the world is based on the UN population data for 2018 [64] and regional MSW production rates reported by the World Bank's Urban Development and Local Government Unit of the Sustainable Development Network [74]. The average MSW incineration rate in the European Union (EU) member countries (the EU-27) [75] is assumed for Europe. The MSW incineration rate for the USA [76] is used for N. America (excluding Caribbean and Central America) and no incineration is assumed in Latin America [77]. The population weighted average incineration rates for India [78] and China [79] are used for Asia. Commercial incineration of MSW is not common practice in Oceania [80], so the overall incineration rate has been calculated by averaging the amount of incineration in Australia [81] over the entire region. No formal MSW incineration is assumed for Africa. The ash content of MSW is assumed to be 27.1% [93].

The amount of dry solids in paper sludge has been estimated from global paper production figures [82], and the assumption that paper sludge contains 4.5% air-dry solids [83]. It is assumed that 54% of sludges are incinerated (the reported rate in 2012 [84]). The ash content of paper sludge is assumed to be 25 wt.% of air-dry solids [94].

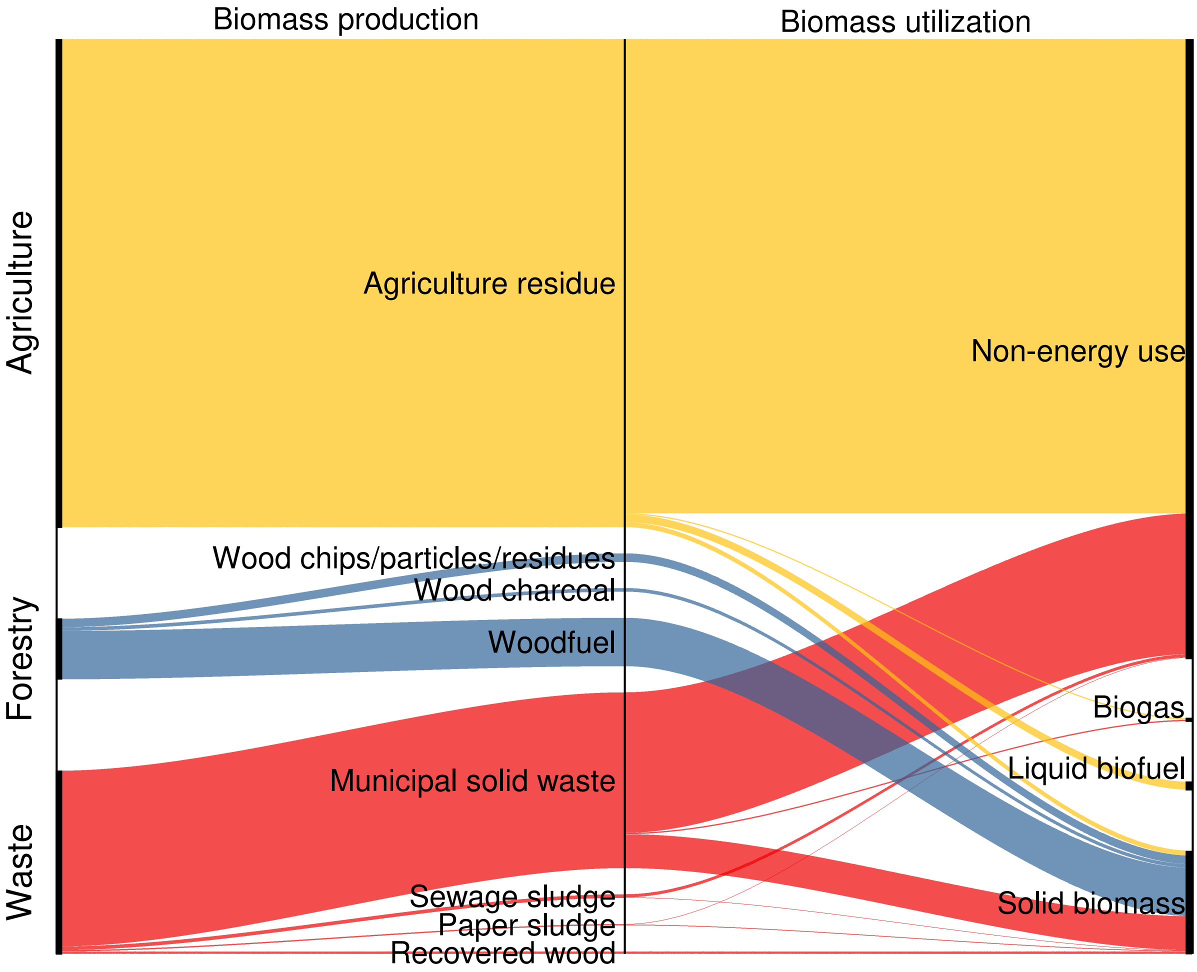

Fig. 1. Global biomass production and utilization (production is based on Table 1, and proportion of biomass used as a solid, liquid or gaseous fuel was determined from World Bioenergy Association data [3]).

Overall global biomass supply and the utilization patterns are presented schematically in Fig. 1. However, dedicated energy crops and some other wastes like animal manure and industrial waste are not shown in Fig. 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 [3].

Fig. 2 illustrates the geographical distribution of current biomass incineration and resulting ash production broken-down by feedstock category, together with the estimated maximum future amounts. The breakdown of biomass utilization by geographic region (Fig. 2a) shows that wood fuel is the main biomass feedstock used in Africa, where it is used for traditional cooking and heating [3]. 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 (Fig. 2c) differs markedly from that for fuel use due to the differing ash contents. MSW incineration is the main source of biomass ash in Americas, Asia, and Europe due to its high ash content. Currently, agricultural residue utilization is low [3], but there is great potential for future bioenergy supply (Fig. 2b), similarly there is scope for increased recovery of energy from MSW [16]. Thus, future biomass ash production is likely to be dominated by MSW and agricultural residue ash.

