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Compositional variation and hazards of wood ash in Ireland

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A thesis submitted to the National University of Ireland, Cork in fulfilment of the requirements for the degree of Doctor of Philosophy.

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism.

Lucas S. Jagodzinski

Abstract

Wood energy on an industrial scale is becoming increasingly popular, not only in forest related industry where the fuel accrues as a by-product (i.e. sawmills) but also for environmental image gain in non-forestry businesses. A major selling-point is that energy from renewable fuels such as wood is supposedly sustainable. While it has been pointed out that 'true' sustainability requires the nutrient minerals in ash from energy conversion to be returned to wood fuel producing soils, this fact remains widely unacknowledged. Primary obstacle to closing the nutrient cycle and achieving sustainable status for wood energy is that ash materials are classified as waste. As per European regulation, a waste may cease to be such via end-of-waste and/or by-product status declarations from the producer. The relevant paragraphs of European regulations have been transposed into Irish law in 2011 but demonstration of compliance with the criteria therein is hampered by lack of local data on ash material composition and environmental safety of its potential after-use.

This study compiled the first compositional account of energy wastes and corresponding leachates as they accrue from ten untreated wood-fired power plants in Ireland today. Compositionally distinguished are the two principal waste-constituting ash types, bottom and fly ash as well as their leachates, from five boilers that allowed for separate sampling. A case study on a combined heat and power (CHP) wood energy model plant investigated the separate bottom and fly ashes' composition over-time. The initial samples of these ashes were examined for their quality as plant nutrient sources and their toxicological properties in an aquatic test battery. The MICROTOX test, *Pseudokirchneriella subspicata* growth inhibition test, *Daphnia magna* immobilization assay, *Lemna minor* growth inhibition and *Oncorhynchus mykiss* acute and prolonged survival tests comprised the ecotoxicological test battery. Further to this, the two ash types from the case study site were sieve fractionated and the particle size fractions tested with a small battery of MICROTOX and *L. minor*.

Some of the major findings from this study are that, from a compositional perspective, leachates are more variable than their parent solid ashes. A large part of the variability and chemical hazards observed in the wood energy waste may stem from the fly ash portion therein. Given the variability of ash, data on the composition

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of a specific wood ash cannot be extrapolated from the compiled summary of wood ashes from Ireland. However, the segregation of the ash types (bottom and fly ash) allows for higher compositional consistency and thus better predictability of the materials' hazardous as well as desired properties. The case study site ashes were variable over time, but some compositional consistency is given. Ecotoxicological assessment revealed fly ash from the case study site to be both relatively more variable and more toxic than bottom ash. Single cell organisms within the test battery were most likely to be adversely affected by exposure to ash. Measurable effects of ash on aquatic species were affected by the test regime (native leachates were more toxic than pH neutralized counterparts). Given the observed variability, a case-by-case evaluation of ashes from distinct boilers (over-time) is recommended.

Chapter 1
Introduction

Renewability versus sustainability

'Natural resources underpin our economy and our quality of life. Continuing our current patterns of resource use is not an option, as is stated by the Resource Efficient Europe Initiative (European Commission, 2011). However, efficient use of resources comprises only part of the conditions to be met in order to advance on harmonization of the needs of modern society with the natural environment. The greater goal has to be the sustainable use of resources. Currently, the ever growing energy demand is mostly met by exhausting the finite fossil fuel reserves. The transition to renewable energy sources (RES) is thus inevitable in the long-run. The European Renewable Energy Directive (2009/28/EC, European Parliament, 2009) initiated the move towards RES in requiring that 20% of all energy in the EU shall be generated from renewable sources by 2020. For example, wind energy is a renewable (in fact inexhaustible resource) form of energy that can be exploited in a sustainable manner. With other RES, such as biofuels, the question of sustainability is more complex.

Utilization of renewable resources, such as biomass, for energy generation is predicted to be one of the most important steps towards environmental protection in the 21st century (Demirbas et al. 2009). Wood fuels are a common component of the biomass fuel mix and promising energy vectors for exploitation in Ireland (van den Broek et al. 2001). The RES character of wood fuel is clear. However, for wood energy in particular, the misconception that renewable equals sustainable prevails. It has been argued that the use of (wood) biomass as fuel is currently not sustainable (Vassilev et al. 2010). This assessment is founded on the shortfall of recycling of the combustion ashes, in fact the nutrient minerals retained therein (Stupak et al. 2007; Vassilev et al. 2010). Wood ashes are known to contain nutrients and to have liming properties (Steenari et al. 1999; Pitman 2006; Augusto et al. 2008; James et al. 2012). The main obstacle to closing the nutrient cycle and achieving sustainable status for energy from biofuels such as wood is that ashes are classified as waste, more specifically 'waste from thermal processes' in the European Waste Catalogue (2000/532/EC, European Commission, 2000).

Wood ash as waste and routes to recycling

The increased use of biofuels as a component of renewable energy portfolios results in increased ash production (Thurdin et al. 2006; Kuba et al. 2008; Demirbas et al. 2009; Vassilev et al. 2010; James et al. 2012). To date, in agreement with their classification as waste, these ashes are largely landfilled (Reijnders 2005). This practice disregards the ash as a nutrient mineral resource. This is particularly striking for phosphorus which is already limited (Neset and Cordell 2012). However, caution is advised in dealing with biomass energy ashes as they may have hazardous properties (Reijnders 2005; Vassilev et al. 2010; Vassilev et al. 2013). In fact the classification as waste can be seen as a precautionary measure as some biomass ashes have been shown to contain a considerable contaminant burden (Pöykiö et al. 2009b; Vassilev et al. 2010). Römbke et al. (2009) stated that waste material recovery and after-use, if precaution-oriented, may aid the protection of natural resources, lead to the closure of element and material cycles as well as, eventually, have economic benefits.

Waste prevention and preparation for re-use (recovery) are priorities set in the revised European Waste Framework Directive (WFD, European Parliament and Council 2008). Therein, By-product (Article 5) and End-of-waste criteria (EoW, Article 6) allow for the reclassification of waste materials. When by-product criteria are fulfilled, a material ceases to be waste, the latter introduces a pathway for a waste to become a by-product under a distinct set of criteria. The EoW pathway requires a recovery operation to be passed and may thus be assumed the more precautionary approach. While basic criteria for both these re-classification pathways are set, they need to be further specified. This has already been done for a few major volume waste streams such as glass cullet or scrap metal (Villanueva et al. 2010). Considering that the various types of energy ash constitute one of the world's largest solid waste streams today (Reijnders 2005), the specification of WFD articles 5 and 6 is expected soon. Ashes and slags are regarded under 'streams used in applications that imply direct exposure to the environment'. For ashes EoW criteria are expected to involve limit values for pollutant content or leaching (Villanueva et al. 2010). The conditions guiding waste preparation for re-use (via EoW) are that the material composition is known, that the waste is clean and with low potential risk of environmental and health damage (Villanueva et al. 2010).

Wood ash in the environment

One proposed after-use of combustion residues from wood fuel is as a soil-improver (Pitman 2006; Augusto et al. 2008). Such use may counter soil impoverishment which has occurred due to removal of biomass or erosion. Particularly phosphorus (P), potassium (K) and base cations may be replenished. Guidelines for the use of wood ash in the environment exist in some European countries and have been summarized (Stupak et al. 2007; Haglund 2008). These guidelines, however, predate by-product and end-of-waste regulations in WFD and are valid in a national context only. Considering that also potentially hazardous elements and compounds are present in ash, caution has to be exercised when application in the environment is intended. A summary by Aronsson and Ekelund (2002) pointed out that ashes would best be applied in stabilized form to prevent shock effects to biota by pH or leachable hazardous substances, but that adverse effects are still likely to occur. The recommendation of the ash stabilization process is consistent with EoW-required recovery operations.

Laboratory data on the physico-chemical composition of ashes from wood fuels, and their potential toxicity (Aronsson and Ekelund 2005; Aronsson and Ekelund 2006; Stiernström et al. 2011; Barbosa et al. 2013) are still scarce. This is particularly the case for ashes from untreated wood fuels. Moreover, very little is known about the compositional consistency of wood ash, and it remains largely unknown whether the wood ash generated by a particular boiler varies across time, whether wood ash generated by different boilers is different, and whether different types of ash (fly ash and bottom ash) or different size fractions have a different composition. At present, wood combustion residues are mostly a priori classified as non-hazardous and the bulk is landfilled (Reijnders 2005). Among existing studies, one biofuel fly ash takes up a middling rather than low biological hazard rank among municipal and industrial waste incinerator ashes (Stiernström et al. 2011). Other biomass ashes from a pulp and paper industry boiler are even classified ecotoxic (Barbosa et al. 2013). Caution is thus advised in dealing (disposal or preparation for after-use) with supposedly 'clean' biomass ashes.

Aim-I

This study aims to provide local reference data on the chemical composition of the ash waste in Ireland. Currently, no data on the chemical composition of wood ash is available within the public domain in Ireland. Ash from untreated wood is expected to be less contaminated than ash from e.g. reclaimed wood (Demeyer et al., 2001; Emilsson, 2006; Koppejan and van Loo, 2012) and free of exogenous compounds. In this study, only wood energy operations burning untreated wood fuels were considered for the analysis.

Aim-II

The second aim is to provide separate compositional data for comparison of bottom and fly ash. The waste, as it currently accrues, is composed of these two ash types, which are reportedly different (Narodoslawsky and Obernberger 1996; Steenari et al. 1999; Pöykiö et al. 2009a; Park et al. 2012; Barbosa et al. 2013). Their segregation may thus yield an improvement of ash quality (hazard, liming potential or nutrient content) in comparison to the composite waste.

Aim-III

The third aim is the conduction of a case study on a modern wood energy CHP model plant. The focus for the investigations here are the properties of the separate bottom and fly ash as nutrient sources as well as hazard incurring agents. To address this aim both physico-chemical characteristics were determined, as well as toxic effects on a test-battery of model species.

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Chapter 2
Wood energy residues in Ireland; Environmental burden or valuable resource?

Abstract

Energy ashes from wood combustion are classified as waste materials in the European Waste Catalogue (EWC). As such, existing knowledge on ashes accruing at industrial sites in Ireland is often limited to waste hazard characterization mandatory prior to disposal. A local compositional record of nutrient and base cation content, significant for the assessment of potential after-use such as in fertilising or liming agents, is lacking. By merging existing databases with new analysis, this study generates the first comprehensive record of the composition of wood ash predominantly derived from combustion of untreated Sitka spruce (*Picea sitchensis*) processing residues. The material, as a waste, cannot be considered entirely non-hazardous. Arsenic and lead outliers were identified in solids, mobile selenium levels were detected above acceptable limits and shortcomings in PAH analysis practice are unveiled. The waste material, as it accrues today however fulfils basic requirements of a Phosphorus-Potassium (PK)-fertilizer and base cation source.

Introduction

Wood energy contributes to the overall target (European Renewable Energy Directive 2009/28/EC) that 20% of all energy in the EU shall be generated from renewable sources. For Ireland, this means that 16% of total energy consumption is to come from renewables by 2020. The Sustainable Energy Authority Ireland states that by 2020 renewable sources are to cover 40%, 10% and 12% of electricity, transport and heat demand, respectively (Howley et al. 2014). The utilization of biomass resources (for energy) will be one of the most important factors for environmental protection in the 21st century (Demirbas et al. 2009). The Irish government white paper on energy (DCENR 2007) specified national renewable energy targets for electricity and heat. To achieve these targets, the Combined Heat and Power (CHP) plant capacity is to be increased, and co-firing with biofuels promoted. Wood fuels are a common component of the biomass fuel mix and promising energy vectors for exploitation in Ireland (van den Broek et al. 2001).

Processed wood in Ireland mainly comprises Sitka spruce (*Picea sitchensis*). Some 53% of all forests, 59% of wood stock increment and 79% of harvested share is Sitka spruce (Forest Service 2013). This makes Ireland and its wood energy operations (often sawmills) a good natural laboratory for low variance, untreated wood fuel species. Thinning residues from working forests are ideal wood fuels since few marketing options are available for this low diameter timber. While these forest residues only play a subordinate role in wood energy in Ireland today, forecasts assume increased exploitation in the future (North et al. 2003). Similarly, by-products from the wood processing industry are good fuel candidates. In the Irish forest and bioenergy sectors wood energy ashes predominantly originate from sawdust as well as debarking and shaving residues from untreated wood. The burning of untreated (virgin) wood for energy is nationally endorsed by not being subject to EPA licensing (Office of Environmental Enforcement 2010). This is based on the assumption that wood fuels, sometimes biofuels in general, are per sé environmentally friendly. Still, major questions remain unanswered about the sustainability of wood energy especially with regard to the wood ash waste issue.

Renewability of fuels and carbon emission budgets are central aspects in bioenergy policies but the issue of accruing waste is inadequately addressed. In the Irish Draft

Bioenergy Plan (DCENR 2014), biofuel supply chain reliability is the focal aspect. The handling of combustion residues, just as relevant for environmental protection, seems neglected. Ashes are residues from thermal processes and as such fall under the remit of the European waste catalogue (EWC, European Commission, 2000). The majority of combustion residues (ashes) is sent to landfill (Reijnders 2005). Based on round wood equivalents ($1.017 \cdot 10^6$ m^3, Knaggs and O'Driscoll, 2013), density (0.39 kg·m^{-3}) and ash content (1-3%, Owens and Cooley, 2013) of Sitka spruce we estimate a production of 4000-12000 tonnes of pure wood ash in 2012). In Ireland, in accordance with European regulation (EWC), wood ash is classified as waste and is subject to licensing via permit or other, for transport, handling, processing, intermediate storage and stockpiling (Ireland 2011). Chapter 10 of EWC specifies that bottom and fly ashes as well as their mixture, generated from peat and untreated wood fuels can be considered non-hazardous wastes (absolute EWC entries). In contrast, wood ash residues accruing at recycling or waste recovery facilities (EWC chapter 19) are considered in a mirror entry 'potentially containing hazardous substances', and are thus either hazardous or non-hazardous wastes. Data on wood ash characteristics in Ireland are relatively scarce and are either the result of 'Duty of Care' regulations, confounding the non-hazardous status of the EWC chapter 10 compliant ash, or aimed to avoid hazardous waste status (UK Environmental Agencies 2013) for ashes falling under chapter 19 criteria. Different scope of these data accounts for variable extent of analyses. By default, due to competitive confidentiality, these data also usually remain within the files of producing companies and receiving landfills. As a consequence, there are no published records of wood ash composition in Ireland. Producers and potential industrial consumers are unable to bench-mark an ash in an industry-wide context, moreover, national regulatory bodies cannot advance on the issue of wood ash after-use in an informed fashion. Thus, the development of wood biofuels in Ireland to date is not in line with EU Council Directive on Waste (Council of The European Communities 2003) which states that "where waste is produced, it is to be recovered".

One proposed after-use of combustion residues from clean wood fuel is as a soil-improver (Pitman 2006). Such use may counter soil impoverishment due to removal of biomass. Reduction of overall nutrient budgets in a forest due to timber extraction ranges up to 60, 230, 30 and 290 kg/ha for Phosphorus, Potassium, Magnesium and

Calcium, respectively, over a 70 year rotation (Serup et al. 2005). Actual sustainability of wood or bioenergy needs to incorporate the entire life cycle of the fuels (Vassilev et al. 2010), the recycling of nutrients retained in ash advances this aim. This important conclusion is reflected in proposed and existing guidelines on wood ash fertilization in Europe (Emilsson 2006; Haglund 2008; Obernberger and Supancic 2009). Wood ash application on productive soils, possibly admixed to sludges, could be based on existing quality criteria for the spreading of biosolids such as sewage sludge on agricultural plots (Nilsson 1998; Anderson and Swedish Forest Agency 2007). Alternatively, non-fertilization ash applications exist (Reijnders 2005; Vassilev et al. 2013), amongst many others in construction of forest tracks or generally as earth construction agent (Pöykiö et al. 2009). In order to enable any further use of wood ash, the material either needs to be declared a by-product, or as a production residue, needs to qualify according to end-of-waste criteria to be used as secondary raw material.

Respective European by-product (Article 5) and end-of-waste (Article 6) status regulations in the Waste Framework Directive (2008/98/EC, European Parliament and Council, 2008) have been transposed into Irish law (Ireland 2011). Producers may declare a current waste material to be a by-product if four principal criteria are fulfilled. These are (i) certainty of use, (ii) applicability without further processing; (iii) accruing material being integral part of production processes and (iv) after-use is lawful and no environmental or human risk is associated (Ireland 2011). Alternatively, end-of-waste criteria may apply, (i) common use for specific purpose, (ii) existence of market and demand, (iii) technical requirements of specific purpose, legislation and product standards are met and (iv) use will not imply overall adverse environmental or human health effects. The European chemicals agency (ECHA), for instance, has registered different combustion residues enabling their marketing as Substance of Unknown or Variable composition, Complex reaction products or Biological materials (UVCB).

At present there is a gap in our knowledge of the physicochemical characteristics of wood ash generated in Ireland, a gap that impedes the development of after-use policy and practice. Therefore, this investigation set out to (i) collate existing knowledge of the composition of wood energy ashes in Ireland today, and (ii) generate a detailed dataset of wood ash composition based on 33 samples from ten

wood burning boilers. The investigation includes waste properties and linked hazard potential of wood ash, but also its nutrient content and potential recycling value.