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.

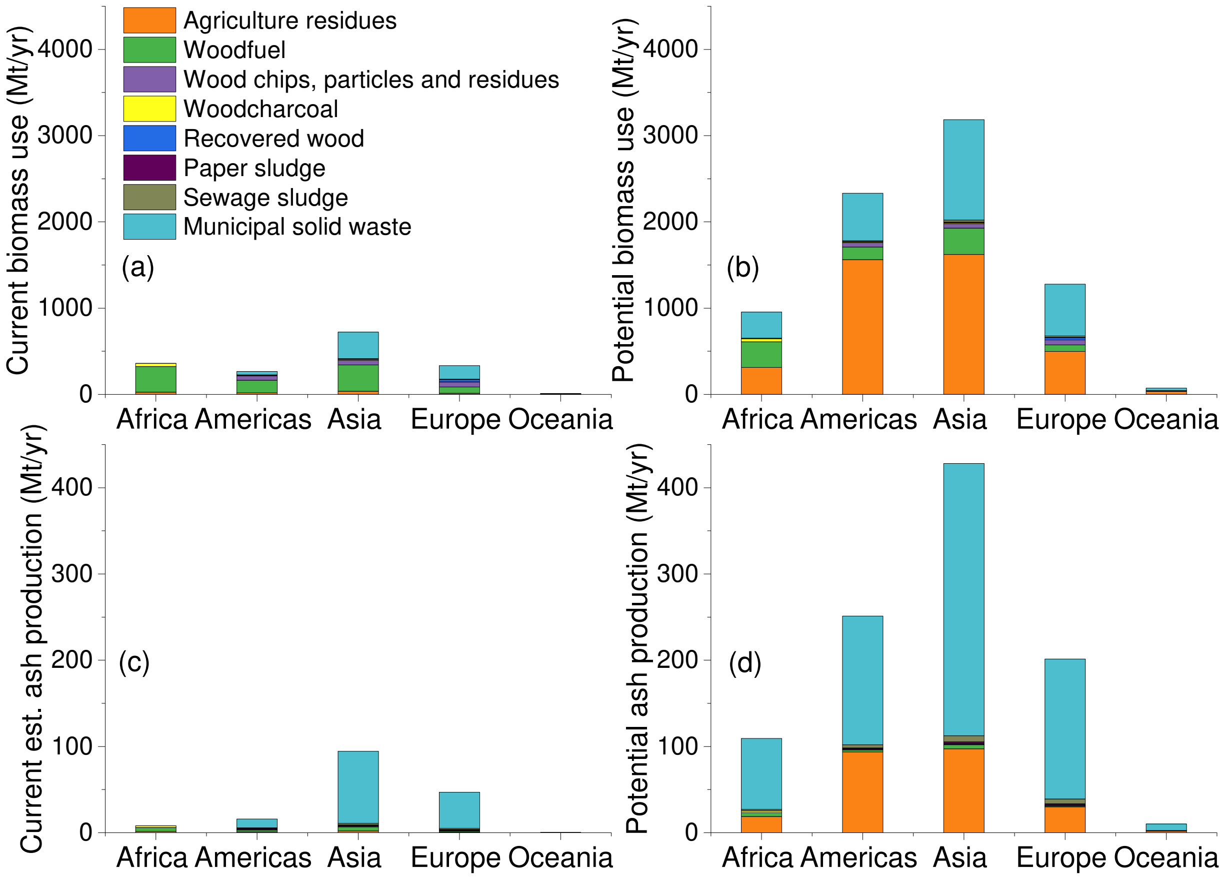

Fig. 2. Current biomass utilization level (a) and potential biomass utilization if used to maximum level (b); current estimates of ash production (c) and potential ash production (d) if used to maximum level.

3. Ash characteristics

3.1 Ash from agriculture residues

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 [3]. Therefore 13 separate reports of maize ash, 10 reports of rice ash and 12 reports of wheat ash were identified in the literature for relevant ash compositional analysis [see SI Table S1 for further details 19, 27, 28, 67, 94-109]. The mean composition (and compositional range) is shown in Table 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 [27, 94, 100, 110-115]. 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 [61, 94, 96, 116]. 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 [117, 118]).

The agricultural residues reported in Table 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 [22] 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) [119, 120].

Table 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 [121, 122], 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 [123-126]: gas phase formation at 400~800 °C [124, 125, 127], and two surface catalysed pathways that typically occur at 200~400 °C [124, 128-130]. 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 [131]. However, transition-metal species associated with the ash particles, especially copper compounds, promote PCDD/Fs formation [124, 130, 132, 133].

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 [134, 135]). 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 [136]. 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 [134]. 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 [137]. 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 (Fig. 3).

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 [129]. 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 [129]. 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 [129]) and these ashes must be consigned for disposal where PCDD/F concentrations are >1000 ng TEQ/kg.

3.2 Ash from forestry derived biomass

Current forestry derived biomass ash estimates are dominated by wood fuel ashes (~68% of global forestry ash total; Table 1). Wood fuels are sourced from tropical hardwood[1], temperate hardwood, and softwood. Therefore 10 separate reports of tropical hardwood ash [94, 138-140], 11 reports of temperate hardwood ash [94, 101, 108, 141-144] and 12 reports of softwood ash [6, 28, 67, 94, 101, 141, 145, 146] have been identified in the literature for relevant ash compositional analysis and the results are shown in Table 2. Tropical hardwood and temperate

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[1] Tropical hardwoods refer those hardwoods grown in tropical areas such as Central and South America, West and Central Africa and South East Asia.