Material and methods

Site identification

A survey of the business register (Spring 2013) for the Republic of Ireland yielded 59 businesses associated with the term 'sawmill'. Information on the operation of on-site heat generation could be obtained for two thirds of these companies. About 70% of the contacts stated that no boiler was run on their premises, 5% specified the use of oil as fuel and the remainder burned wood. Further (non-sawmill) sites were described in COFORD publications on wood energy (North et al. 2003; Serup et al. 2005). In total, we identified ten working boilers burning wood biomass (sawdust, wood and bark chips). This included board and sawmills burning on-site wood processing residues as well as non-forest industry burning purchased wood fuels. Boilers (Table 1) were of variable age (3 to 35 years) and thermal output, all featured moving grate firing technology while according to company declaration wood fuel was predominantly untreated, Irish grown Sitka spruce (*Picea sitchensis*).

Table 1: Fuel specification, manufacturer, model name, year of manufacture and thermal output of wood energy furnaces sampled within the study

Woodfuel specification	Manufacturer, build (year)	Type	Themal output
sawdust	Kara, unknown (unknown)	linear	4.85 MW
sawdust, bark, wood chips	Järnforsen, 9125 (1992)	linear	4.0 MW
sawdust, bark, wood chips	Wärtsilä, Biograte (2004)	circular	3.8 MW
sawdust, bark, wood chips	Geka, THZ (1994)	linear	11.7 MW
sawdust, bark, wood chips	Kara, min 1700 (1984)	linear	2.0 MW
wood chips	Weiss, Multicratboiler (2011)	linear	1.6 MW
sawdust	Danstoker, unknown (unknown)	linear	unknown
sawdust, bark, wood chips	unknown	linear	unknown
sawdust, bark, wood chips	unknown, unknown (1979)	chamber	unknown
sawdust	Danstoker, Multimiser (1989)	linear	0.9 MW

Sampling and analysis

Wood energy ashes destined for disposal were grab-sampled from temporal holding facilities (waste skips and silos) at seven commercial boiler installations between March and June 2013. Samples were stored until dispatch for analysis in opaque 1 L

HDPE containers in a cold room at 4 ± 2°C. Particle size distribution (PSD) of the ashes was determined in the range between 63 μm and 6.3 mm by dry sieving according to DIN 18123 (DIN 1996). Analysis of loss on ignition (LOI) by DIN 18128 (DIN, 2002) at 500 °C was performed for bulk ash samples as well as size fractions obtained by dry sieving. Chemical analysis for *aqua regia* extractable metals and metalloids from bulk solids exceeded the element requirement for waste hazard characterization laid down in Waste Acceptance Criteria on landfills (WAC, Council of the European Union, 2003). Solid contents were determined by ICP-OES after drying at 30°C and crushing to pass through a 2 mm mesh size. The standard compliance test for leaching of granular waste materials (BS EN 12457-2, CEN, 2002) was applied to determine total mobile concentrations (waste assessment relevant) as well as the mobility of these elements relative to the parent solid content. Crushed, dried samples were leached with 10 l/kg distilled water for 24 h on an overhead rolling-shaker followed by filtering and analysis by ICP-MS. The scope of leachate analysis was extended for mobile nutrients (colorimetric determination). Organic compounds were analysed by GC-FID. All analyses were performed by a certified laboratory (UKAS #0754). Methods for ash analysis undertaken as part of this study were chosen to be congruent with pre-existing analyses conducted by wood ash producing companies.

Other data sources

Existing compositional data on EWC chapter 10 wood ash waste in Ireland is limited to the 'Murphy suite analysis' (Figure 1) which encompasses a set of (i) descriptive observations such as colour, grain size and inclusions, (ii) some physical measurements such as moisture and TOC, (iii) solid concentrations of 7 PCB species (congeners 28, 52,101, 118, 138, 153 and 180, analysed by GC-MS), gasoline related organics such as C4-C12 BTEX (Methyl tertiary butyl ether, Benzene, Toluene, Ethylbenzene, m,p-Xylene and o-Xylene, analysed by GC-FID), mineral oil (C10-C40, by GC-FID) and 16 PAH species (by GC-FID) as well as (iv) pH and concentrations of 13 elements defined in WAC (Council of the European Union 2003) in standard waste leachate (BS EN 12457-2). Murphy suite waste compliance data (18 datasets from 4 sites) do not include concentrations of the 13 WAC elements present in the solid materials by default. In contrast, ash waste of some boilers is assessed according to the WM2 document (UK Environmental Agencies

2013). Main criterion here is less than 2.5 g/kg solid content of hazardous substances and by default includes analytical determination of the most toxic (2,3,7,8 chlorinated) p-dioxins and furans (HRGC/HRMS). These seven datasets from two sites or Murphy suite datasets are to accompany ash waste for its disposal and normally remain within the files of receiving landfills and the producing company. In this study, only analyses from certified laboratories (UKAS #1291, #1549 and #4225), with applied methods clearly stated were considered.
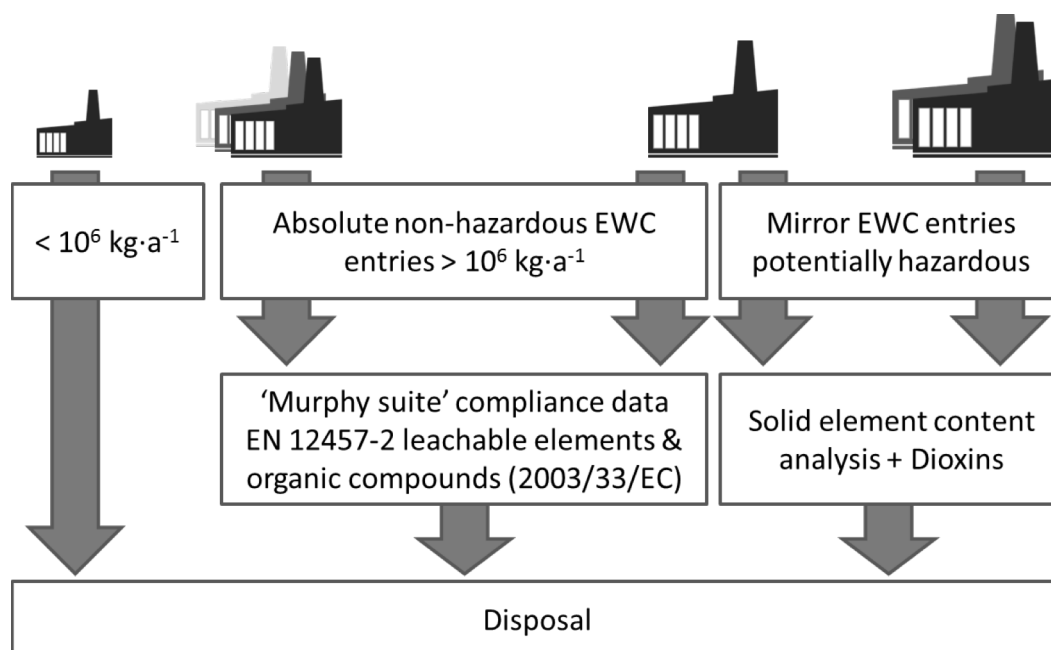
Figure 1: Sources of data and common assessment pathways of wood ash waste in Ireland; Small (no existent data) and larger wood energy operations with variable, European Waste Catalogue (EWC) classification dependent waste compliance requirements and corresponding data availability at disposal.

Data-management and statistics

Particle size distribution and ash content was determined in triplicate for the ash waste from each of the seven sites sampled in 2013. For presentation and statistical analysis of PSD and ash content (Figure 2) all replicates were pooled. No pre-existing waste data were included here because certificates of analysis did not provide the necessary detail.

Compositional data presented in this study comprise a mixture of pre-existing waste data from five sites, and data generated for seven sites including two with already existing records. Compositional data were calculated as the average with standard

deviation (SD) and coefficient of variation (CV), as well as medians with range and quartile coefficient of dispersion (QCOD) of site means in order to prevent varying number of pre-existing data points (per site) to skew the resulting 'national' average. Below detection limit results were not considered in averages, frequency of detection (FOD) is calculated as portion of successful detections. The combination of existing waste data and analyses done as part of this study, comprised a total number of 19 individual metal and metalloid analyses of solids, 26 element analyses of leachates, 18 solid concentration analyses of PCB, gasoline related organics (BTEX), mineral oil and PAH as well as seven solid content determinations of dioxin and furan compounds. Variation in ash composition (Tables 1 and 2) was determined across the average concentrations of up to ten sites. QCOD is used with larger numbers of represented sites, when data basis was limited to few sites CV was employed as only measure of spread. Relative mobility, the leachable proportion of an element's content in the parent solid, additional to leachable concentration per kg bulk ash (waste assessment criterion in WAC), was calculated for samples where both solid and corresponding leachate analyses were available. Liming capacity (CaO%) was calculated from solid concentration of Na, Mg, K and Ca (Zhang et al. 2002). Data provided by companies, was made anonymous. The Prism 5 (Graph Pad, La Jolla) package was used for plotting and determination of descriptive statistics.

As part of our assessment of wood ash properties, the following comparisons were made; (i) average to median concentrations, (ii) medians to literature values as well as (iii) averages to limit values defined in regulatory guidelines, all were based on their quotient. Where values differed by less than 5% values were considered matching. Differences of up to 25% of the numerator are considered similar while divergence above this threshold is considered disparate.

Results

Physical appearance

Some pre-existing reports accompanying ash samples for disposal (18 Murphy suite compliance datasets representing four sites) included observations providing a rough description of the sample matrix. Reported matrix descriptions state colour (black and brown: 56 and 44% of samples respectively), appearance (sand, wood and

gravel: 46, 31 and 15% of samples) and inclusions (stone, vegetation and ash/soot are most common: 56, 31 and 20% of samples). Total organic carbon (TOC) analyses stated >2 g/kg in 96% of these samples. The average reported TOC ± standard deviation (SD) for these four sites was 11.9 ± 11.9% w/w. Some of that carbon was water solvable (DOC 64.3 ± 95.5 mg/L). Apart from carbon, a great amount of solids were dissolved (TDS 6.85 ± 3.63 g/L) in standard waste leachate. The leachates from these four sites were generally strongly alkaline (pH 12 ± 0.49) and of high electrical conductivity 7.72 ± 3.27 mS/cm. Physical description from 18 pre-existing waste compliance datasets for four sites outlines the range of particle sizes in parent solid waste, as <0.1 mm for 13% of the samples, as between 0.1 and 2 mm for the majority of ashes (69%) while another 13% were stated to be coarser.

More detailed sieving analysis of waste ashes as part of this investigation (seven samples collected in 2013) showed diverse PSD (Figure 2). For different sites (i.e. boilers), average particle diameter (D_{50}) of the bulk ashes ranged from 0.1 to 1.13 mm, similar to particle size estimates from the four sites above. Overall, D_{50} ± SD across the seven sites was 0.41 ± 0.37 mm.
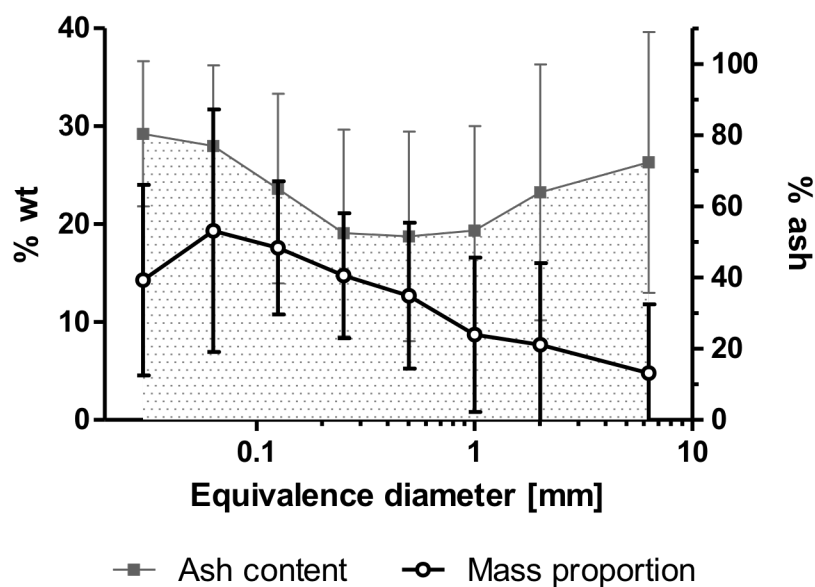
Figure 2: Size distribution of Irish wood ash waste (as disposed) between <0.063 and 6.3 mm particle equivalence diameter (% weight, left y-axis, black open circles) with corresponding ash content (% ash, right y-axis, area fill, grey squares), Average ± SD, n=7

By average weight proportion of the bulk, the >0.063 to <0.125 mm size fraction was the largest. Standard deviations for the individual fractions within PSD were

between 7 and 12%. Even higher variation among waste ash samples was found in total organic carbon (TOC). The reciprocal ash content (pure wood ash, Figure 2) was highest for particle size fractions at the margins of our analysis range (75-80%). Particles in the fraction >0.125 to <2 mm exhibited the largest content of unburned, ash-able material. The average TOC content in these seven ashes (33.3 ± 25.5%) was higher than in pre-existing data. The overall average of site means resulted as 27 ± 26.2%.

Further waste assessment relevant element composition

Potentially hazardous trace elements are present in Irish wood ash wastes (Table 2). In solids, the frequency of detection was 1 for all regarded elements apart from Sb (0.9) and Hg (0). Number of represented sites, shows that pre-existing solid analyses cover differing sets of analytes. Both solid and leachate concentrations and derived relative mobility of the elements show considerable variation. Average and median *aqua regia* extractable solid contents were determined across all ten sites (pre-existing waste compliance data as well as results obtained from analysis performed for this study). The elements Sb, Cd, Co, Mo, Se, Ag and T were present between 1 and 10 mg/kg. Cr, Li, Ni, Sn and V occurred in the 10 to 100 mg/kg band and Ba, Cu, Sr, Ti and Zn up to 1 g/kg ash.

Table 2: Trace and waste assessment relevant metal and metalloid elements in wood ash solids accruing at ten commercial sites in Ireland with leachate concentrations (BS EN 12457-2: 10 L of water per 1 kg of dry sample) from eight sites; Solid content averages with standard deviation (SD), coefficient of variation (CV), number of represented sites (n), frequency of detection (FOD) median concentrations with min to max (Range) and quartile coefficient of dispersion (QCOD); Average leachate concentrations with SD, number of represented sites and FOD

	Aqua regia extractable content [mg/kg]									Leachate concentrations [µg/L]			
	Average	SD	CV [%]	n*	(FOD)	Median	Range		QCOD	Average	SD	n	(FOD)
Antimony (Sb)	6.38	3.55	56	8	(0.9)	4.24	1.87 ..	20	0.53	22.4	19.4	6	(0.75)
Arsenic (As)	43.5	116	267	10	(1)	7.5	1.37 ..	372	0.74	19.5	16.7	4	(0.5)
Barium (Ba)	467	395	85	8	(1)	380	82.1 ..	1300	0.54	3973	3523	3	(0.43)
Beryllium (Be)	0.26	0.20	79	7	(1)	0.19	0.1 ..	0.64	0.54	<2			(0)
Cadmium (Cd)	9.86	8.2	83	10	(1)	8.6	0.408 ..	30.5	0.35	3.29	4.17	5	(0.63)
Chromium (Cr)	90.3	59.3	66	10	(1)	63	26.6 ..	262	0.44	1195	1934	8	(1)
Cobalt (Co)	9.9	7.22	73	9	(1)	7.9	3.5 ..	27.7	0.20	5.90		1	(0.14)
Copper (Cu)	173	82.47	48	10	(1)	140	73.1 ..	293	0.30	170	205	6	(0.75)
Lead (Pb)	203	412	203	10	(1)	46	7.05 ..	1339	0.65	232	345	6	(0.75)
Lithium (Li)	12.1	6.41	53	7	(1)	12.0	1.12 ..	21.3	0.21	n.d.			
Mercury (Hg)					(0)		<0.1 ..	<1		3.60	4.94	2	(0.25)
Molybdenum (Mo)	2.17	1.21	56	7	(1)	1.56	1.36 ..	4.77	0.16	171	189	7	(1)
Nickel (Ni)	29.6	16.4	55	10	(1)	22.2	10.7 ..	65.4	0.21	17.2	20.2	6	(0.75)
Selenium (Se)	5.65	3.85	68	9	(1)	5.59	1.13 ..	12	0.59	23.3	26.5	7	(0.88)
Silver (Ag)	3.57	2.75	77	8	(1)	2.71	1.26 ..	9.05	0.48	n.d.			
Strontium (Sr)	920	552	60	7	(1)	946	193 ..	1620	0.47	2483	1972	3	(0.43)
Thallium (Tl)	5.82	3.66	63	8	(1)	4.5	1.87 ..	12.8	0.32	<4			(0)
Tin (Sn)	25.2	36.8	146	8	(1)	7.04	1 ..	105	0.81	11.9		1	(0.14)
Titanium (Ti)	500	305	61	7	(1)	486	177 ..	995	0.48	46.1	38.2	3	(0.43)
Vanadium (V)	15.9	7.74	49	8	(1)	21.2	5.8 ..	35	0.45	93.1	68.8	5	(0.71)
Zinc (Zn)	893	506	57	10	(1)	960	244 ..	1932	0.44	399	483	8	(1)

* Data from up to 10 sites, number varies for FOD and differences in pre-existing analysis scope

Average solid content of Li, Se, Sr and Ti matched their median concentration, only for the elements V and Zn the average was slightly below median. More disparate average and median values were determined for Co, T, Ag, Ni, Be, Mo, Cr, Sb, Sn, Pb and As. In fact, average concentrations for As and Pb (43.5 and 203 mg/kg) were an order of magnitude higher than their respective medians (7.5 and 46 mg/kg). Highest coefficients of variation (CV) were found for Sn (146%), Pb (202%) and As (266%). Apart from these elements with highly variable content in ash, the average CV for the remaining (waste relevant) analytes ranged from just below 50% for Cu and V to 80% and more for Be, Cd and Ba.

Cr, Mo and Zn are present in all leachates, other commonly mobile elements, detectable in ash leachate of at least half of the 8 represented sites were Sb, As, Cd, Pb, Ni, Se and V. Highest average concentrations were found for Ba, Cr and Sr (3.97, 1.19 and 2.48 mg/L respectively, Table 2). Still detected above 0.1 mg/L are the metals Zn, Pb, Cu and Mo. SD associated with average leachate concentrations is generally in the range of the calculated average signifying CV around 100%. Relative mobility (% water soluble amount, data not shown) was assessed, Mo and Cr show the highest relative mobility (78.7 and 10.7%), most elements exhibit relative mobility below 10%, among those V, As and Ba showed >5% dissolution of parent solid content in water. Excluding Mo and Cr, average relative mobility was $2.81 \pm 2.86\%$. However, in all cases the relative mobility showed considerable CV (80-180%).

Nutrient and macro elements

Nutrient and macro elements (Table 3) are not usually covered by waste compliance data. However, data on Mn, Fe and B solid content were available in pre-existing data from one site. The analysis done as part of this study showed that residual carbon in seven wood energy ash solids range from 2.26 to 47.4%, the average is 24.3% and matched the median. *Aqua regia* extractable Nitrogen in ash accounted for 0.4% of ash dry weight (dw) but SD was twice as high as this value; accordingly the range in which the element can be found was wide (0.2 to 23.3 g/kg). Solid content of Phosphorus accounted for $1.33 \pm 0.58\%$ of waste ash dry weight, the coefficient of variation was the lowest among macro and nutrient elements (43.5%). Average and median content of P were matching, the average content of Potassium

(5.1 ± 3.46% of ash dw) was still considered similar to its median concentration (<10% difference). Calcium solid content displays lower average (140 ± 71.2 g/kg) than median concentrations. The QCOD of Ca concentrations was low compared to other nutrients while the range from min to max (30.2 to 233 g/kg) was the second largest after Carbon. Magnesium average concentrations matched their median. The CV for Magnesium was the second lowest in the dataset. Manganese content was by CV and QCOD most variable, the average solid content was different from the median (34% difference). Sodium made up 0.37 ± 0.21% of the ash dw and QCOD was the second lowest in the dataset. Average solid content of iron (Fe, 1.7% of ash dw) both exceeded the median values.

Fe displayed the least variation within QCOD. Solid content of the trace nutrient boron displayed, apart from N, the largest divergence between average and median (41% difference). Average calculated liming potential from solid concentration of Na, Mg, K and Ca in seven wood ashes (CaO%, Zhang et al. 2002) was 24.9 ± 12.5%; CaO% ranged from 5 to 42%. Leachable concentrations (Table 3) included waste compliance data for Chloride and Sulphate from four sites. Two of these sites could be visited during the 2013 sampling campaign; the averages from pre-existing waste compliance and own data were considered here. In waste ash leachate, Potassium and Sulphate concentrations exceeded 1 g/L. Calcium, Chloride and Sodium were present above 100 mg/L. Average leachate concentrations of these elements, apart from Na (CV 41.4%) were associated with a CV close to 100%. K was found leachable in samples of all seven represented sites, with a relative mobility of 73% (CV 116%) a substantial amount of the solid content of K was detected in leachate.

Only 0.001% of P transferred into aqueous leachate, although P was detectable in 86% of samples. In less than half of the samples (43%) orthophosphate was detected. N as nitrite and total oxidized N (NO_x-N) were found in 71% of leachates with relative mobility of 0.02 and 0.07% of *aqua regia* extractable N in the solids. Sodium leached from the same number of samples and relative mobility was the highest among nutrient and macro elements (1.23 ± 2.36%). Ca, Sulphate and B were found leachable from ash in more than half of the seven represented sites (57%). Ammonium, Mg (both at 0.01% of the solid content of the respective samples) and Fe (0.44%) were found to be mobile from ash of only one site.

Table 3: Macro and nutrient elements and compounds in wood ash solids accruing at commercial sites in Ireland (n=10) with leachate concentrations (BS EN 12457-2: 10 L of water per kg of dry sample); Solid content averages with standard deviation (SD), coefficient of variation (CV), number of represented sites (n), frequency of detection (FOD), median concentrations with min to max (Range) and quartile coefficient of dispersion (QCOD), Average leachate concentrations with SD

	Aqua regia extractable content [g/kg]										Leachable content [mg/L]			
	Average	SD	CV	n	(FOD)	Median	Range		QCOD		Average	SD	n	(FOD)
Carbon (C)	243	169	69	7	(1)	236	22.6 ..	474	0.41					
Nitrogen (N)	4.07	8.50	209	7	(1)	1.08	0.20 ..	23.3	0.60					
										NH$_3$-N	12.2		1	(0.14)
										NO$_2$-N	1.98	1.19	5	(0.71)
										NO$_x$-N	6.13	3.93	5	(0.71)
Phosphorus (P)	13.3	5.79	44	7	(1)	13.7	6.57 ..	21.5	0.33		0.91	0.85	6	(0.86)
										PO$_4$-P	1.52	0.07	3	(0.43)
Potassium (K)	51.0	34.6	68	7	(1)	46.5	5.49 ..	97.8	0.39		3095	3446	7	(1)
Calcium (Ca)	140	71.2	51	7	(1)	156	30.2 ..	233	0.27		355	408	4	(0.57)
Magnesium (Mg)	18.7	11.0	59	7	(1)	18.3	2.03 ..	32.9	0.34		20.7		1	(0.14)
Manganese (Mn)	10.5	8.34	79	8	(1)	7.86	1.98 ..	24.8	0.63		1.44	1.26	3	(0.43)
Sodium (Na)	3.72	2.14	58	7	(1)	3.09	0.40 ..	6.96	0.25		174	72.2	5	(0.71)
										Cl$^-$	315	400	9	(0.86)
										SO$_4^{2-}$	1578	1337	7	(0.57)
Aluminium (Al)	11.1	8.58	77	8	(1)	8.53	3.24 ..	28.3	0.53		3.32	3.47	7	(1)
Iron (Fe)	15.6	9.61	62	8	(1)	13.3	4.90 ..	36.5	0.17		5.49		1	(0.14)
Boron (B)	0.23	0.14	60	8	(1)	0.16	0.09 ..	0.45	0.33		5.49	4.58	4	(0.57)

Polychlorinated biphenyls, Gasoline related organics and mineral oil

Across all pre-existing waste compliance data samples (n=18, from 4 boilers) polychlorinated biphenyls (PCB) were not detectable. Limits of detection (LOD) for PCB compounds varied between analyses and were 3 or 5 µg/kg. The sum of 7 PCB species was therefore either <21 or <35 µg/kg. The sum of petroleum derivate compounds (BTEX as benzene, toluene, ethylbenzene and xylenes), was given as <24 to <30 µg/kg, though one of 18 samples yielded detectable amounts of toluene and o-xylene, 4.2 and 7.1 µg/kg respectively. LOD of BTEX varied for the different compounds between 2 and 10 µg/kg. Mineral oils with carbon chain lengths of 10 to 40 were detected frequently (in 14 ash samples from three sites, but not in ash from one site where LOD was 30 mg/kg). Average mineral oil (n-decane, C10 to n-tetracontane, C40; also referred to as Hydrocarbon Index) concentration for three sites (186 ± 253 mg/kg) was based on very variable values, individual site CV was 20, 76 and 223%. The site with the largest coefficient of variation included a sample where 'oil/petroleum' contamination was, prior to analysis, referred to in the sample description. Non site-specific calculation (n=14, number of analyses varied between 2 and 9 per site) exhibited median mineral oil contamination of 58.8 mg/kg with a range from 16.8 mg/kg to 4.25 g/kg.

Polycyclic aromatic hydrocarbons

Pre-existing waste compliance data from four sites showed that all 16 US-EPA defined polycyclic aromatic hydrocarbons (PAH) indicator compounds could be detected in ash of at least one producer (Table 4). Six compounds were found in ash from more than one site. SD was, apart from naphthalene, as large as, or larger than the calculated averages. In these data, the predominant amount of solid samples yielded below detection limit results, LOD of the individual compounds was between 8 and 24 µg/kg.

Table 4: Average concentrations of 16 PAH from four commercial wood energy installations and water leachable concentrations (BS EN 12457-2) from seven sampled waste ashes

	Solid concentrations (µg/kg)				Water leachable concentrations (µg/L)		
	FOD	Average	SD	%CV	FOD	Average	SD
Naphthalene	0.75	1768	965	55	0		
Acenaphthylene	0.75	540	770	143	0.14	0.148	
Acenaphthene	0.25	348			0		
Fluorene	0.25	797			0		
Phenanthrene	0.75	1395	1316	94	0.14	0.525	
Anthracene	0.25	710			0		
Fluoranthene	0.50	826	812	98	0.14	0.556	
Pyrene	0.50	853	797	93	0.14	0.549	
Benz(a)anthracene	0.25	1346			0.14	0.1	
Chrysene	0.50	302	404	134	0.14	0.213	
Benzo(b)fluoranthene	0.25	1250			0.29	0.394	0.3
Benzo(k)fluoranthene	0.25	411			0.14	0.119	
Benzo(a)pyrene	0.25	1539			0.14	0.285	
Indeno(1,2,3-	0.25	580			0.14	1.02	
Dibenzo(a,h)anthracen	0.25	1276			0		
Benzo(g,h,i)perylene	0.25	820			0.14	0.794	
∑16PAH	0.75	8049	9833	122			

Water leachable concentrations of PAH analysed in seven samples from 2013 (detection limit 0.02 µg/L) showed seven and four compounds to be mobile from two ashes respectively. Benzo(b)fluoranthene was the only compound leachable from both these ashes, one showed exclusively lower molecular weight PAH while the other released PAH more complex than benzo(b)fluoranthene only.

Table 5: Quality of analysis, recovery of deuterium labelled PAH surrogates across all available analyses of Irish wood ashes obtained from four producers, number of analyses per producer varied, Average ± SD, coefficient of variation, median and range.

	Average	SD	n	CV [%]	Median	Range		
Naphthalene-d8	39.0	28.3	15	73	33.6	0.36	..	93.4
Acenaphthene-d10	42.4	31.4	15	74	31.7	0.49	..	93.3
Phenanthrene-d10	17.8	26.7	16	150	4.93	0.06	..	87.1
Chrysene-d12	8.6	17.9	15	209	0.19	0.04	..	65.5
Perylene-d12	6.5	14.0	15	214	0.09	0.02	..	51.1

Striking in context of PAH solid content were the very low recovery values of deuterium labelled surrogate PAH that were used to spike samples (Table 5). Consequently, most of the 18 available, pre-existing analyses had to be considered at least partially invalid and/or inconclusive (<60% recovery). Presented average concentrations (Table 4) mainly resulted from two samples (from one site) where quality of analysis was acceptable as average recovery for the five surrogates ranged between 52 and 57%. One of these was a-priori labelled 'oil/petroleum contaminated'.

Dioxins and Furans

Analysis results for polychlorinated dibenzodioxins and furans (PCDD/F) were available for seven ash samples from two sites (Table 6, pre-existing but unpublished 'EWC chapter 19' ash analyses). In ash from one site, only 1,2,3,4,6,7,8-heptachlordibenzodioxin (1,2,3,4,6,7,8-HpCDD) and octachlorodibenzodioxin (OCDD) were detectable. Considering all available samples, 1,2,3,4,6,7,8-HpCDD and OCDD are detectable in all samples, average concentrations are 17.2 and 25.5 ng/kg with a CV of 58 and 57% respectively. In order of decreasing frequency of detection (FOD), one 1,2,3,6,7,8-hexachlordibenzodioxin (1,2,3,6,7,8-HxCDD) was detected in 4 of the 7 ashes, the other two 1,2,3,7,8,9-HxCDD and 1,2,3,4,7,8-HxCDD as well as 1,2,3,7,8-pentachlordibenzodioxin (1,2,3,7,8-PeCDD) and 2,3,7,8-tetrachlordibenzodioxin (2,3,7,8-TCDD) were detectable in 3 ash samples. Among dioxins, the International Toxic Equivalency Factor reference compound TCDD was found in low concentrations (0.73 ng/kg at 81% CV) in 3 ashes.

The most frequently found furans, chlorinated in positions 2,3,7,8, are 1,2,3,4,6,7,8-heptachlordibenzofuran (1,2,3,4,6,7,8-HpCDF) in 4 out of 7 samples from two sites as well as 2,3,7,8-tetrachlordibenzofuran (2,3,7,8-TCDF) and octachlorodibenzo-furan (OCDF) detected in half of all samples. Again, considering all available samples, TCDF and OCDF were the most variable compounds.

Table 6: Overall average of 17 (2,3,7,8 chlorinated) Dioxin and Furan concentrations (ng/kg) from two commercial wood boiler installations in Ireland, additionally all seven available analyses of these two sites specifying analysis variability

	Overall average				All available samples				
	Average	SD	FOD	n	Average	SD	CV [%]	FOD	n
2,3,7,8-TCDD	0.73		0.5	2	0.73	0.59	81.3	0.43	3
1,2,3,7,8-PeCDD	2.53		0.5	2	2.53	1.20	47.4	0.43	3
1,2,3,4,7,8-HxCDD	4.87		0.5	2	4.87	5.34	109.6	0.43	3
1,2,3,6,7,8-HxCDD	4.63		0.5	2	4.63	1.41	30.4	0.57	4
1,2,3,7,8,9-HxCDD	3.97		0.5	2	3.97	1.50	37.9	0.43	3
1,2,3,4,6,7,8-HpCDD	15.63	5.06	1	2	17.2	9.91	57.8	1.00	7
OCDD	26.13	2.16	1	2	25.5	14.4	56.5	1.00	7
2,3,7,8-TCDF	3.75		0.5	2	3.75	3.21	85.6	0.57	4
1,2,3,7,8-PeCDF	1.07		0.5	2	1.07	0.41	38.4	0.43	3
2,3,4,7,8-PeCDF	2.60		0.5	2	2.60	1.50	57.7	0.43	3
1,2,3,4,7,8-HxCDF	1.23		0.5	2	1.23	0.40	32.8	0.43	3
1,2,3,6,7,8-HxCDF	1.11		0.5	2	1.11	0.35	31.6	0.43	3
2,3,4,6,7,8-HxCDF	1.70		0.5	2	1.70	0.56	32.8	0.43	3
1,2,3,7,8,9-HxCDF	0.45		0.5	2	0.45	0.01	1.6	0.29	2
1,2,3,4,6,7,8-HpCDF	6.12		0.5	2	6.12	3.31	54.1	0.71	5
1,2,3,4,7,8,9-HpCDF	0.51		0.5	2	0.51	0.23	46.2	0.29	2
OCDF	3.52		0.5	2	3.52	4.27	122	0.57	4

The furan compound considered most toxic (2,3,7,8-TCDF) was detected in the second highest concentration (3.75 ng/kg). Total 2,3,7,8 chlorinated dioxin and furan International toxic equivalents (ITEQ) found for two sites were between 2.7 and 6.4 ng/kg (lower and upper margins), CV was 117 and 59% respectively.

Discussion

This study is the first overall record of the content of crude commercial wood energy ashes generated in Ireland. It combines pre-existing, variable scope waste assessment data from major producers (exceeding 1000 tonnes of ash per annum) and supplements these with more in-depth physico-chemical analyses of ashes from seven sites. Small and medium scale businesses are not usually obliged to provide compositional and hazard data on accruing ash wastes (Figure 1). Also, reporting of nutrient or base cation content is not common for waste, therefore this analysis and summary extend our knowledge of wood ash composition and variability in Ireland. The examined ash sample population can be characterized by the relative uniformity of burned wood fuels (Sitka spruce) but rather variable boiler size and age. Thus, the focus of this study is on chemical analysis of elemental, parent fuel borne constituents, more than the strongly combustion process related occurrence of organic contaminants.

Waste properties and compliance

A principal observation arising from this study was, that visually, wood ashes appear very diverse (i.e. colour and granulation). Boiler diversity, build and set-up are likely sources of variation in wood ash appearance, that is by changing the ratio (and indeed separation) between bottom and fly ash (Someshwar 1996; Pitman 2006; Augusto et al. 2008; Vassilev et al. 2010). Some installations are for example working with a strong stream of air blowing all ashes out of the firing chamber, resulting in large amounts of fly ash; others produce off-white, near completely combusted ashes with very low carbon residual. Brown colour appears to be associated with bulk ash samples containing <10% TOC, while ash samples described as black commonly contain between 10 and 20 but sometimes even up to 40% TOC. Ash sample appearance named 'wood' is commonly associated with a TOC >20%. Described inclusion of 'stones', most likely boiler slag (i.e. clinker, dross or scoria), generally corresponds with <10% TOC unless jointly stated with

'vegetation' (between 10 and 20% TOC). High, unburned organic matter content (7 to 50%) is a common phenomenon with commercial, industrial size boiler wood ashes (Someshwar 1996; Tollin 2000; Pitman 2006). PSD (Figure 2) shows 5-10% w/w of particles larger than 1, 2 and 6.3 mm, the majority of solids in these fractions are molten ash (slags) and lumps of char. Thus, crude ash as it accrues from wood energy generation contains impurities. These are, amongst others, combustible matter residue, sand and boiler slags or stones, distinguishing the waste ash from pure ash, as it is obtained from experimental, small scale combustions under laboratory conditions (Serup et al. 2005). 'Crude' ashes in Ireland contain only between 50 and 80% pure ash (Figure 2). Therefore, the weight of crude wood energy residues disposed on landfills may well exceed (up to a factor 2) the pure ash estimates that are based on biomass fuel dry weight.