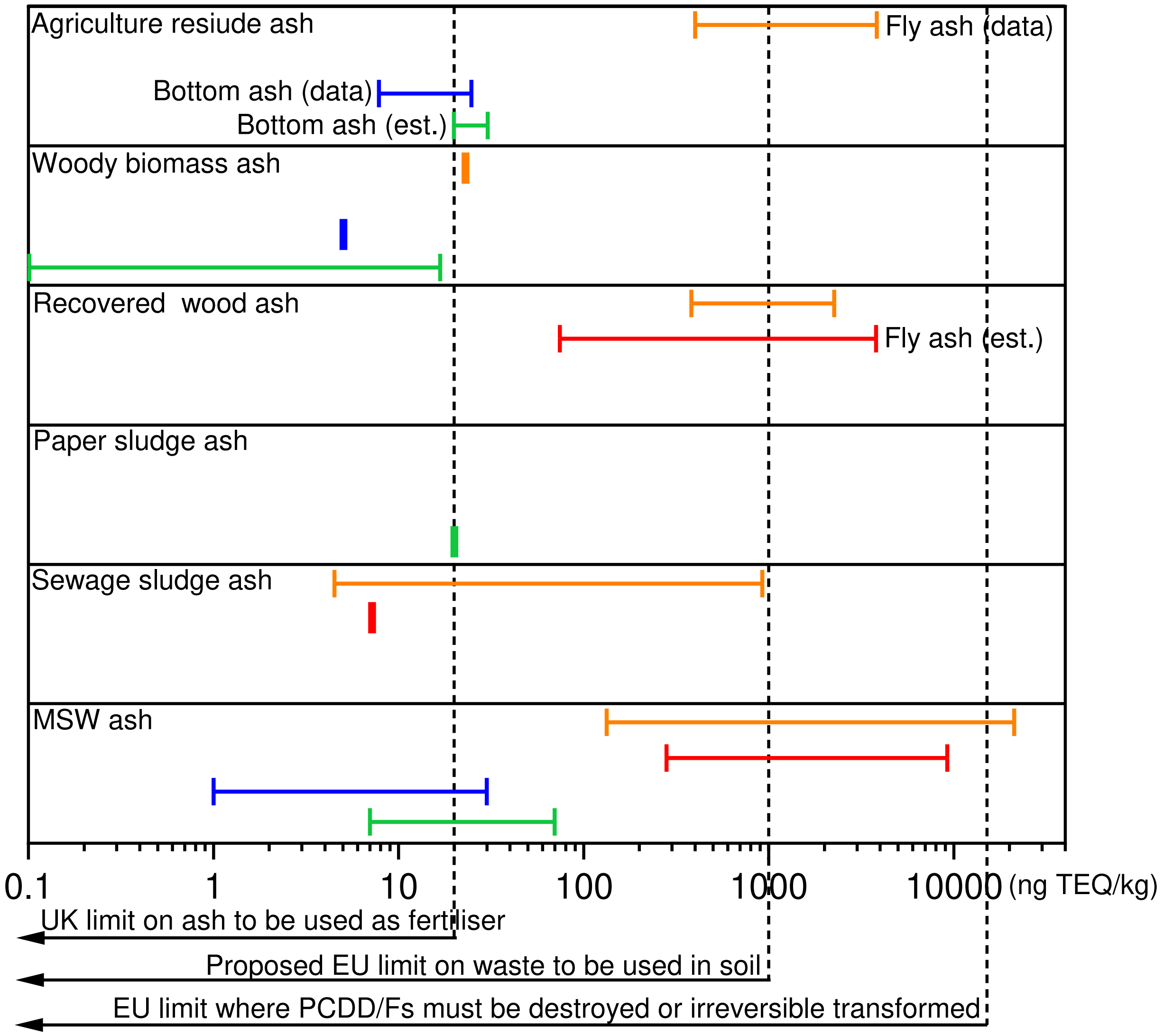

Fig. 3. PCDD/Fs content in biomass ash and current regulations on PCDD/Fs content limits for ash management (blue line and orange lines are reported values of bottom ash and fly ash, respectively [129, 147-154]; dark green lines are estimates for bottom ash (MSW and paper sludge) or combined bottom and fly ash (agriculture residue ash and woody biomass ash) [135]; red lines are estimates for fly ash [135]).

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 and SiO_2 (23%) and less K_2O (10%) (differences between hardwood and softwood ash composition have been shown to be statistically significant [22]).

Chemical compositions of ashes from temperate hardwood bark (based on 9 separate records [96, 155]) and softwood bark (6 records [96, 142]) are reported in Table 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.

Wood charcoal ash is currently estimated to make up ~18% of global forestry ash quantities (Table 1), but its ash compositional analysis is not conducted because specific data is limited. As charcoal is wood carbonized by partial combustion, and it is reasonable to assume that the final ash of wood charcoal will be similar to their parent/original wood (tropical/temperate hardwood or softwood).

Fig. 4 presents concentration of contaminant trace elements in 26 different wood/forest-residue combustion boiler ashes [156] (raw data in SI Table S2; there is insufficient published data to consider different types of wood and forestry residue separately). The Swedish limits for ash as a forestry fertiliser [120] are also shown for comparison. Generally, ash from burning of untreated wood and forest residues is thought to be relatively innocuous [38, 39, 157], and the data in Fig. 4 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

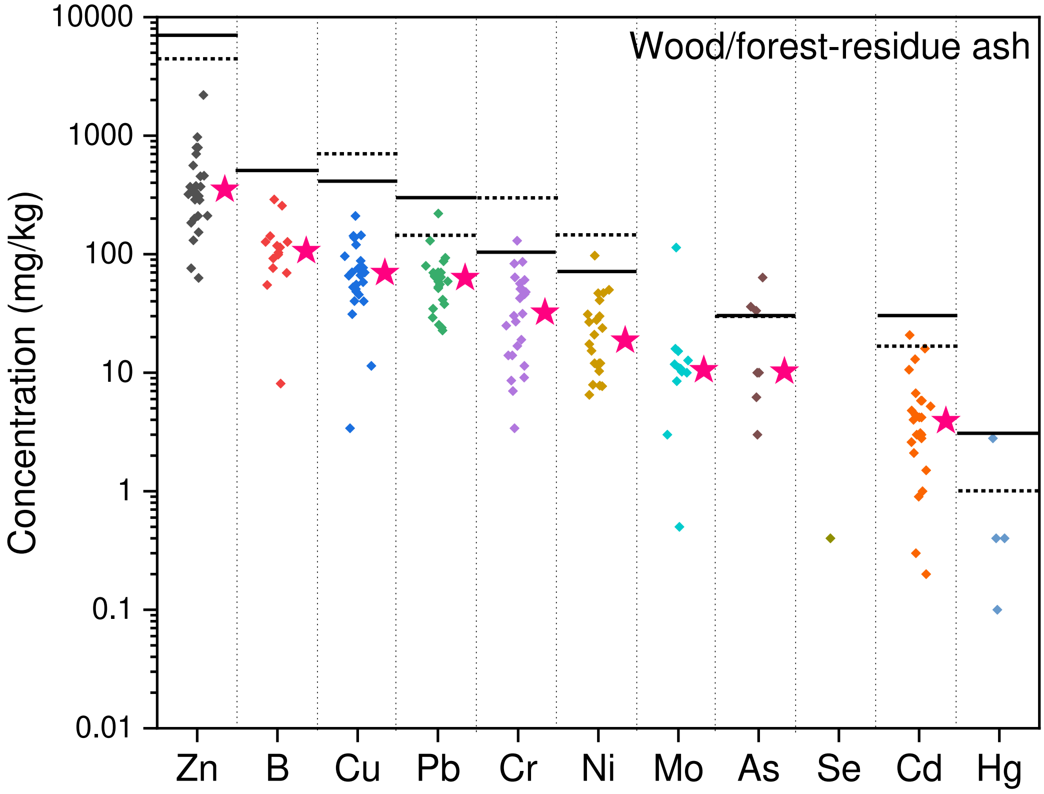

Fig. 4. Concentration of contaminant trace elements in wood/forest-residue combustion ashes ([156] and references therein). The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median element concentration (median values of Se and Hg are both zero and therefore not shown).

than those in ash from agriculture residues, which may be associated with the lower ash content of woody biomass [22].

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 [156]. 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 [129] making it suitable for fertiliser use by the same criteria applied to agricultural residue combustion ashes (see Section 3.1 above). 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 [156]. In recent years, some studies show that PAHs content in wood ash ranges from 0 (not detected) to 0.733 mg/kg [158, 159], which is within regulatory standards (e.g. in Sweden the preliminary PAHs limit is 2 mg/kg for ash utilisation as forestry fertiliser [120] and in the Czech Republic the limit is 6 mg/kg for ash reuse in agriculture soil [158]). Therefore, organic contaminants in virgin woody biomass ash are unlikely to restrict its beneficial reuse.

3.3 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 willow and poplar) are herein reviewed.

In this study, 19 separate reports of grass energy crop ash including 10 miscanthus ash [27, 94] and 9 pennisetum purpureum ash [101, 111, 160-163] have been analysed to obtain the compositional results shown in Table 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 [101, 142, 143] and 14 poplar ash [18, 101, 164, 165] have been identified for ash compositional analysis (Table 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 [94], and in total 30 separate records have been found (see SI Table S3). Just one miscanthus ash exceeded the Swedish limits for ash use as forestry fertiliser (it exceeded the limit for Cu) [120]. 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 3.2). A case study [165] 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 [120]. 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 3.1) and forestry biomass ashes (subsection 3.2) may be used as a reference for grass energy crop ash and woody energy crop ash, respectively.

3.4 Ash from wastes and residues

Globally, four biomass derived waste materials are incinerated in large volumes to recover the embedded energy and reduce their volume (Table 1). Thus, this review of biomass combustion ashes will focus on the properties of recovered wood ash, paper sludge ash, sewage sludge ash, and municipal solid waste ash.

Four separate reports of the chemical composition of recovered wood ash have been identified in the literature [20, 94, 101]. 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). 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 [39]. Recovered wood may be partially mixed with plastics and thus increase the potential of PCDD/Fs contamination of combustion ashes [166]. 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) [147]. 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 Fig. 3).

Eight reports of the chemical composition of paper sludge ash have been identified in the literature [94, 167-172]. The composition of paper sludge ash is dominated by SiO_2 (37%), CaO (26%) and Al_2O_3 (23%) (see Table 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 [156]. 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 [156].

Twelve reports of the chemical composition of SSIA have been collated [20, 41, 47, 94, 173] (Table 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%).