The average TOC of Irish wood ash from pre-existing data (four sites) was 12%, our analysis suggests a higher national average TOC of 27% (nine sites represented) both attached to a CV of close to 100%. Some European countries have passed legislation which prevents waste materials exceeding TOC thresholds from being disposed of on landfills. Direct landfilling of residual organic matter contained in ash, apart from unutilized energy content and larger waste volume, seems not objectionable at first. However, a TOC remainder points at incomplete valorisation of the fuel. Thereby leachable elemental contaminant concentrations as well as the absolute content of these elements may deviate from what is expected from a pure ash. Moreover, incomplete combustion and occurrence of organic contaminants are positively linked (Sinkkonen et al. 1995; Wunderli et al. 2000). In Denmark, for example, ash with TOC larger than 5%, needs to pass a <3mg/kg total PAH criterion (Pitman 2006) when spreading is intended. On average, dissolved organic carbon levels in Irish wood ash (data from four sites) do not violate EU WAC criteria for non-hazardous waste (800 mg/kg dry substance at 10 L/kg solvent ratio, Council of the European Union, 2003). However, the large CV of 149% and higher average abundance of TOC combined with alkaline pH reported here suggest that some ashes might. For the same four sites, the total dissolved solids criterion (60 g/kg) is surpassed by average TDS concentrations measured in Irish wood ash leachate (6.85 g/L in a volume of 10 L total leachate per 1 kg of ash waste). Acceptable DOC and TDS limit values are not compound specific, the hazard or potentially beneficial nature of these

mobile burdens needs to be characterized to reach a reasonable verdict on the wood energy ash wastes subject to this study.

Elemental contaminants

The study tracked the concentrations of substances of concern and priority hazardous substances (Parliament and Council of the European Union 2001) in wood ash solids as well as water leachable proportions. Elemental solid composition of Irish wood ash is, with a CV generally over 60%, quite variable. This aspect is consistent with findings for trace and heavy metals reported by Someshwar (1996) who studied 26 wood ashes in the US. Largest CV (up to 200%), were found for Hg, Se and Mo in that study (Someshwar 1996), the analysis was based on sample sizes of 9, 1 and 12 respectively. Even larger variation (CV) was found for Sn (146%), Pb (202%) and As (266%) in Irish wood energy ash waste (n=10) presented here. This is despite being derived from relatively uniform, untreated wood fuel species. Average and median disparity found for a range of elements in this study signifies outliers with unusually high or low concentrations. The ratio between bottom and fly ash as well as boiler size, build and age are likely to entail this variability. However, contaminations of wood fuel or deviations from untreated fuel type cannot be excluded entirely.

To assess the environmental burden of Irish wood ash we interpreted elemental composition in the context of (i) hazardous waste status (WM2, UK Environmental Agencies, 2013), (ii) EU sewage sludge quality guidelines (Council of the European Union 1986), (iii) earth construction agent threshold concentrations (Pöykiö et al., 2009), (iv) the range of solid elemental concentrations in wood ash from a meta study (Augusto et al. 2008) and (v) WAC leachate criteria (Council of the European Union 2003). These five criteria are to cover waste, land application and backfilling as well as allowing for variability comparison; a prominent sub-set of European criteria that apply to waste streams.

    (i)   British technical guidance on hazardous waste status

The upper acceptable limit (2500 mg/kg content of hazardous substances, whereby element concentrations are transformed to represent the common oxides that are predominant in ash) is violated by a single sample of ash waste from only one of ten sites. This ash contains a total of 4775 mg/kg of As, Cr, Co, Pb and Zn oxide

equivalents and certainly classifies as hazardous waste. It is noted that this wood ash arose from a recycling facility (EWC chapter 19 ash) that could not be visited in 2013, and that data were pre-existent but unpublished. Relatively low concentrations of PAH (mg/kg, Table 4) and PCDD/F (ng/kg, Table 6) are unlikely to affect the crude sum of hazardous substances after metal and metalloid compounds have been considered. It is concluded that the majority of Irish wood ash wastes are not hazardous waste according to the WM2 technical guidance document. Nevertheless, caution needs to be exercised as organic contaminants may still cause biological effects.

(ii)   European sewage sludge for land application quality guideline (86/278/EEC)

Apart from the ash sample identified as hazardous waste (above, according to British technical guidance document), thresholds for metals in sewage sludge, defined in annex I B of the Council Directive (Council of the European Union 1986) are well above *aqua regia* extractable concentrations detected in Irish wood ashes. A historic example of long term organic (sludge), char and ash waste use, are the highly fertile anthropogenic terra preta soils. However, suitability of modern sludge, pyrolysis and combustion residues in this fashion remains debatable. Like ash, sewage sludge is a high volume waste containing nutrients; admixture for application or beforehand pelletized fertilizer production have been tried (Nilsson 1998; Anderson and Swedish Forest Agency 2007). Sludge, however, already contains heavy metal elements and admixture to wood ash may lead to higher sum concentrations, closer or possibly exceeding acceptable limits. Interactions of sludge and ash matrices however may decrease their individual effect on drainage water quality (Sajwan et al. 2003). Maximum detected concentrations of Cd in Irish wood energy waste are closest to the defined limits (86/278/EEC) representing 75% of the allowable threshold. Zn, Pb, Cu and Ni content range between 40 to 15% of the upper limits. Was wood ash to be considered like sewage slugde here, ash from 9 out of 10 sites would comply with the set limits.

(iii)   Finnish earth construction agent guideline

In Finland, ash may be used in the construction of roads, cycling paths, pavements, car parks or sport fields if compliance to earth construction agent limits is given.

When Irish wood ashes are compared with these limit concentrations (Poykio et al 2009), Cd, As and Pb limits (15, 50 and 300 mg/kg respectively) are exceeded by two distinct samples out of 19 for each element. Average and median concentrations for Irish wood ash calculated for 10 sites however do not surpass set maximum concentrations. Non-fertilizer, earth construction application would thus be acceptable for most of the ashes investigated here.

(iv)   Common range of element concentrations in wood ash

The elements Cd, Cr, Co, Cu and Zn in Irish wood energy waste have higher medians than common in wood ash (Augusto et al. 2008), the reported common range is exceeded by maximum values found in this study. Median As, Pb and Mo concentrations in Irish wood energy ash waste, in contrast, remain below literature values, here determined ranges are smaller but contained within reported intervals. Thus, Irish wood ashes may, while largely suitable for earth construction according to Finnish legislation, still (by median) contain more than usual amounts of some elements. In addition, exceedance of maximum reported ranges exhorts caution.

(v)   European criteria for waste acceptance on landfills

Waste acceptance criteria for landfills (WAC, Council of the European Union, 2003) defined for inert, non-hazardous and hazardous waste represent the basis for leachable component assessment in wood ash. Fuel ash, due to its large proportion of inert substances, was stated to be a suitable inert material for fluidized bed combustion boilers (North et al. 2003). The general assumption of ash as being inert (in the context of waste) is deceptive as ashes may not be particularly reactive but may still leach considerable proportions of elements considered environmental risks. Further to potential DOC and definite TDS limit violations discussed for four sites with pre-existing data earlier, average selenium leaching surpasses WAC of non-hazardous wastes at two sites and for a total of 11 of 26 individual samples. Based on physico-chemical parameters and elemental content we conclude that some wood energy ashes, as they accrue today, could be classified hazardous, but variability suggests that this is not necessarily the case.

Organics

The seven indicative PCB compounds considered within Murphy suite waste compliance analyses do not seem to be present in measurable concentrations in Irish wood ash. Despite their enrichment in the environment in the past, there seems to be little transfer into growing trees and no noteworthy abundance in wood ashes in general (Pitman 2006). Petroleum associated compounds (BTEX, C4-C12) were only detected once, underlining that these compounds are uncommon in Irish wood ash. In contrast, the hydrocarbon (oil) index representing mineral oils was detectable in nearly all samples. This index mainly represents linear carbon chains (C10-C40) that are not considered particularly harmful but mineral oils may contain other lipophilic toxicants. Their common presence in ash may arise from lubricants, minor amounts possibly from formation of bio or pyrolysis oils during combustion (Zhang et al. 2007).

Polycyclic aromatic hydrocarbons, substances of high molecular mass, are found in ash when fuels and primary flue are not sufficiently burned out (Enell et al. 2008). In accordance with findings from Sweden (Johansson and van Bavel 2003) and despite insufficiencies of PAH analyses of wood ash in Ireland (Table 5), structurally simple naphthalene and phenanthrene were detectable in most ash samples (Table 4). PAH mobility, as well as detectability, in standard soil analysis (ash is mostly treated as such) may be reduced by matrix properties such as organic matter and char residuals (Rey-Salgueiro et al. 2004; Pérez-Gregorio et al. 2010). Difficulties in surrogate recovery during PAH analysis point at strong interactions with the sample matrix (Rey-Salgueiro et al. 2004). We assume that PAH content is masked, possibly by binding to the char content of ash. While PAH are not considered persistent organic pollutants (POP) and may, over time be decomposed, we still consider the inconclusive analysis, even in case of 'safe' disposal on landfills, a possible risk for the environment through leaching or other possible dislocation events. European WAC left PAH limit values to be determined by the member states. The range of allowed concentrations in materials granted permission to be landfilled varies greatly (between 20-100 mg/kg) between, for example, Austria and Ireland or the UK. Below detection limit results may, in case low surrogate recovery is overlooked, be interpreted as low concentrations. However, this is not necessarily the case and clarification on actual PAH content of Irish wood ashes is needed. However, some

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authors have stated that PAH input in to soils due to wood ash recycling remains below the substantial levels generated in prescribed burning or fire clearing, and that ecosystems evolved detoxification potential (Enell et al. 2008).

Dioxins and Furans are POP. The few available analyses suggest the omnipresence of at least some of the 2,3,7,8 chlorinated, most toxic compounds of the group (Table 5). A marine influence on the climate for wood growth on the island of Ireland, as outlined for European wood combustion residues in general, may increase dioxin and furan abundance in fly ashes and soot (Someshwar 1996; Pitman 2006). Thus, the presence of these compounds in waste ashes seems inevitable. Cumulated ITEQ of ashes from untreated wood are reported to be commonly below 10 ng/kg (Wunderli et al. 2000) which is confirmed by available data presented here. Noteworthy in this regard is that PCDD/F analyses were only obtainable for ashes from two sites which also exhibited low organic matter residual. We acknowledge the bias of relatively low sample size and insufficient overlap with the data presented here (where TOC remainder was higher). We conclude that the fragmentation of knowledge on organic contamination presents a major barrier for the development of recycling of wood ashes in environmentally sensitive applications such as liming or fertilizing agents.

Nutrients and fertilizer suitability

Essential for the development of wood ash after-use as soil amendment in Ireland is the confirmation of its nutrient content. The literature supports the feasibility of the recycling strategy (Pitman 2006; Augusto et al. 2008). However, the nutrient yield of ash derived from close to exclusively Sitka spruce is, to our knowledge, and particularly for crude ashes has not yet been described.

The primary nutrient element N is normally volatised during combustion of fuels and virtually absent from ashes (Pitman 2006; Augusto et al. 2008; Obernberger and Supancic 2009). Thus, presence of N is a good indicator for undesired insufficient burn-out and use of fuel (and consequent presence of PAHs). Although N compounds are crucial for biota, we consider ashes to be an inappropriate source because of the presumed organic contaminant burden associated with its presence. Other, non-volatile nutrient elements though may be exploited. Irish wood energy ash contains 4 times more phosphorus (Table 3) than the common median concentration of 3 g/kg that was determined in a meta-study of 151 observations

(Augusto et al. 2008). Both minimum and maximum P concentrations found in the current study also slightly exceed the published range. Pitman (2006) cites P contents between 0.8 and 2.8% for generic wood ash and softwood bark ash respectively. These P levels are similar to those reported in this study (1.33 ± 0.58%). Low mobility of P and phosphate in water is supposedly due to its likely apatite mineral form in ashes (Reijnders 2005; Pitman 2006; Augusto et al. 2008). Potassium content in Irish wood ash is also relatively high, compared with concentrations reported in a large, international meta-study dataset (Augusto et al. 2008). The range of concentrations we determined for Irish wood ash, though, is contained within the published interval. The review by Pitman (2006) again, places Irish wood ash K concentrations just above generic wood ash content but below softwood stem and bark ash. Tree species specific ash element content for Norway spruce (*Picea abies*) cited in Pitman (2006) are much lower than values for generic wood ash or softwood ashes, which are the basis for comparison here.

Minimum nutrient contents demanded in existing and proposed guidelines for wood ash application (Emilsson 2006; Haglund 2008; Obernberger and Supancic 2009) are satisfied. Ca, K and Mg requirements are surpassed by average and median solid concentrations of these elements in Irish ash. Average and median content of P and Zn in crude Irish wood energy ashes is even twice as high as the guidelines from Sweden and Finland demand. Thus, Irish wood energy waste is a resource and may serve as a PK-fertilizer and base cation source. Maximum allowable values are defined for elements of concern, which includes Zn. Out of ten listed elements, maximum admissible concentrations for six (B, total Cr, Hg, Ni, V and Zn) are not surpassed by either average nor median values determined for Irish wood ash. As and Pb average concentrations in Irish wood energy ash waste exceed defined limits (20-40 and 100-300 mg/kg respectively), however median concentrations comply. Further compliance issues exist for Cd and Cu, where average and median values in the Irish ashes tested exceed the strict limit values from Germany (defined for bottom ash).

Average calculated liming potential (CaO%) was 24.9%, concurrent with the range of 10-30% common for waste ashes (Zhang et al. 2002). The minor contributors K and Na show a high relative mobility, only 1.29% liming potential may be lost due to leaching.

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The Irish case

The endorsement of wood and biomass for heat and electrical power generation in Ireland is in line with European renewable energy targets. The next step has to be a recycling strategy for accruing ash wastes to comply with the recovery dictum and to approach actual sustainability (i.e. closure of mineral cycles) of biomass energies. By-product regulations state that a material must be suitable for after-use as it accrues. We identified high As and Pb outliers, leachable Se, large quantities of readily dissolvable compounds, low reliability of PAH content determination and largely lacking knowledge of PCDD/F burden make a general by-product classification of wood energy waste, as is today, premature. The use of wood energy waste as secondary raw material under application of end-of-waste criteria seems more reasonable as recovery operations may alleviate the contamination issues. Currently prevailing wood ash waste management strategies are, at least in part, based on 'dilution' of fly ash (low quantity, comparatively burdened) with bottom ash, which accrues in greater amounts and is generally less contaminated (Narodoslawsky and Obernberger 1996). A separate assessment is needed to clarify the actual hazard and resource potential of the major ash fractions. Different recycling pathways may, even with ashes from largely clean biofuel, be necessary to account for distinct ash fraction properties (Vassilev et al. 2013).

Conclusion

Wood energy ashes accruing in Ireland today are variable. This compendium of all known, available data provides a needed basis for comparison of ashes produced in the geographic area. However, the constituting fractions of these ash wastes have to be more closely investigated as they pose a likely source of wood energy ash waste variation. Particular attention should be dedicated to mitigation of As, Pb and Se contents, more reliable analysis of PAH, Dioxin and Furan contamination. Nutrient and base cation content clearly confound the resource character of the current waste and at least some Irish wood energy ashes show properties suggesting application and recycling in the environment with beneficial outcome is possible. Finally, biological hazard assessment, potentially in a case-to-case manner, is needed to support the transition of wood energy ashes from waste to resource.

Acknowledgements

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Chapter 3
Wood ash residues cause of mixture of growth promotion and toxicity in *Lemna minor* (L.)

Abstract

Wood ash contains high amounts of plant nutrients such as phosphorus, potassium, calcium as well as several micronutrients. In this study the growth enhancing properties of Sitka spruce (*Picea sitchensis*) wood ash were contrasted with its toxic action. The growth of common duckweed exposed to wood bottom and fly ash solids and corresponding leachates was assessed in ultra-oligotrophic and eutrophic media. For purpose of comparison to standard waste toxicity data, ash solids and leachates were also tested as neutralized preparations. Suspended ash solids improved *Lemna minor* growth up to concentrations of 2.5-5 g/L. Leachates promoted growth up to 10 g ash equivalents per litre, but for bottom ash only. Beneficial effects of ash were most pronounced on ultra-oligotrophic medium. Severe inhibition (EC_{50}) of *L. minor* biomass and frond growth by fly ash was observed in nutrient deficient (12-18 g/L), standard (18-22 g/L) and neutralized standard media (37-61 g/L). Higher doses of bottom ash were required to incur that level of growth retardation in ultra-oligotrophic and eutrophic media (35-50 g/L) and in neutralized standard medium (70-95 g/L). It is argued that phytotoxicity is due to the elemental composition of the ash, its alkaline character, and possible interactions between these two factors. Growth promotion is due to the substantial content of plant nutrients. Thus, the margin between growth promoting and toxicity inducing concentrations can be enlarged through ash neutralization. This study underlines the importance of the receiving environment (nutrient status and pH) in determining the balance between toxicity and growth promotion.