Fig. 5 shows the concentrations of contaminant trace elements in SSIA (full dataset in SI Table S4) [41, 47, 174-178]. 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 [120]. 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 [149]. PCDD/Fs from sewage sludge incineration have been investigated using three different sludges (two from municipal wastewater one from

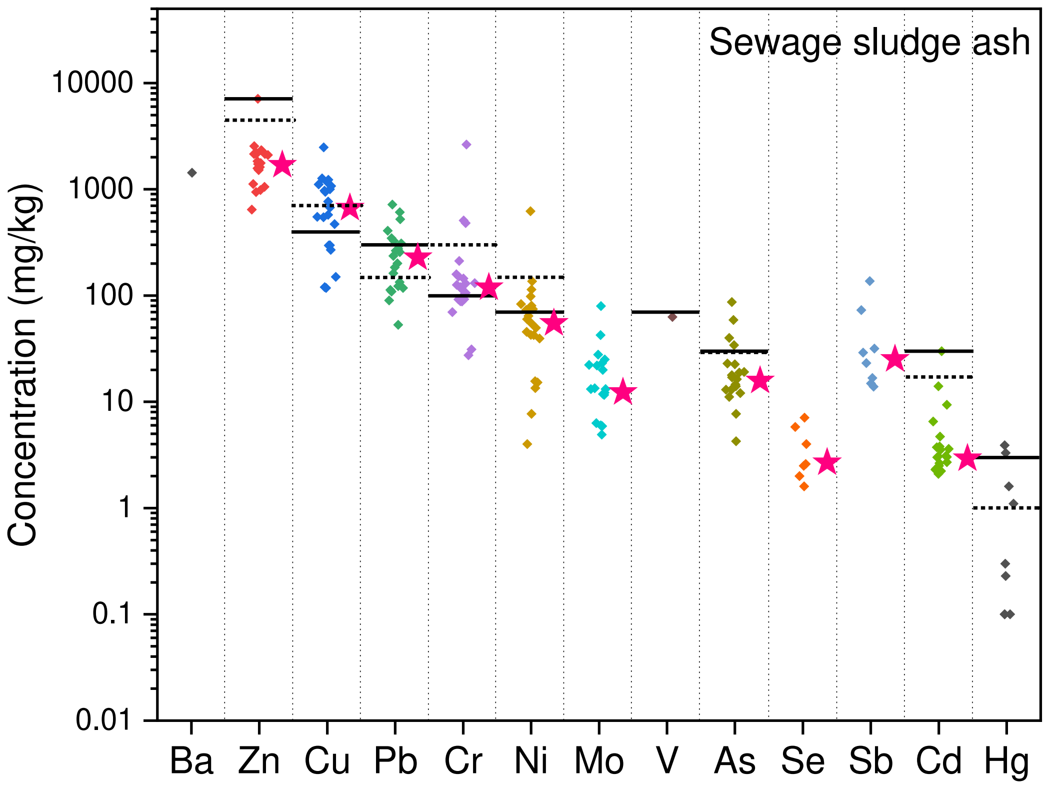

Fig. 5. Concentrations of some reported trace elements in sewage sludge ashes. The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median value: median values of Ba and V are not shown because of only one available sample; median value of Hg is zero and therefore not shown).

industrial wastewater treatment) and the filter ash contained 9 - 909 ng TEQ/kg [148] (an ash content of ~33 wt.% of dry solids of the fuel has been assumed [90-92]). Even the high value, which was for the industrial wastewater sludge and probably related to the high chlorine and copper content in this sample [148], is below the proposed EU limit on waste to be used in soil (1000 ng TEQ/kg [134]; see Fig. 3), and therefore, PCDD/Fs content in sewage sludge ash is not the main factor restricting beneficial reuse.

Data from 10 separate studies has been used to analyse the major element composition of MSW ash [20, 43, 49, 94, 179-183]. 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). Contaminant trace element concentration in MSW bottom and fly ash are reported separately in Fig. 6 (raw data in SI Tables S5 & S6) [43, 49, 179, 181, 182, 184-195]. 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 [120] (the median concentration of Hg in fly ash is just below the Swedish limit, but above the equivalent Finnish limit [119]). 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 (Fig. 6; the former are volatile at typical incineration temperatures [196-199]).

PCDD/Fs concentrations in MSW fly ash ranged from 980 to 1500 ng TEQ/kg in Shanghai [150], 780-2860 ng TEQ/kg in Taiwan [151], 140 to 18,000 ng TEQ/kg in Sweden [152], 130 to 21,000 ng TEQ/kg in Korea [153], and 1098 to 1839 ng TEQ/kg in UK [154]. 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 [134]), and sometimes exceeds the EU PCDD/Fs content limit for hazardous waste disposal in landfill, even after solidification (15,000 ng TEQ/kg [136]), and thus may require destruction or irreversible transformation of the PCDD/Fs prior to landfill disposal (see Fig. 3).

4. Biomass 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 [22], and thus slagging, fouling and corrosion within the furnace [20, 107, 200], 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.