Introduction

The increased use of biofuels as a component of sustainable energy portfolios, results in increased ash production (Demirbas et al., 2009; James et al., 2012; Kuba et al., 2008; Thurdin et al., 2006; Vassilev et al., 2010). Ash residues remaining after combustion of wood and/or other types of biomass in power plants are highly heterogeneous and consist mostly of inorganic mineral matter (amorphous to crystalline), smaller amounts of char and organic mineral solids, as well as fluid to gaseous inclusions of both inorganic and organic matter (Vassilev et al., 2013). In order to prevent the accumulation of large amounts of wood ash, numerous potential after-use options for these complex materials have been proposed and are practised. *Inter alia*, these include the use of ash for soil amendment and fertilization, production of construction materials and sorbents as well as element/mineral recovery (Vassilev et al., 2013). Notwithstanding the valuable plant nutrient content of ash, the bulk of biomass energy ashes is still defined as waste and often landfilled.

Minerals contained in biomass ashes originate from bio-accessible sources. Thus, returning such ashes to the original ecosystem can be considered a form of re-cycling. It has been argued that ash from untreated biofuels (as opposed to timber treated with paint and/or other preservatives) poses a comparatively low contaminant risk to the environment (Demeyer et al., 2001; Emilsson, 2006; Koppejan and van Loo, 2012). However, the chemical composition of biomass ashes can be extremely variable and depends, amongst others, on biomass source and origin (Pitman, 2006; Vassilev et al., 2010). Some biomass ashes have been shown to contain a considerable contaminant burden (Pöykiö et al., 2009; Vassilev et al., 2010). Wood ash may contain contaminants such as lubricants (machinery or spills), metals (abrasion/scrap) or silicon (sand) as well as residues of intentionally introduced compounds such as wood preservatives. Therefore, neither the fertilising-value nor the environmental innocuousness of wood ash can be assumed without case evaluation.

Modern biomass and solid fuel fired power plants accrete two major residue fractions; bottom ash (BA) and fly ash (FA). Additional precipitation techniques (i.e. cyclone or bag filters) allow for further partitioning of the FA. Even though

the different ash types accrue in separate parts of the furnace, the waste streams are commonly combined and both ashes are collected in a single waste bay. As a result few studies distinguish the two prime ash types (Park et al., 2012; Poykio et al., 2011; Steenari et al., 1999). Rather, the literature on wood ash composition and recycling describes either the composite material (Augusto et al., 2008; Demeyer et al., 2001; Etitgni and Campbell, 1991; Pitman, 2006; Someshwar, 1996), or just one ash fraction (Aronsson and Ekelund, 2006; Pöykiö et al., 2009; Steenari and Karlfeldt Fedje, 2010). Data on both the toxicity and growth promotion potential of these distinct types of ashes from clean (i.e. un-treated) wood fuel are scarce. Such data are important to inform policies for the recycling of clean wood ash (i.e. see Emilsson and Swedish Forest Agency, 2006; Haglund, 2008).

Exposure of terrestrial organisms to the potentially toxic components of ash depends on their distribution within the soil, and on interactions with soil solids. Weathering, transfer but also re-adsorbtion of ash compounds within soils largely depends on dissolution in water. The ecotoxicological assessment of solid waste materials commonly involves testing this mobile fraction, for example water based leachates (Barbosa et al., 2013; CEN, 2002; Jenner and Janssen-Mommen, 1993; Lapa et al., 2002; Tsiridis and Samaras, 2006; Wadge and Hutton, 1987). Such leachates may naturally occur following heavy rain and flooding and represent a worst case scenario of ash components being leached into downstream habitats. The testing of native, suspended, solid material in an aquatic environment, though likely with such events, is often neglected. Given the complexity of ash, dissolution of compounds from the residue may not be the only property determining its environmental effects. Mineral, as well as organic matter from ash, have been shown to adsorb and precipitate dissolved elements and compounds (Chirenje et al., 2006; Chojnacka and Michalak, 2009).

Standard aquatic toxicological testing has been used to quantify wood ash impacts on a range of species (Barbosa et al., 2013; Stiernström et al., 2011). However, standardised testing with photoautotroph models (i.e. plants and algae) is based on the premise of supplying non-limiting nutrient levels in media, which will therefore nullify any growth stimulating effect of ash. The additional use of a nutrient-poor medium allows the assessment of such growth stimulating (i.e.

fertilizing) properties. The alkaline pH of wood ash creates a further dilemma for ecotoxicological assessments. The validity of standardised toxicological test results is typically conditional upon the pH being within the defined range of the test organism tolerance. Therefore, the pH of non-neutral waste extracts is commonly adjusted to pH 6-8 (Lapa et al., 2002; OECD, 2006; Römbke et al., 2009). This practice is inadequate when assessing the toxicity of ash to be reintroduced to the natural environment, as any pH dependent risk will be underestimated, while pH dependent changes in solubilisation and speciation may be promoted (Barbosa et al., 2013).

This study set out to assess growth stimulating and toxic effects of clean wood ash on the model plant *Lemna minor* (L.). The study assesses these effects under different trophic conditions, using both native and pH neutralized solid ash and ash leachate (Figure 1), to generate a comprehensive overview of the impacts of ash recycling on this plant species. Results will be discussed in the context of recent wood ash recycling recommendations.

Material and Methods

Characteristics of wood ash and corresponding leachates

Origin and sampling
The wood ash used in this study was collected in May 2011, directly from the conveyors of a 3.8 thermal MW rotating grate wood boiler, located at a commercial sawmill in Co. Cork, Ireland. The wood-fuel comprised a mixture of Sitka spruce sawdust, wood chips and bark shavings (sawmill wood processing residues) which was burned at 700-800°C. The wood burned in the boiler was sourced locally in south-west Ireland. Bottom ash (BA) accrues below the firing grates at the base of the boiler. This type of ash contains heavy, large constituents such as clinker agglomerates and chunks of char in addition to small, powderous particles. Fly ash (FA) was collected from the post-furnace filter system where it had been transported with the flue gas. In contrast to bottom ash, fly ash consists of powderous, light weight ash and small char particles. Ash samples were stored in opaque 50 L barrels (HDPE, with clamp top lid) in a sheltered area at outside ambient temperature.

Physico-chemical analyses

Particle size distribution of bottom and fly ash was analysed in the range between 63 μm and 6.3 mm by dry sieving according to DIN 18123 (DIN, 1996). Analysis of loss on ignition (LOI) at 500 °C was performed for bulk ash samples following DIN 18128 (DIN, 2002). Ash sub-samples for each replication and leachate were dried at 30°C for 3-4 days until the weight remained constant, and the particle fraction > 4 mm was removed. Leachates were prepared according to the EN 12457-2 one stage leaching test for granular waste (CEN, 2002) at 10 l/kg water ratio, with 24 h contact time and filtering (Fisherbrand, FB 59031). Fresh leachates were applied in bioassays. Titration of ash leachates was performed with 0.02 N H_2SO_4 to pH 4.

Chemical analyses of bulk solids (*aqua regia* extractable elements) and corresponding leachate (water leachable elements and nutrient compounds), biological (BOD) and chemical oxygen demand (COD) were performed by UKAS accredited ([#]0754) National Laboratory Services (NLS, Leeds, UK). Total metal and metalloid content was determined by ICP-OES from *aqua regia* digested reflux extractions, water leachable concentrations were detected by ICP-OES or MS.

Growth inhibition test with *Lemna minor*

Lemna minor Linnaeus (Asimatales, Araceae) is an aquatic macrophyte with close to ubiquitous distribution. This species is commonly used in single substance phytotoxicity tests (OECD, 2006) as well as water quality assessment in wastewaters and leachates (Jenner and Janssen-Mommen, 1993; Mackenzie et al., 2003). *L. minor* is furthermore described as a sentinel species for ash settling ponds of coal fired power plants (Dorman et al., 2010). The pH optimum of *L. minor* growth is 6.2, the species tolerates conditions between pH 3-4 and 10.5 (McLay, 1976). *L. minor* single frond lifespan is reported to be 31.3 days during which period it asexually produces daughter fronds (Lemon et al., 2001). A 7 day exposure can be considered acute to sub-chronic. Axenic specimens were from University College Cork, School of Biological, Earth and Environmental Sciences laboratory stocks. These stocks originated in the Blarney area of southwest Ireland. *L. minor* was cultured in half-strength Hutner's medium

(Lahive et al., 2011) in 1 L crystallizing dishes (Pyrex) covered with watch glasses. Growth medium was renewed every two weeks and the laboratory culture stock was continued from a sub-sample of its precursor. Culturing and bioassays were conducted using a 16/8 h photoperiod (light intensity of 50 μmol m^{-2} s^{-1}) at 22 ± 2 °C.

Growth inhibition assay

Growth inhibition tests with *L. minor* were conducted following OECD guideline 221 (OECD 2006) recommendations. Effects of solid ash (i.e. ash suspensions) and ash leachates on plant growth were tested, using a medium of either half-strength Hutner's or distilled water (Figure 1). Solid ash suspension gradients were prepared by pouring medium onto the appropriate weight of dry ash sample (particles >4 mm excluded) followed by a 24 h maturation period. Leachate test solutions were obtained as dilutions of fresh ash leachate in Hutner's medium (with appropriately reduced water content) or distilled water; concentrations are expressed as ash equivalents per litre (g aeq/L). Test suspensions and leachates compliant with the pH 6-8 guideline criterion (neutralized) were prepared by adjusting the medium to pH 6.1 ± 0.7 using H_2SO_4, after 24 h contact with the solid sample. Measurements of pH (resolution 0.001) in the test medium were taken at the beginning and the end of the 7 d experimental period while electrical conductivity (ElC, resolution 0.1 μS/cm) was determined after the test (Multi 3420 SET G, WTW). Exposure vessels were 300 ml magentas (HDPE) with punctured lids and cotton wool plugs. Clean test vessels were autoclaved prior to being filled with the test dilutions and suspensions and afterwards to ensure batch sterility.
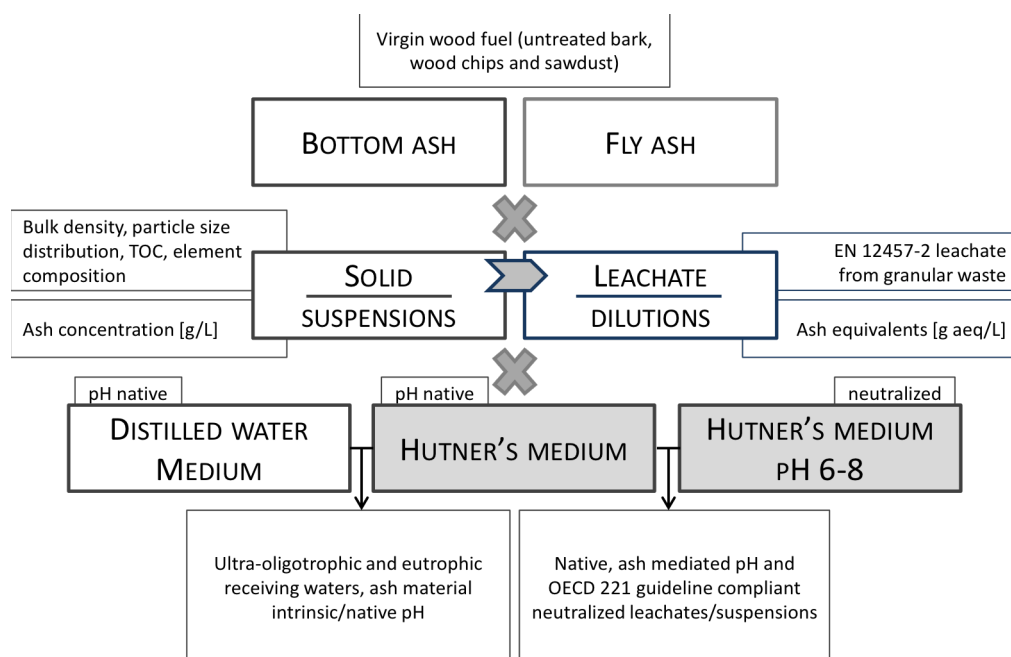
Figure 1: Test design; Biomass (fresh weight) and frond (number) growth rates tested in gradients of wood ash preparations under ultra-oligotrophic, eutrophic (nutrient medium) conditions, and eutrophic at set pH; 2 wood ash solids × 2 preparations (suspension and leachate) × 3 exposure conditions × 4 replications

Calculations and statistics

Ash NPK content ratios were calculated as %wt of elemental N and assuming all P and K were present as P_2O_5 and K_2O respectively. Enrichment factors for solids (EF_S, $[FA]\cdot[BA]^{-1}$, Pöykiö et al., 2009) were calculated as ratio between fly and bottom ash *aqua regia* extractable solid concentrations. Likewise, enrichment factors for leachate (EF_L, $[FAL]\cdot[BAL]^{-1}$) were based on BS EN 12457-2 extract concentrations (Table 1). These measured concentrations represent a tenth of total water soluble amounts and relative element mobility was calculated as ratio of total soluble amount in 10 L to *aqua regia* extractable concentration per kg.

Biological endpoints of the *Lemna minor* exposure studies (Figure 1) were average specific growth rates (OECD, 2006) for biomass fresh weight and frond number after 7 days. Statistical analysis was performed with Graph Pad Prism 5 (Graph Pad Software, La Jolla, USA). For plotting in Figures 3-4, *L. minor* growth in each replication was normalized to the average growth rates in the controls (half-strength Hutner's medium, SD shown as grey band). In ultra-oligotrophic medium, the ash treatment exhibiting the best growth response was

used for normalization and calculation of EC_{10} and EC_{50}. Significant difference to the controls for No Observed Effect Concentrations (NOEC) and Lowest Observed Effect Concentrations (LOEC) determination in each experiment were tested by one-way ANOVA with Dunnett's post-test (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$). The number of replicates per treatment was 4-5 with twice the amount of control vessels, total count of experimental units was 384.

Results

Physico-chemical characteristics

Ash solids

Fresh bulk samples of bottom ash had a density ($\pm$ SD) of 0.64 ± 0.07 g/cm^3, 3-fold higher than flue gas borne fly ash (0.23 ± 0.02 g/cm^3), a difference that is a result of the collection of BA in a water trough. Consistently, dried ashes had a more similar bulk density (BA; 0.27 ± 0.04 g/cm^3 and FA; 0.21 ± 0.001 g/cm^3), and this material was used for all further experiments. Levels of combustible matter residue in fly ash (LOI $44.7 \pm 1.84\%$) were twice as high, but less variable, than in bottom ash ($25.1 \pm 4.05\%$). The average particle diameter of BA was 0.91 ± 0.08 mm, whilst FA was much finer (0.19 ± 0.01 mm). Gravel sized particles due to ash melting (>2 mm) were exclusive to BA. Removal of clinker and dross (>4 mm sized fractions, 15% of bottom ash), strictly a combustion product and not ash, resulted in a rather similar particle size distribution. The sieved material was used to determine elemental content and biological impacts.

NPK content of both ashes was similar, yet the N-P-K ratios (%wt) of bottom ash (0.1-2.7-6.9) were slightly smaller than of fly ash (0.2-2.8-8.6). Macro element content was similar, and enrichment factors (EF_S) varied between 0.75 and 1.25 (Table 1). Only Fe and Al displayed relative enrichment as they were 2-fold more concentrated in BA than in FA. Plant micro nutrients were present in both ash types although Cl, Zn, B, Mo were enriched in fly ash while Fe, Cu, Mn and Ni tended to present in higher concentrations in bottom ash. Among non-essential trace elements, Ba showed a strong enrichment in bottom ash (EF_S 0.06), while the heavy metal elements Co and Cr were slightly more abundant in

bottom ash. FA, in contrast, contained relatively higher amounts of Cd
(EF_S 5.99), Pb, As and Se (EF_S 1.39).

Ash leachates

Bottom ash leachates (BAL) exhibited both a lower pH and conductivity (pH
10.6 ± 0.18 and 3.56 ± 2.3 mS/cm) than those of fly ash (pH 11.5 ± 0.11 and
12.7 ± 6.43 mS/cm). Titration to the pH 4 yielded two equivalence points for
bottom ash, BAL required 0.006 meq H_2SO_4/ml for titration to pH 7. Fly ash
leachate (FAL) exhibited only one equivalence point and required 3.7-fold more
sulphuric acid to neutralize. BAL had a greyish brown tint, FA aqueous eluates
were clear. Biological Oxygen Demand (BOD) was <1.4 mg/L for both
leachates. Chemical Oxygen Demand was very similar for the two types of ash
(46.2 ± 19.6 mg/L and 49.7 ± 1.26 mg/L in BAL and FAL respectively),
although variability was a magnitude higher for bottom ash leachates.

No ammonical N was detected (< 0.5 mg/L) in either ash leachate. FAL
contained at least 6-fold more total oxidized nitrogen (TON, Nitrate and Nitrite)
than leachate of bottom ash (Table 1, EF_L). Orthophosphate was detectable only
in BAL (2.3 mg/L). In terms of elemental composition the difference between the
leachates was striking. BAL was enriched with P (EF_L 0.04), Mg, V (EF_L
0.25), As, B (EF_L 0.39) and Cu. Fly ash leachate contained relatively more K
(EF_L 4.47), Ca (EF_L 36.6), Zn, Al, Sr, Ba, Se, Ti, K, Cr, Mo, Pb, and Na than
BAL. Particularly noteworthy is the observation that FAL contained 620 times
more Zn than BAL. Finally, saliferous chloride (EF_L 11.1) and sulphate (EF_L
13.9) concentrations in fly ash leachate were more than an order of magnitude
greater than those in bottom ash leachate.

Relative mobility of elements (Table 1) was different for the two ash types. Some
21.3 and 23.1% of K and Na, respectively, were leached from BA into BAL. In
comparison, 76.6 and 57.4% of K and Na, respectively, leached from FA into
FAL. Other particularly mobile elements in bottom ash were B, V, As, Cr, and
Se. Strongly mobile elements in fly ash were Cr, Ca, V, B, Ba, Sr, Se and Zn. Mo
was entirely transferred into solution in the case of both ashes.

Table 1: Element analysis of wood bottom and fly ash solids and corresponding BS EN 12457-2 leachates (100 g ash extracted with 1 L distilled water) with relative mobility and enrichment factors in the solids (EF$_S$) and leachate preparations (EF$_L$); TON: Total Oxidized Nitrogen (NO$_2$ + NO$_3$), Average ± Standard Deviation (SD), n=4, no SD when analyte detected only once.

	Bottom ash	Bottom ash leachate	Relative mobility	Fly ash	Fly ash leachate	Relative mobility	EF$_S$	EF$_L$
	g/kg	mg/L	ppm	g/kg	mg/L	ppm		
N	0.66 ± 0.24			1.72 ± 0.18			2.62	
NH$_3$-N		<0.5			<0.5			
NO$_2$-N		<0.1			0.63 ± 0.01			6.32
TON		<1			6.98 ± 0.19			6.98
P	11.8 ± 1.34	1.87 ± 0.39	1583	12.4 ± 0.49	0.08	61	1.05	0.04
PO$_4$$^{3-}$		2.19 ± 0.22			<0.5			0.23
K	57.2 ± 9.73	1217 ± 306	212855	71.1 ± 3.48	5445 ± 320	765823	1.24	4.47
Ca	113 ± 11.5	11.9 ± 4.46	1052	98.0 ± 5.3	437 ± 280	44636	0.86	36.6
Mg	16.5 ± 1.86	1.65 ± 0.08	999	15.7 ± 0.67	<0.3	<191	0.95	0.18
Na	4.32 ± 0.54	99.9 ± 16.6	231192	3.70 ± 0.06	212 ± 12.4	574425	0.86	2.13
Fe	11.1 ± 0.97	<0.03	<27	5.05 ± 0.10	<0.03	<59	0.45	
Al	13.4 ± 1.61	0.03 ± 0.03	25	6.32 ± 0.13	1.96	3104	0.47	58.1
Mn	11.9 ± 1.27	0.02	14	10.5 ± 0.44	<0.01	<10	0.88	
Cl		111 ± 41.3			1243 ± 20.8			11.2
SO$_4$		297 ± 12.4			4133 ± 92.4			13.9
	mg/kg	µg/L	ppm	mg/kg	µg/L	ppm		
Sb		5.12 ± 1.43			<20			
As	2.66 ± 0.15	23.4	87887	5.44 ± 0.05	8.05	14798	2.04	0.34
Ba	1228 ± 64.0	19.2 ± 4.19	157	72.9 ± 12.0	247 ± 116	33938	0.06	12.9
Be	0.35 ± 0.03	<20	<566572	0.16 ± 0.02	<20	<1277955	0.44	
B	105 ± 6.28	2015 ± 430	192042	192 ± 1.71	789 ± 901	41147	1.83	0.39
Cd	1.62 ± 0.13	0.19	1146	9.67 ± 0.25	<2	<2069	5.99	
Cr	19.0 ± 1.91	81.7 ± 17.4	42930	14.0 ± 0.60	254 ± 21.0	181900	0.73	3.11
Co	8.75 ± 0.59	1.04	1189	6.24 ± 0.17	<20	<3208	0.71	
Cu	84.0 ± 26.0	8.89 ± 3.89	1058	76.5 ± 1.3	4.26 ± 0.31	557	0.91	0.48
Pb	11.5 ± 1.53	<2	<1743	38.5 ± 0.90	4.45 ± 0.29	1156	3.35	2.22
Li	12.1 ± 1.10			7.40 ± 0.31			0.61	
Hg	<0.2	<0.01	<500	<0.2	<0.01	500		
Mo	<1	104 ± 24.9	<1041000	1.68	243 ± 43.5	1447917		2.34
Ni	17.0 ± 1.26	<1	<589	12.9 ± 0.21	<10	<7737	0.76	
Se	3.01 ± 0.68	8.53	28362	4.18 ± 0.75	99.5	238181	1.39	11.7
Ag	<1			1.41				
Sr	817 ± 83.5	73.2 ± 21.0	896	725 ± 83.5	1858 ± 1013	25649	0.89	25.4
Tl	3.95	<1	<2532	4.23	<10	<23641	1.07	
Sn	1.45	<2	<13793	1.72	<40	<232558	1.19	
Ti	719 ± 49.5	8.15 ± 1.03	113	290 ± 24.6	78.1 ± 12.5	2691	0.40	9.58
V	18.6 ± 1.49	183 ± 13.2	98522	10.9 ± 0.24	45.5	41935	0.58	0.25
Zn	325 ± 25.2	5.29	163	1833 ± 58.0	3296 ± 2191	17989	5.64	623

Lemna minor bioassays

Electrical conductivity and pH conditions in the test

Electrical conductivity (ElC) of native ash suspensions in distilled H_2O and Hutner's media differed due to the base electrical conductivity of the nutrient medium itself (1.66 ± 0.16 mS/cm). However, the difference in ElC between ultra-oligotrophic and eutrophic test solutions decreased as ash concentration was increased (Figure 2A, D). The difference in pH values of ultra-oligotrophic and eutrophic medium was substantial and related to the buffer capacity and the slightly acidic pH 5.01 ± 0.28 of Hutner's medium. The difference in pH values decreased with increasing pH value. Suspensions of fly ash in oligotrophic or eutrophic medium displayed consistently higher pH and ElC than respective bottom ash suspensions. BA and FA leachates had similar effects on ElC and pH as ash solids. Notable was that the increases in ElC and pH caused by supplementation with leachate were smaller than those caused by the equivalent mass of suspended solids (Figure 3A, D). To determine potential pH effects on toxicity, medium was neutralised at the start of the experiment. During the 1 week exposure, both solids and leachates facilitated a drift of test solution pH towards the alkaline, and this was most pronounced with suspended solids. ElC of neutralized suspensions and dilutions of neutralized leachates in Hutner's medium (Figure 4A, D) displayed the same ash dose dependent increase as their respective native counterparts.

Lemna minor growth on native ash solids and leachates under differing trophic conditions

Suspended bottom ash solids

When suspended in Hutner's medium, bottom ash concentrations of 1.25, 2.5 and 5 g/L neither impaired nor benefitted the growth of the test organism relative to the corresponding control (Figure 2B, C). However, BA concentrations of 40 g/L ($p < 0.05$, LOEC) and above ($p < 0.001$) significantly decreased biomass growth rates. EC_{10} and EC_{50} for biomass growth rate were 10.1 g/L and 50.9 g/L (95% CI: 33 to 78.5 g/L, Table 2), respectively. The LOEC for frond growth was lower

than for biomass growth (20 g/L, $p < 0.05$) but EC_{10} and EC_{50} values were similar.

When cultured under conditions of extreme nutrient scarcity (ultra-oligotrophic medium), *L. minor* biomass average growth rates were just $38.5 \pm 19.2\%$ of those achieved in Hutner's medium (lower dotted line in figure 2B). However, under these conditions the addition of solid BA at concentrations of 1.25 and 2.5 g/L strongly stimulated biomass growth ($p < 0.01$). In fact, the addition of these low concentrations of BA to the ultra-oligotrophic medium resulted in biomass growth responses that were similar ($79.5 \pm 19.2\%$) to those achieved on the Hutner's control medium. Frond growth rates (Figure 2C) were significantly stimulated at 1.25 g/L BA ($p < 0.05$) only.

Higher concentrations of BA added to ultra-oligotrophic medium impaired the growth of plants (Figure 2B, C). Up to BA concentrations of 40 g/L biomass and frond growth rates decreased gradually, however at a concentration of 80 g/L BA ($p < 0.05$, LOEC) both growth rates declined markedly. Compared to Hutner's medium, the biomass EC_{10} was higher on ultra-oligotrophic medium.

Suspended Fly ash solids
High concentrations of fly ash suspensions added to Hutner's medium caused negative effects on plant growth (Figure 2E, F). These inhibitory effects occurred at lower concentrations than observed for bottom ash, the plateau stage of the dose-response relationship in Hutner's medium spanned the FA concentrations from 0.625 to 2.5 g/L. Significant reductions of biomass growth occurred at 20 g/L ($p < 0.05$, LOEC) and 40 g/L ($p < 0.01$) FA. The biomass growth EC_{10} and EC_{50} in Hutner's medium were 8.6 g/L and 20.5 g/L (95% CI: 15.6 to 27.1 g/L, Table 4), respectively. Again the LOEC for frond growth (10 g/L, $p < 0.05$) was lower but the EC_{10} and EC_{50} values were the same as for biomass growth.

When low concentrations of solid FA was added to an ultra-oligotrophic medium growth was stimulated (Figure 2E). Compared to the control, a significantly stronger growth response was observed in medium with 0.625 and 1.25 g/L added FA ($p < 0.01$). Biomass of plants grown on medium with 2.5 and 5 g/L fly ash also increased faster than the corresponding control ($p < 0.05$).
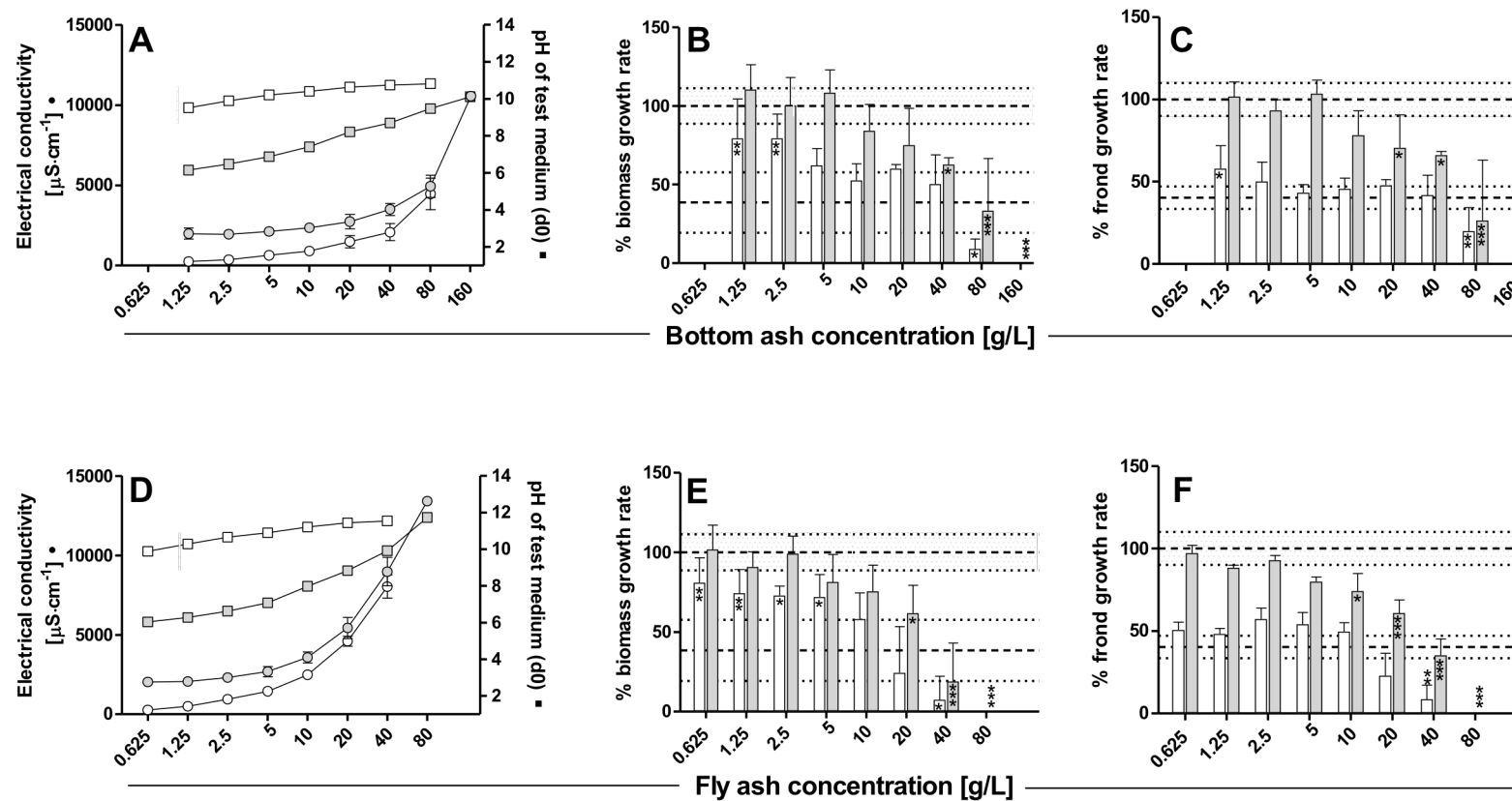
Figure 2: Biomass and frond growth rates of *Lemna minor* exposed to wood ash solid suspensions under two trophic regimes; bottom ash (A-C), fly ash (D-F); pH and electrical conductivity of ultra-oligotrophic medium (empty squares and circles respectively) and Hutner's growth medium (grey squares and circles respectively); growth response in ultra-oligotrophic medium (empty bars) and Hutner's growth medium (grey bars), Normalized to respective Hutner's Control growth rates (100%, dashed line with grey SD range), growth rate in distilled Water below (dashed line with clear SD range).

A significant reduction of biomass growth occurred at 40 g/L FA ($p < 0.05$, LOEC). Biomass EC_{10} and EC_{50} for FA suspensions in ultra-oligotrophic medium were both slightly lower than in Hutner's medium. The stimulation of frond growth was not significant. The LOEC for frond growth was 40 g/L ($p < 0.01$) and EC_{10} and EC_{50} values were very similar to the values found in FA supplemented Hutner's medium.

Bottom ash leachates

Bottom ash leachate added to Hutner's medium (Figure 3B), and diluted to 0.625 and 1.25 g aeq/L, did not alter the biomass growth rate of *L. minor*. Higher concentrations of 2.5 to 20 g aeq/L BAL improved biomass growth compared to the control, but not significantly. A significant reduction of biomass growth ($p < 0.001$) was observed at 40 g aeq/L (LOEC). Plants exposed to 80 g aeq/L were necrotic. The calculated biomass EC_{10} was 25 g aeq/L, while the EC_{50} for BAL was 33.1 g aeq/L (95% CI: 20.2 to 54.2 g aeq/L). The frond growth LOEC was also 40 g aeq/L, while the EC_{10} and EC_{50} for BAL were 14.8 g aeq/L and 33.1 g aeq/L, respectively. Plants grown on ultra-oligotrophic medium supplemented with BAL (Figure 3B) exhibited significantly higher biomass growth rates in the concentration range between 0.625 to 10 g aeq/L, when compared to the non-supplemented control. The fastest growth was observed on medium with 2.5 g aeq/L BAL added. The biomass growth EC_{10} for BAL was calculated to be 25.9 g aeq/L. The EC_{50} was 43.9 g aeq/L (95% CI: 34.3 to 56.3 g aeq/L). In contrast, the frond growth rate did not respond to increasing BAL doses in the nutrient deficient medium up to 40 g aeq/L. Plants were found to be necrotic at 80 g aeq/L.