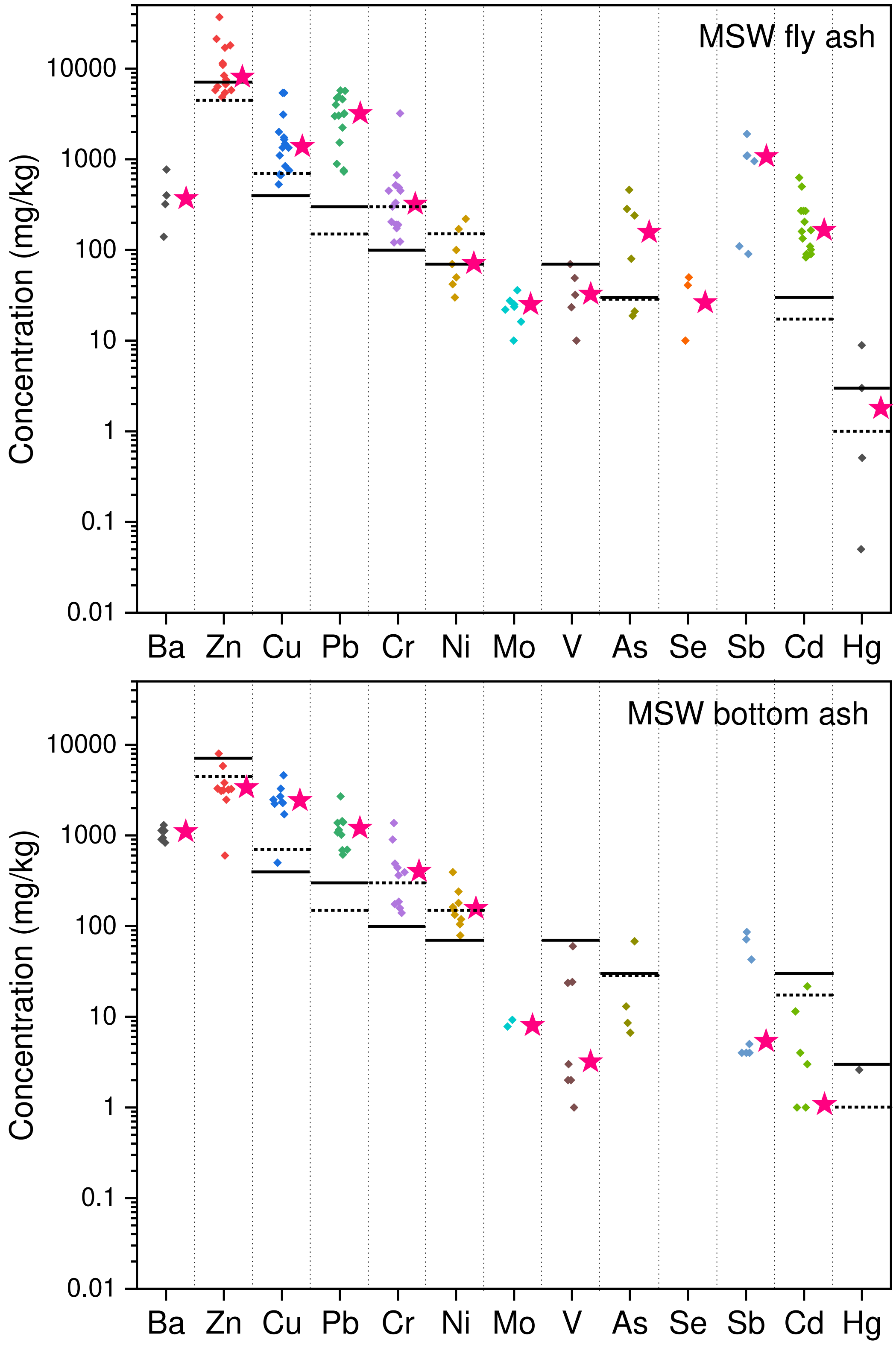

Fig. 6. Concentrations of some reported trace elements in municipal solid waste ashes. The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) for ash to be used as a forestry fertiliser are shown for comparison; ★ represents the median value: median value of As, Se and Hg in bottom ash is zero and therefore not shown).

Coal ash classification has been widely investigated and has proved to be a useful aid to ash reuse [201-204], 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 [205]. 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 [22]. 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 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 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. The mean compositions of the biomass ashes (Table 2) have been used to calculate relative abundances of CaO, K_2O and SiO_2 and thus create the ternary diagram in Fig. 7. This shows that there are compositional groupings amongst the biomass ash categories:

Table 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 Fig. 7.
- 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 [22]).