Fly ash leachates

Fly ash leachate diluted in Hutner's growth medium (Figure 3B) did not significantly affect the biomass or frond growth rates in the concentration range between 0.625 and 5 g aeq/L. However, a significant reduction of biomass growth, compared with the control, was observed at 20 (LOEC) and 40 g aeq/L ($p < 0.001$). The EC_{10} and EC_{50} were 6.92 g aeq/L and 17.9 g aeq/L (95% CI: 13.2 to 24.1 g aeq/L), respectively. The LOEC for frond growth was lower (10 g aeq/L, $p < 0.05$) than the one for biomass growth, but EC_{10} and EC_{50} values were very similar.
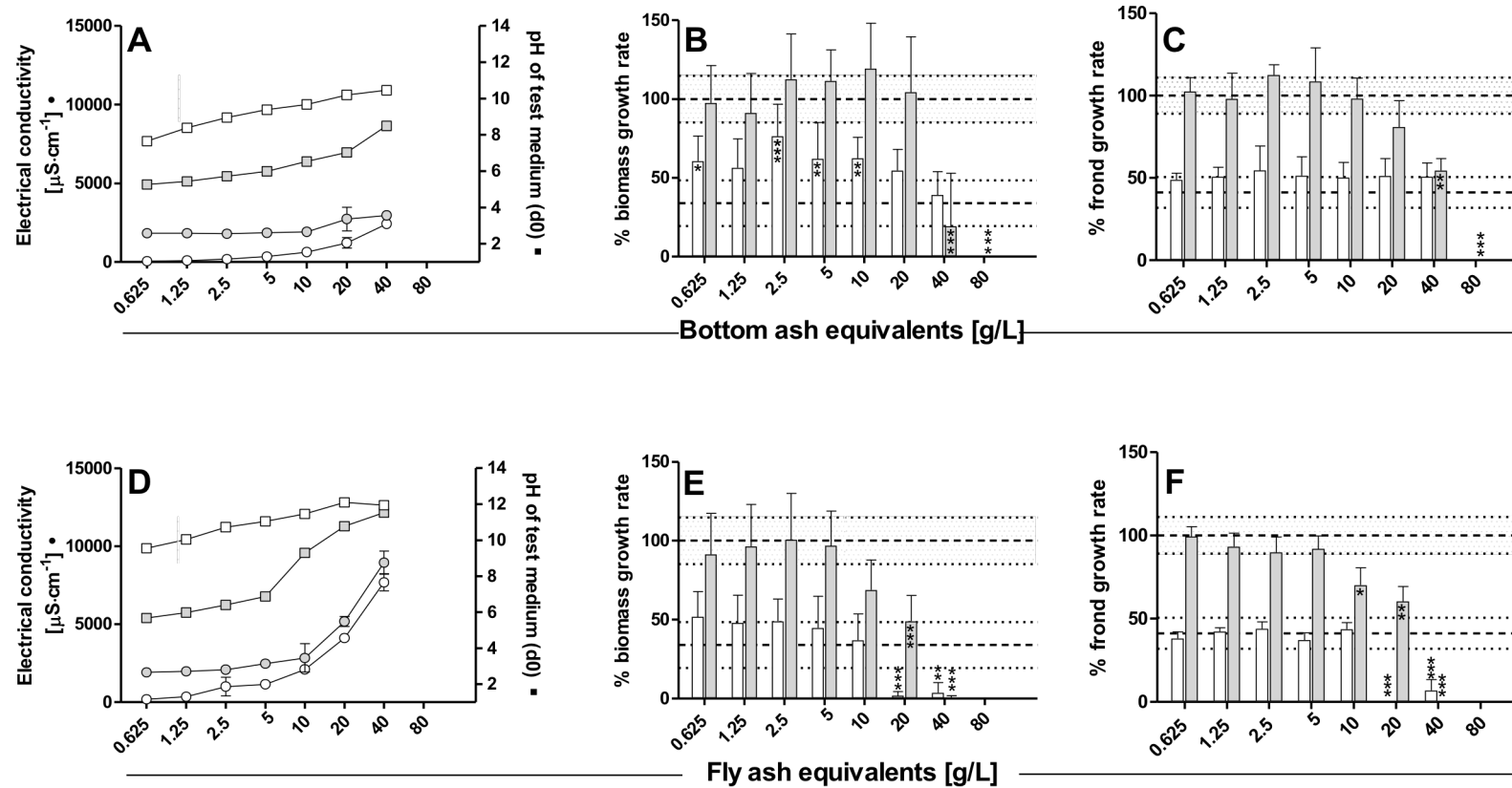
Figure 3: Biomass and frond growth rates of *Lemna minor* exposed to wood ash leachate dilutions under two trophic regimes; bottom ash (A-C), fly ash (D-F); pH and electrical conductivity of ultra-oligotrophic medium (empty squares and circles respectively) and Hutner's growth medium (grey squares and circles respectively); growth response in ultra-oligotrophic medium (empty bars) and Hutner's growth medium (grey bars), Normalized to respective Hutner's Control growth rates (100%, dashed line with grey SD range), growth rate in distilled Water below (dashed line with clear SD range).

When ultra-oligotrophic medium was supplemented with fly ash leachate, no significant plant growth stimulation was observed, neither of biomass nor frond growth. Significant decreases ($p < 0.001$) in biomass and frond growth rate were observed for the 20 (LOEC) and 40 g aeq/L FAL treatments. In fact plants were necrotic. The biomass EC_{10} was slightly higher and the EC_{50} was lower compared to the equivalent values using Hutner's medium. Frond growth EC_{10} and EC_{50} were >10 g aeq/L and <20 g aeq/L FAL, respectively.

Neutralized suspensions and leachate dilutions

Lemna minor exposed to the neutralized suspensions of either bottom or fly ash solids in Hutner's medium (Figure 4B, C) maintained biomass and frond growth up to relatively high concentrations. Growth could be observed on Hutner's medium supplemented with 160 g/L bottom ash solids or 80 g/L fly ash solids. Thus, dose-inhibition curves for bottom and fly ash solids were stretched and quite flat, compared to those observed with non-neutralised ash suspensions. For bottom ash suspensions, the biomass EC_{10} and EC_{50} were 9.7 g/L and 74.4 g/L (95% CI: 56.7 to 97.6 g/L), respectively. For fly ash suspensions, the biomass EC_{10} and EC_{50} were 4.49 g/L and 37.1 g/L (95% CI: 25.9 to 53.3 g/L), respectively. Despite the lack of growth inhibition at lower bottom ash concentrations, increasing chlorosis at frond edges could be observed in plants on bottom or fly ash suspensions exceeding 10 g/L. Necrosis was not observed with either of the two neutralized ash suspensions. Low concentrations of neutralized ash leachates added to Hutner's growth medium (Figure 4E,F) had very little impact on biomass and frond growth rates. The shape of the dose-response curve for plants exposed to neutralized BAL displayed an abrupt increase in effect severity above 40 g aeq/L. The biomass growth rate EC_{10} and EC_{50} for neutralised BAL were 51.6 g aeq/L and 87.9 g aeq/L (95% CI: 69 to 112 g/L), respectively. The shape of the dose-response curve for plants exposed to neutralized FAL displayed a slightly more gradual decrease in biomass and frond number growth, and EC_{10} and EC_{50} values were both markedly increased compared to the equivalent values for neutralised BAL.
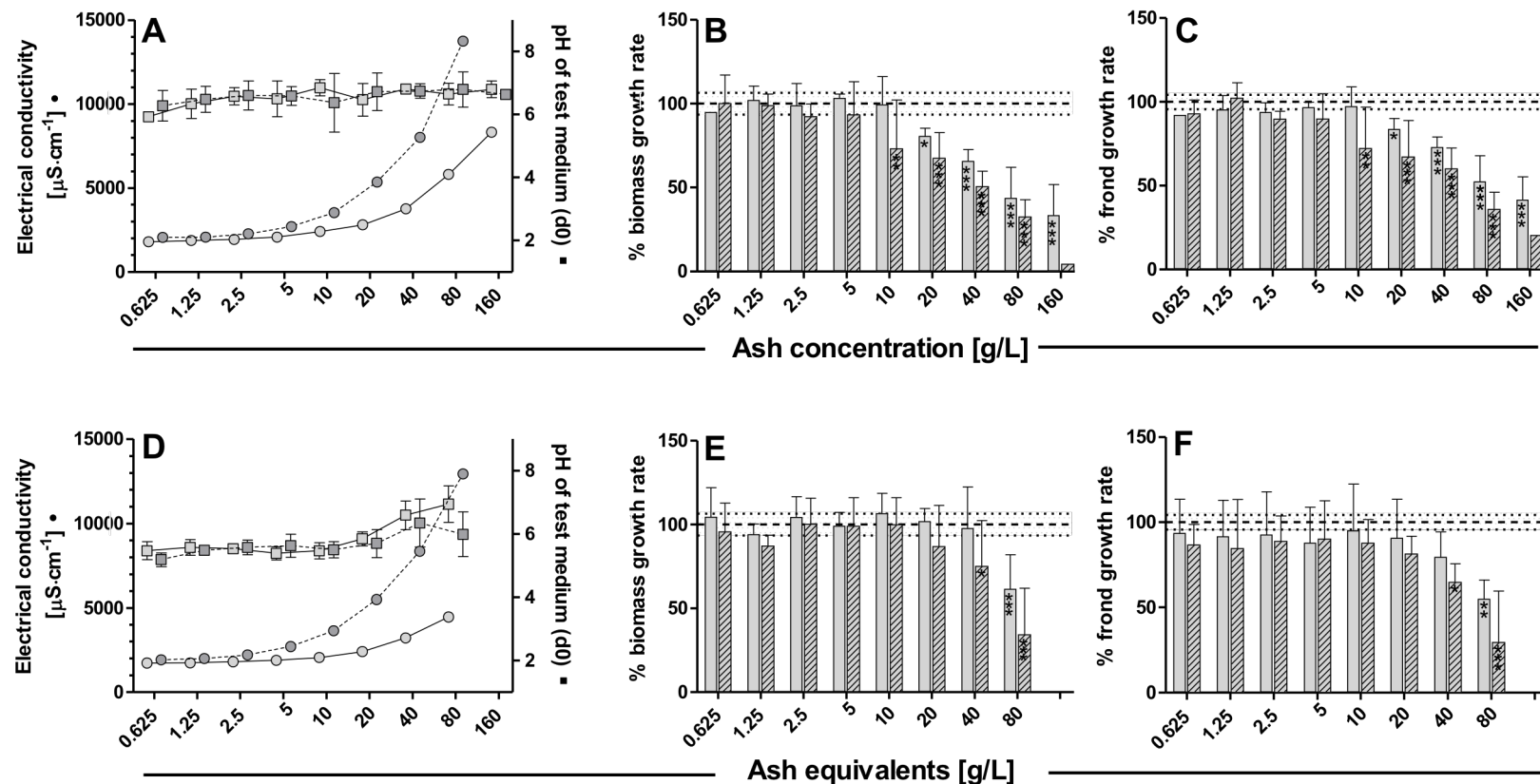
Figure 4: Biomass and frond growth rates of *Lemna minor* exposed to neutralized wood bottom (light grey) and fly ash (dark grey symbols) solid suspensions (A-C) and leachate dilutions (D-F); pH and electrical conductivity of Hutner's growth medium (squares and circles respectively); growth response in Hutner's growth medium (grey bars), Normalized to respective Hutner's Control growth rates (100%, dashed line with grey SD range)

Discussion

Wood ash solids and corresponding leachates

Wood ash solids

Fast growing, and commercially important Sitka spruce (*Picea sitchensis*) is considered to be a promising biofuel species for parts of western Europe. Combustion of this Gymnosperm species generates comparatively large (>2% w/w) amounts of ash (Owens and Cooley, 2013). Grate fired biomass ashes contain substantial amounts of charred organic fuel residuals (Emilsson, 2006; Tollin, 2000). In this study, highest levels of organic combustible residues were found in fly ash (44.7%), and this value is well within the reported range of 7 to 50% (Someshwar, 1996). The average particle diameter for FA is also similar to a reported FA particle size of 0.23 mm (Etitgni and Campbell, 1991). BA generated in an industrial size furnace is coarser due to its clinker and dross content. However, the removal of molten agglomerates somewhat aligned the ash particle size distributions minimising the difference in surface area between FA and BA.

Contents of primary and secondary plant macro nutrients in the two types of ashes differ only slightly. Bottom and fly ash thus appear equally suited as sources of these desired elements. Levels of P and K in the studied ashes are above median concentrations reported for generic wood ash (Augusto et al., 2008) and exceed cited literature values in Park et al. (2012) markedly. Minimum limit concentrations are set for plant nutrients in wood ash as a prerequisite for ash application in forests (Emilsson, 2006; Haglund, 2008; Pitman, 2006). Nutrients P, K and Mg in both bottom and fly ash exceed required minimal amounts of these plant nutrients. Yet, wood ashes used in this study contain only about half as much Ca as expected from medians reported in a meta-study of wood ashes by Augusto et al. (2008). Swedish requirements (Haglund, 2008) for the secondary macro nutrient Ca (125 g/kg) are met for 90 and 79% for BA and FA, respectively. Based solely on the plant nutrient contents, both ashes could be considered for land application.

Our data show that the micro nutrient and trace element concentrations in BA and FA are distinct, likely implying distinct hazards. Relative enrichment of Fe and Al in bottom ash used in this study is higher than reported in Park et al. (2012) and Pöykiö et al. (2009) but matches earlier findings (Narodoslawsky and Obernberger, 1996). B, Cu, Mn and Zn are present in both ashes at expected levels (Augusto et al., 2008). Mo and Ni contents in the tested Sitka spruce ashes are slightly lower than commonly reported. Among micro nutrients, a minimum nutrient content for ash spreading (Haglund, 2008) has been defined for Zn (0.5 g/kg) only. BA supplies 65% of required Zn content, while FA exceeds the requirement by 3.6-fold. Elements of concern, defined in 86/278/EEC (Council of the European Union, 1986), such as Cd, Pb and Zn are enriched in fly ash, as was found earlier (Park et al., 2012; Pöykiö et al., 2009). As and Se are also enriched in fly ash, but the partitioning between FA and BA is less pronounced than in Park et al. (2012) and the opposite of what was described for As by Pöykiö et al. (2009). Enrichment prevalence is commonly linked to condensation on fly ash particles (Izquierdo and Querol, 2012; Narodoslawsky and Obernberger, 1996; Pitman, 2006) and also affected by incomplete combustion. Based on the comparison of the chemical composition of Sitka spruce wood ash with a meta-analysis data set of various wood ashes (Augusto et al., 2008), bottom ash from un-treated Sitka spruce can be considered above average quality for its high content of P and K, and its low content of the toxic metals As and Pb (below reported minimum values). In comparison, fly ash from *P. sitchensis* also has above median levels of K and P, but contains above median levels of undesired Cd. Contents of the elements As, Pb, Cd, Cr, Hg, Ni and V in bottom and fly ash from untreated Sitka spruce sawmill residues remain below published maximum allowable concentrations (Haglund, 2008).

Wood ash leachates

EN 12457-2 one-stage 10 l/kg batch leachate from granular ash waste serves as a model for mobilization of ash constituents in water. Given the use of distilled water as an eluent, the pH conditions during mobilization are essentially determined by the alkaline pH of the wood ash. The titration profile of BAL exhibits the same carbonate-like characteristics as published for general wood ash (Etitgni and Campbell, 1991). This profile is, however, distinct from that of

FAL which shows a strong hydroxide presence. The alkalinity of FAL is 3.6 times higher than that of BAL. Conductivity tests also reveal a much higher ionic strength and quantity of readily dissolvable components in FAL.

Striking quantitative differences were observed in the concentrations of dissolved, plant nutrients in leachate of the two ash types. Oxidized N is exclusive to FAL, while orthophosphates are mostly dissolved in BAL (Table 1). Scarce N in wood ash is usually associated with unburned biomass and largely insoluble although small amounts of N condensed on FA particle surfaces can be mobile (Demeyer et al., 2001; Someshwar, 1996). Small amounts of P and Mg are found in BAL, these elements are likely bound to the silicate matrix (Izquierdo and Querol, 2012) and appear immobile in the case of fly ash. Among macro elements, the leachates are quantitatively distinct in K, Ca, Na, Al, Cl and SO_4, levels which leach more readily from FA. Unsurprisingly, the saliferous alkali metals K and Na are the most mobile elements in one stage leachates from both types of wood ash. In coal fly ash (Izquierdo and Querol, 2012), the elements Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Sn and Zn attain their lowest solubility in neutral to alkaline conditions (pH 7-10), such as used in this study. Oxyanionic-forming As, B, Cr, Mo, Sb, Se and V are of particular environmental concern because their maximum mobility occurs in neutral to alkaline conditions (Izquierdo and Querol, 2012), similar to the wood ash leaching conditions used in this study. Differences in particle size and element composition of the two ash types are also likely to contribute to distinct leaching behaviour of nutrients and hazardous substances in the ash (Stiernström et al., 2014; Tsiridis and Samaras, 2006; Wadge and Hutton, 1987). Strong acid extractable elements in the ash solids demonstrate desired nutrient contents to be rather similar in bottom and fly ash. Leaching into water and consequent plant availability, in contrast, prove to be distinct.

Distinct test conditions with solids and leachates

Leachates (Table 1) carry a finite amount of dissolved elements, the impacts of which can be studied in a *Lemna* growth assay. In contrast, the presence of suspended, particulate ash for the duration of the toxicity test, similar to differing liquid to solid ratio during leaching (Stiernström et al., 2014), will result in a

continuous influence on the water chemistry due to on-going dissolution, precipitation, electrostatic adsorption and ion exchange reactions (Chojnacka and Michalak, 2009). Metal removal from waste waters using washed ash sorbents has been documented (Chirenje et al., 2006; Horvat et al., 2007), and a similar sorption process may potentially have affected results of this study. In ultra-oligotrophic medium ash samples are likely to only release their components, while in eutrophic growth media ash may also act as a sorbent. Particulate ash contains between 25 and 45% residual organic matter that may remove ions due to chelation and surface adsorption. Calcite and gypsum minerals (Chirenje et al., 2006) are capable of exchanging Ca^+ ions for cations present in solution. Dissolved organic matter, ettringite or other secondary phase minerals in leachate may also trap dissolved ash elements. Measurements of the ElC in medium supplemented with either ash solids or the equivalent leachate amounts, shows that with increasing ash dose the ElC per mass unit of introduced ash decreases. This indicates saturation and/or removal of dissolved elements from the medium. Thus, it appears that the introduction of ash into standard eutrophic medium impacts on mobilization and adsorption equilibrium, irrespective of whether particulate matter or leachate were used, and this may affect both plant growth promotion and toxicity.