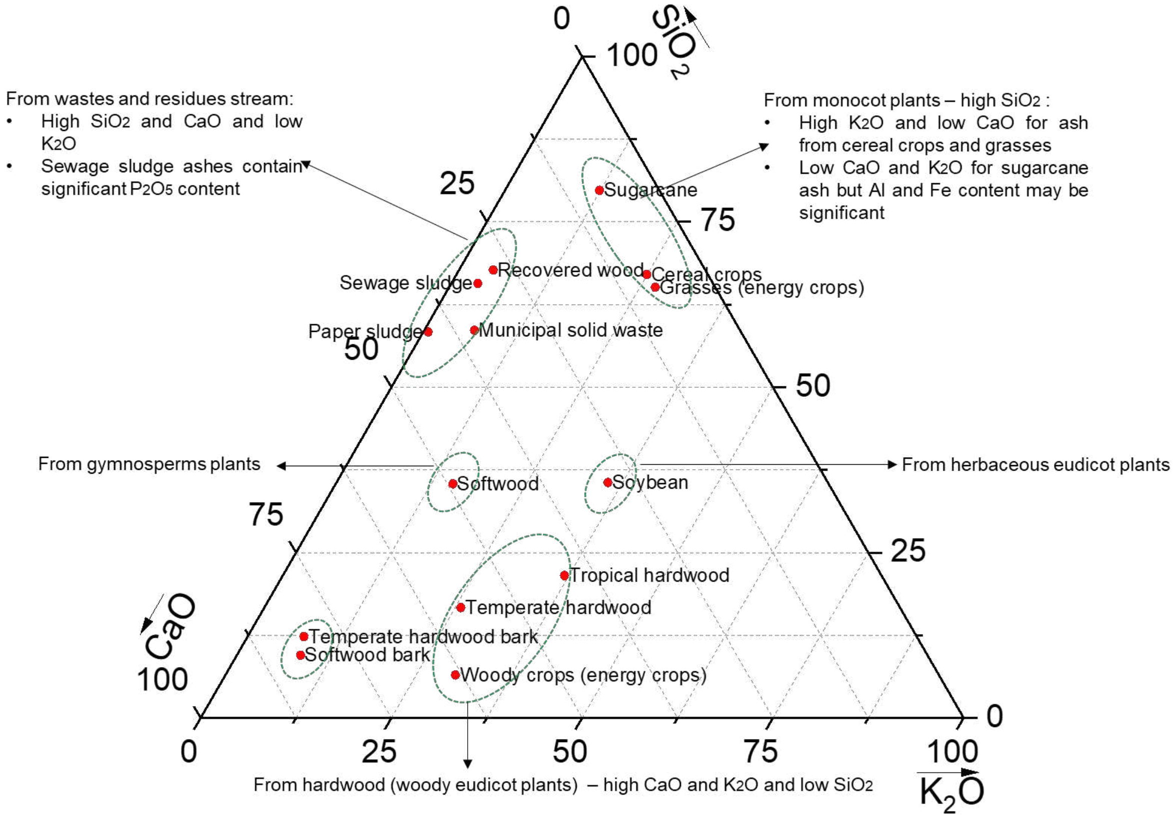

Fig. 7. Ternary diagram for the classification of biomass ash based on its CaO, K_2O and SiO_2 contents. Composition of different categories of biomass ash is based on the mean values as shown in Table 2.

- 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 Fig. 7.
- Perhaps surprisingly, ashes from disparate wastes and residues form a single group in Fig. 7. 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).

5. Beneficial 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 [206, 207]. 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 [208-210]. Ca, Mg and S can also be growth limiting in some soil types and are added to agricultural soils when required [211-213]. 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 [214] (see Table 4), but only if contaminant concentrations are acceptable for specific recovery options.

5.1 Ash from agricultural residues

5.1.1 Grass and cereal residue ashes

Ash derived from cereal crop residues is rich in potassium compounds (Table 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 [215-217]. It thus has a comparable potassium grade to commercially exploited potash deposits (from 11% to 25% in operating potash mines) [218]. 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.

Table 4. Recommend resource recovery priorities for different combustion ashes.

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.

In addition to KCl, potassium in ash can also be present as carbonate and sulphates [215-217, 219]. 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 [215], which is similar to commercial recovery of potassium from Cl bearing ores [220]. Water leaching is preferable to H_2SO_4 acid leaching, even though K_2SO_4 is used in fertiliser mixtures [221, 222], because the enhancement in K extraction is small and it may increase leaching of undesirable impurities [219]. Some challenges with water leaching of potassium from biomass ashes are: (1) unburnt carbon in ash can decrease K recovery by about 9-19% [219]; and (2) the proper disposal of residues and waste brines [216].

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 [223]. Similarly, the use of rice husk ash [224] and miscanthus ash [225] as cement substitutes, and wheat straw ash [226], rice straw ash [227], corn stalk ash [98] 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 [228, 229]. 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 [98, 224, 226, 229, 230], 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 [231], so recovery of SiO_2 from grass and cereal crop ash has also been investigated. Mesoporous silica has been recovered from miscanthus bottom ash [232]. Similarly, zeolites have been synthesised from wheat straw ash [233], sugarcane straw ash [234], and rice husk/hull/straw ash [235]. 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 [236], and meanwhile, it can capture/store atmospheric CO_2 simply by exposure to air [237, 238].

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 a 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 [231], particular as the process appears to be compatible with an initial water extraction step for K_2O recovery.

5.1.2 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). 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 [216]. 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 [230, 239, 240]. 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.

5.2 Ash from forestry derived biomass

5.2.1 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, particularly Ca, K, P, and Mg (Table 2). It also contains relatively low levels of toxic trace elements and organic contaminants (as discussed in subsection 3.2). 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 [7, 241-246]. 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 [39]. 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) [39, 247, 248]. Nutrient deficient soils, such as tropical red soils [249-251], 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 [252-254]. 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 [206, 255, 256], although the high solubility of the dominant phases in wood ash means that it will not persist in soil for long periods [257].

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 [218]. 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 [258]. 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 [259, 260]. Similarly, it 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) [261-265]. 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 [266]. However, as the unburnt carbon content of wood ashes is one of the limiting factors [262], the ash from modern commercial biomass power stations where there is careful combustion control may be more suitable than the ash used 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 [267, 268]. Surface modification, such as surface coating by alkaline metal salts or amines, can enhance the CO_2 capture ability of wood ash [236, 267].

5.2.2 Forest residue ashes

There are only very modest differences between the composition of temperate hardwood bark ash and softwood bark ash (Table 2; there is very little data for tropical hardwood ash bark). 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 [269-272]. Also, while its other principal components (SiO_2, K_2O and MgO) have value (the first as a pozzolan [273] and the other two as plant nutrients [206]), their concentrations may not make their recovery an attractive proposition, however all are compatible with application to soil [269-271].

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 [274-277].

5.3 Ash from wastes and residues

5.3.1 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) [39, 278]. 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), 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) [279].

5.3.2 Paper sludge ash

Paper sludge ash has a high CaO content (mean value 26%, Table 2) and could be used as a soil amendment via land spreading [280, 281]. Paper sludge ash also contains high silica and alumina contents (mean nominal oxide value 37% and 23%, respectively; Table 2), which can be exploited in: (1) construction materials production (which also exploits the calcium content) [282-287]; and (2) zeolite synthesis via the alkaline (NaOH) hydrothermal method [167-169, 288]. 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 [282-284] and enhanced sulfate attack resistance [283]). 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 [169], or the Si content must be supplemented [167].

5.3.3 Sewage sludge Incineration 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 [35], as it has a similar P content (typically ~14%) to commercially exploited phosphate minerals (5-40%, wt. % as P_2O_5 [42]). Also, it could be used as supplementary cementitious material due its high SiO_2 and Al_2O_3 contents (~30% and ~10%, respectively) [44, 47]. 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 [119, 120]).

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 [42, 289-294], but H_2SO_4 is 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 ($CaSO_4 \cdot 2H_2O$) [44]. Alkaline (NaOH) extraction of P from SSIA has also been attempted but recovery is lower than with HCl [295]. The challenges that remain for P recovery from SSIA by leaching are: (i) selective separation of valuable phosphorus with impurity elements like heavy metals [293]; and (ii) management of leaching residues and waste brines [44].

An alternative strategy is thermal treatment of SSIA to remove the heavy metals, so it can be used as a P-fertiliser [175, 176, 296-298]. 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 [175]; (2) potential P loss [296]; and (3) the limited removal of largely non-volatile Cr and Ni [175, 296]. Another thermal method is to treat SSIA with sodium (Na_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 [174], 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), 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 [44, 47, 299, 300]. 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 [35, 44, 301, 302]).

5.3.4 Municipal solid waste ash

Ferrous and non-ferrous metals (e.g. Al, Cu, Zn) are routinely recovered from the MSW bottom ash from energy to waste plants, leaving a material suitable for restricted use as aggregate [48, 303-309]. Several studies have shown construction materials made with bottom ash and bottom ash reuse as aggregate in pavement applications meet the regulatory standards [194, 308, 310], but an environmental risk assessment is often required before use is permitted [309]. There has also been research into exploiting the pozzolanic properties of MSW bottom ash [194, 310-313]. 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 [179, 311, 314-316]. 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 [48].

Heavy metal recovery from MSW fly ash is technically viable via thermal or hydrometallurgical methods [187, 317-319]. About 70% Cu, 80% Zn, >90% Pb and >92% Cd can be leached from the fly ash using HCl solution [49], 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 [189]. 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.) [320]. As a result APC residue is usually handled as a hazardous waste unless treated [321] (recently developed commercial treatments involve either carbonation and incorporation into a binder [316, 321, 322], or plasma treatment to extract hydrochloric acid and separate hazardous elements [323-325], to produce secondary aggregates).

5.4 Future Perspectives on beneficial management of biomass ash.

This review shows that that much has been published on the current production and properties of, and reuse options for ash derived from the common biomass feedstocks used for energy generation. However, knowledge gaps and research opportunities remain, particularly with regards to the beneficial reuse of ash. Currently industrial scale reuse of ash is limited to direct use of forestry residue bottom ash as a fertiliser/soil conditioner, and the recovery of secondary aggregates from MSW bottom ash by simple mechanical processing. The potential to use biomass ash as a pozzolan or to incorporate it into cementitious materials has been clearly demonstrated, but more research on the long-term durability of these material is needed. Looking forward, 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. Potentially, multiple valuable elements can be recovered in a sequence of compatible recovery steps, which would maximise economic return while minimise secondary wastes, but more research is required. Finally, beneficial use of biomass fly ash is currently far more challenging than bottom ash due to higher concentrations of problematic constituents. Fortunately fly ash is usually produced in smaller volumes than bottom ash, but nonetheless it should be a target for future research.

6. Conclusions

- It is estimated that about 3 Gt/yr of biomass is used globally for energy production (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, 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.
- 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 biomass feedstocks that are burnt as fuel can usefully be categorised as hardwood, softwood, grass (cereal) crop residues, non-grass crop residues, and biomass containing

wastes. The abundant nominal oxide phases (>5 wt.%) in tropical hardwood ash are $CaO>K_2O>SiO_2>P_2O_5$, in temperate hardwood ash are $CaO>K_2O>SiO_2> P_2O_5>MgO$, in the softwood ash are $CaO>SiO_2>K_2O$, and in grass crop residues are $SiO_2>K_2O> CaO$. 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.

- POPs and POP precursor molecules tend to partition to the flue gases, so fly ash (and APC residues) are likely to require controlled disposal (virgin wood fly ash may be an exception due to the low Cl content of the feedstock).

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List of Tables and Figures:

Table 1: Global estimate of biomass production rate, current incineration rate and ash production rate broken down by region.

Table 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).

Table 3. Summary of abundant chemical components of biomass ash (mean value >5%, wt. %).

Table 4. Recommend resource recovery priorities for different combustion ashes.

Fig. 1. Global biomass production and utilization (production is based on Table 1, and proportion of biomass used as a solid, liquid or gaseous fuel was determined from World Bioenergy Association data [3]).

Fig. 2. Current biomass utilization level (a) and potential biomass utilization if used to maximum level (b); current estimates of ash production (c) and potential ash production (d) if used to maximum level.

Fig. 3. 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 [129, 147-154]; 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) [135]; red lines are estimates for fly ash [135]).

Fig. 4. Concentration of contaminant trace elements in wood/forest-residue combustion ashes ([156] and references therein). The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) 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).

Fig. 5. Concentrations of some reported trace elements in sewage sludge ashes. The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) 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).

Fig. 6. Concentrations of some reported trace elements in municipal solid waste ashes. The Swedish limits (black solid lines [120]) and Finnish limits (black dotted lines [119]) 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).

Fig. 7. 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.