Growth promotion

Wood ash contains a range of plant nutrients as well as contaminants (Table 1). In ultra-oligotrophic or eutrophic media the relative contribution of ash-derived plant nutrients to plant growth differs. In the ultra-oligotrophic medium nutrients are virtually absent. Plant growth in the ultra-oligotrophic water control (dotted lines in Figure 2 and Figure 3) is sustained for the short duration of the test by stored nutrients. Under these conditions, the only nutrients present are those supplied with wood ash. This study shows substantially increased growth rates for *L. minor* in ultra-oligotrophic medium supplemented with ash (Figure 2B, C, E and 3B). In ultra-oligotrophic media, bottom ash solids and leachates, up to concentrations of 2.5 g/L and 10 g aeq/L respectively, increase biomass and frond growth significantly (Figure 2B and 3B). Fly ash stimulates biomass growth when applied as a solid (up to 5 g/L, Figure 2E). Arguably, osmotic stress in the ultra-oligotrophic medium (distilled H_2O) control (20 µS/cm) may reduce

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plant growth performance, thus artificially emphasizing the stimulatory effects mediated by ash. However, this scenario is unlikely, as significant increases in growth occur at ash concentrations that barely affect electrical conductivity. Moreover, no significant growth stimulating effect is observed for any of the ashes or their leachates in eutrophic medium. Therefore, growth promoting effects under oligotrophic conditions are likely to be caused by improved nutrient supply. Given the key role that nitrogen plays in mediating plant growth, it could be argued that fly ash leachate should cause a more pronounced growth stimulation. However, Hutner's medium provides 560 mg/L NO_3 and the 10 g aeq/L fly ash dilution only carries 0.7 mg/L NO_x, and therefore the latter is unlikely to significantly resolve nitrogen deficiency. There have been previous reports of wood ash mediated growth enhancement. For example, Aronsson and Ekelund (2006) showed that growth of the water moss *Fontinalis antipyretica* was increased when the growth medium was supplemented with extracts of a crushed wood ash. Other studies did, however, fail to show any growth stimulation by wood ash. For example, Park et al., (2005) failed to show enhanced biomass production by willows (*Salix purpurea*) and it was hypothesised that this was due to the fact that growth was predominantly limited by Nitrogen. Our data confirm the growth stimulation potential of wood ash solids, and to a lesser extend leachates, but also emphasise the role of plant nutrients from other sources in facilitating growth promotion.

Phytotoxicity

Lemnaceae are an excellent group of model species for ecotoxicity assessment, considered representative for aquatic macrophytes, and also to a lesser extent for vascular plants in general. Out of eight common aquatic test organisms *Lemna minor* is among the most metal tolerant species (Wu et al., 2013). Common duckweed ranks first or second for tolerance against 60% of the studied metal and metalloid elements, while conversely being particularly sensitive to Co, Cr and Cu (Wu et al., 2013). *L. minor* is a sentinel species (Dorman et al., 2010) that is commonly used for phytoremediation. This not only suggests that obtained EC_{50} outline an aquatic worst-case scenario but also facilitate the distinction between growth promotion at low ash concentrations and toxicity at higher levels for this study.

Table 2: EC_{10} and EC_{50} values with 95% CI calculated for the inhibition of biomass and frond growth rate in respective media

		Bottom ash EC with 95% CI			Bottom ash leachate EC with 95% CI			Fly ash EC with 95% CI			Fly ash leachate EC with 95% CI		
Native sample in distilled water (ultra-oligotrophic) medium													
Biomass growth rate	EC_{10}	28.5	16.3 to	50	25.9	13.5 to	49.5	6.44	3.15 to	13.1	8.03	4.79 to	13.4
	EC_{50}	**35.4**	22.3 to	56.2	**43.9**	34.3 to	56.3	**14.2**	10.7 to	18.7	**12.5**	8.67 to	17.9
Frond growth rate	EC_{10}	41.9	22.1 to	79	>40			8.03	1.53 to	42.2	>10		
	EC_{50}	**52**	33.2 to	81.5	**<80**			**18.1**	12.1 to	27.1	**<20**		
Native sample in Hutner's (eutrophic) medium													
Biomass growth rate	EC_{10}	10.1	3.67 to	28.1	25	8.18 to	76.6	8.6	4.28 to	17.3	6.92	3.25 to	14.7
	EC_{50}	**50.9**	33 to	78.5	**33.1**	20.2 to	54.2	**20.5**	15.6 to	27.1	**17.8**	13.2 to	24.1
Frond growth rate	EC_{10}	13.3	5.1 to	34.3	14.8	9.82 to	22.2	8.6	4.28 to	17.2	8.33	3.87 to	17.9
	EC_{50}	**42.9**	30.8 to	60	**36.9**	29.7 to	45.7	**21.8**	16.8 to	28.3	**19.6**	14.1 to	27.2
Neutralized sample in Hutner's medium													
Biomass growth rate	EC_{10}	9.7	3.56 to	26.5	51.6	27.7 to	96.4	4.49	1.06 to	19.1	26.7	13.6 to	52.3
	EC_{50}	**74.4**	56.7 to	97.6	**87.9**	69 to	112	**37.1**	25.9 to	53.3	**61.6**	48.9 to	84.5
Frond growth rate	EC_{10}	9.71	3.56 to	26.5	35.7	12.8 to	99.1	4.5	1.06 to	19.1	24.8	12.4 to	49.7
	EC_{50}	**68.3**	48.2 to	96.9	**94.2**	56.7 to	156	**36.7**	22.2	60.6	**60.8**	44.3 to	83.3

When exposed to bottom and fly ash, *Lemna minor* growth performance exhibits distinct dose-response relationships (Figure 2, 3, 4). Fly ash is always more hazardous than bottom ash. Severe toxic effect concentrations (EC_{50}, Table 2) of bottom and fly ash solids are significantly different, regardless of the use of oligotrophic or eutrophic growth conditions or native or neutralised ash applications. Plant nutrition provided by the medium has no effect on the toxicity of native fly ash solids or leachates (Table 2). However, severe toxicity (EC_{50}) is decreased due to pH neutralization (Table 2). For neutralized bottom ash leachates, both EC_{10} and EC_{50} are about 2-fold higher compared to native samples, while the difference is 3-fold for neutralized fly ash leachates. Thus, careful management of pH during fertilization with ash may avert detrimental effects (toxicity) and this can have important management implications for ash spreading.

Phytotoxicity of wood ash and wood ash leachates can potentially be caused by several different factors individually, as well as through interactions. Two main factors include toxicity of single elements and adverse effects of extreme pH of the medium. Here we have explored these factors, and assessed their potential role in causing phytotoxicity.

(i) We have reviewed the literature for threshold and toxicity concentrations (EC_{10} and EC_{50}) for single elements. Subsequently, we compared these concentrations with those present in wood ash and/or ash leachate. Naumann et al. (2007) rank the toxicity of toxic metals to *Lemna minor* (based on thresholds as EC_{10}) as Ag^+ (6-14 µg/L) > Cd^{2+} > Hg^{2+} > Cr(VI) > Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Tl^+ > As (3-12 mg/L). Based on lowest reported EC_{50} values for metal and metalloid elements under standard test conditions (Davis et al., 2002; Duester et al., 2011; Naumann et al., 2007; Simmons, 2012; Wang, 1990; Wu et al., 2013), bottom ash leachate contains 0.44 toxic units (TU, as presented in Horvat et al., 2007) in contrast to 9.75 TU in fly ash leachate. In bottom ash leachate, the toxic units are linked to the presence of the elements B, Cr and Cu which make up 38.3, 31.9 and 21.3% of total TU, respectively. When considering a threshold value of 0.5% of total TU, the elements Zn, As, Co, Tl and Ni with 2.49, 2.26, 1.12, 0.91 and 0.59% may be added to this list. In fly ash the situation is essentially different. In fly ash 92.4% of total TU are contributed by dissolved Zn

while Cr accounts for 4.46%. Furthermore above the arbitrary 0.5% threshold are Co and B with contributions of 0.97 and 0.67%, respectively, towards total TU. Thus, elemental contamination theoretically causes less than 50% effect of the toxic effect of bottom ash leachate, while fly ash leachate, even when diluted 10-fold, may still reduce growth by nearly 50%.

(ii) In eutrophic medium the reduction of *L. minor* growth coincides with a 10-fold decrease in H^+ ion concentration from pH 7 to 8, irrespective of ash type and form of introduction. High pH values were associated with a near total cessation of growth (Figure 2 and 3). *Lemna minor* is reported to survive and grow in a pH range between 3-4 and 10.5 (McLay, 1976). Growth optima derived from regressions of average frond number growth rates place the pH optimum for growth between 6.2 and 6.9, although in practice there is a broad optimum ranging between pH 5 and 8 (McLay, 1976). The growth rate for fronds is reduced to an average of about 80 and 50% of optimum growth at pH 9 and 10, respectively (McLay, 1976). When medium was neutralised following ash-addition (i.e. less alkaline pH) toxicity decreased and in most cases both EC_{10} and EC_{50} values increased. Thus, we conclude that the alkalinity of wood ash contributes to its phytotoxicity. However, the pH effect is rather complex. For example, the addition of 1.25 g/L bottom ash to oligotrophic medium increases the pH of the medium to 9.5, but this was associated with a marked stimulation of growth (Figure 2B,C) consistent with other findings (Aronsson and Ekelund, 2006). Therefore, it is concluded that observed ash toxicity is unlikely to be due to just the alkalinity of the medium. Rather, it appears that at higher ash concentrations a toxicity threshold is approached due to a combination of exposure to contained contaminants, and the alkaline nature of the ash.

Conclusion

The after-use of ashes creates a dilemma between preventing contaminants from re-entering ecosystems and recycling of beneficial plant nutrients. This dilemma is particularly strong in the case wood-based ashes, where it is, in principle, feasible to return minerals to the place where they were extracted from the soil. This study demonstrates both the plant growth promoting, as well as the toxic characteristics of wood ash that fulfils the minimal element content criteria for

spreading. It is argued that phytotoxicity is due to both the elemental composition of the ash, its alkaline character, and possible interactions between these two factors. In turn, growth promotion is due to the substantial content of plant growth nutrients. Interestingly, this study shows that the margin between growth promotion and toxicity incurring concentrations can be enlarged through ash neutralisation. This study underlines the importance of the receiving environment (nutrient status and pH) in determining the balance between toxicity and growth promotion, and thus the impact of ash spreading on plant growth.

Acknowledgements

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Chapter 4
Compositional consistency of ashes from untreated wood fuel

Abstract

Ashes from virgin wood fuels like untreated sawmill or forest harvest residues are, from a risk and regulation based perspective, considered less hazardous than ashes from, amongst others, coal, peat and treated-wood fuels. Ashes from virgin wood are therefore likely suitable for ecologically sensitive recycling options. In this study the compositional consistency of wood ash was analysed. Six years of composite wood ash from a single boiler, three years of separate wood bottom and fly ash from that same boiler, and one year of bottom and fly ash from five further boilers. Results show that furnace and flue-gas borne ash fractions exhibit distinct hazard potentials that are masked in chemical compliance analysis of the composite waste material. Moreover, results show that variations over time are distinct for the ash types and their extracts. Highest compositional consistency is found for ash solids. In his study, we argue that in depth appraisal and separation of the waste stream, commonplace with other fuels is needed also for 'clean' biomass ashes, particularly where ecologically-sensitive after-use is considered.

Introduction

Forest thinning and harvest residues as well as some wood processing by-products are untreated, renewable biomass resources which have, as of yet, relatively low commercial value. Traditionally, wood processing residues were applied as animal bedding, mulch or as a resource for composting, but nowadays such residues are increasingly sought after and exploited for their calorific, added value. Vassilev et al. (2010) reports that while the traditional applications of wood biomass are sustainable, their use as a fuel is currently not. The main reason for this lack of sustainability is the shortfall of mineral recycling (Stupak et al. 2007; Vassilev et al. 2010). Keys to sustainable wood energy production thus remain the recovery and ecologically sensitive recycling of minerals in residual ash. Waste material recovery and after-use, if precaution-oriented, may aid the protection of natural resources, lead to the closure of element and material cycles as well as, eventually, have economic benefits (Römbke et al. 2009). The various after-use options for thermal residues from biofuel, including their use as fertilizing or liming agent, are being widely researched (Reijnders 2005; Pitman 2006; Kuokkanen et al. 2009; Vassilev et al. 2013). It has further been argued that ashes from untreated renewable biomass are, for their chemically virgin nature and thus low extraneous contaminant burden, superior and possibly exclusive candidates for mineral recycling to soils (Demeyer et al. 2001).

Standardization exists for untreated, virgin wooden biomass fuels (FAO 2004; Alakangas et al. 2006), but there are few references available for their corresponding ashes. Wood ashes are known to contain nutrients and to have liming properties (Steenari et al. 1999; Pitman 2006; Augusto et al. 2008; James et al. 2012). The recycling of phosphorus (P), potassium (K) and base cations may counter mineral losses occurring due to harvest or erosion without adding to nitrogen leaching. However, caution is advised in dealing with supposedly 'clean' biomass energy ashes, even from virgin fuels such as untreated wood, as they may contain some hazardous properties (Reijnders 2005; Vassilev et al. 2010; Vassilev et al. 2013). In a review-paper, Reijnders (2005) reported that concentrations of arsenic (As), cadmium (Cd) and sometimes zinc (Zn) may be of concern in ash from untreated wood fuel. An investigation of ten distinct energy ashes derived from untreated wood biomass residues (Chapter 2) showed

that hazardous elements are consistently present in wood ash. Concentrations of some hazardous elements, such as As, lead (Pb) and tin (Sn) were particularly variable in ash solids. This variation in fuel borne elemental contaminants raises questions about the compositional consistency of ash derived from untreated wood fuel, and the validity of the virgin wood fuel argument as a guarantee of non-contaminated ash.

Fuel associated factors that influence ash contaminant concentrations include the species of tree (Pitman 2006; Reimann et al. 2008; Werkelin et al. 2010), the biomass type (i.e. stem wood, branches, bark or needles; Werkelin et al. 2010) and the location of cultivation (Preto et al. 2005; Keller et al. 2005; Pitman 2006; Reimann et al. 2008). In Ireland, Sitka spruce (*Picea sitchensis*) is the most common tree species in plantation forests (Irish Forest Service 2007). The geographical position of the island, with predominantly south-westerly winds, virtually precludes exposure to foreign airborne industrial emissions. Thus, wet and dry deposition, affecting the chemical make-up of soils and trees may be presumed to be of only minor significance for the chemical composition of the wood fuel, and corresponding wood ash. Wood energy operations in Ireland may provide an important, supra-regional benchmark and a good test of the hypotheses that untreated wooden biofuel can be converted in a clean ash. Ashes however also vary with type and design of a furnace, including operational parameters such as the combustion temperature (Misra et al. 1993; Spokas et al. 2011), organic material burn-out and applied methods of collection, subsequent storage, conditioning or stabilization of the ash (Steenari et al. 1999; Reijnders 2005; Pitman 2006). Although segregation of particulate matter (fly ash) from flue gas is a standard procedure employed to reduce emissions to air and thus lessen environmental impact, the subsequent mixing of bottom and fly ash fractions into a composite (Chapter 2) is another supposed source of ash waste variability. In absence of alternatives to disposal and facilitated by their common classification as 'absolute non-hazardous' wastes in the European Waste Catalogue (EWC, European Commission 2000), the combining of bottom and fly ash (ash waste) from fuels such as untreated wood is *quasi* routine practice. Also, composite ash disposal is cost effective and thus currently benefits wood energy use (Chapter 2). This range of non-fuel-related, but technical and/or process

variations increases ash compositional variation, and therefore limits the informative value of pre-existing data on (composite) ash waste from untreated wood fuel (Chapter 2).

Some chemical composition data exist for wood ash from untreated fuel (Wunderli et al. 2000; Ludwig et al. 2005; Pöykiö et al. 2009), but is often limited to single sample 'snapshots' which may miss variations in composition over time. Chapter 2 showed considerable variation in wood ash waste composition in Ireland, when composite, clean wood ashes from ten boilers were compared. In fact, one out of ten anonymous wood energy waste samples contained hazardous substances in excess of 2.5 g/kg and was thus considered hazardous waste based on its solid composition (UK Environmental Agencies 2013). Another significant finding (Chapter 2) was that some waste ashes, exhibit leaching properties suggesting they should be designated as hazardous waste: Water mobile selenium (Se) and mobility controlling species such as sulphate (SO_4^{2-}) were often found to exceed admissible European Waste Acceptance Criteria (WAC, 2003/33/EC; Council of the European Union 2003) limits on non-hazardous waste.

The variability of nutrient and contaminant concentrations in ashes from virgin, untreated wood fuel needs to be explored further in a current practice framework. Initially, six years of pre-existing, but unpublished, data on the waste ash from one case study site were compiled. These data comprise the analyses required before landfill disposal according to European WAC. Limit value infringement of these composite (waste) ashes was followed up in a second step, leachate analyses of separate waste constituting bottom and fly ash from the case study site as well as their *aqua regia* extractable solid content over a three year period. Finally, composition of bottom and fly ashes as well as their corresponding leachates from five further wood energy installations operating on virgin wood fuels was analysed. These data provide a baseline for ash stakeholders to benchmark ash residue composition, to assess potential benefits of separation and after-use options (and further aims to advance a practical definition of local, clean, non-contaminated ash in Ireland today).

This study tested the hypotheses that (i) leachates from the case study site ashes (composite ash waste as well as constituting bottom ash and fly ash) would fall within the range of compositional variability expected from wood energy wastes in Ireland (Chapter 2). (ii) Bottom and fly ash solids from the case study site as well as their corresponding leachates would be nonetheless distinct in their composition, and the consistency thereof. Finally, (iii) that single source (case site) bottom and fly ashes as well as their leachates are more consistent in composition than the respective solids and extracts of ashes from five other wood energy operations on average.

Materials and methods

Historic data on wood ash waste and its constituting ash fractions

WAC compliance data on wood ash waste (an 'as accrues' blend/composite of bottom and fly ash) dating from 2007 through to 2013 was made available by a commercial sawmill in Co. Cork, Ireland. These pre-existing analyses were performed by a certified analysis laboratory (UKAS #1291), and their scope is referred to as the 'Murphy suite' (Chapter 2).

To complement pre-existing data on composite ash, separate bottom and fly ash samples were first collected from the 3.8 thermal MW rotating grate CHP wood boiler in May 2011 (Chapter 3). Bottom ash was collected from the solid residue conveyors serving the water pool below the firing grate and the fly ash from the electrostatic precipitator outlet. In dry form, both types of ash had the same matt, dark anthracite colour and were stored in opaque barrels until testing. The parent fuel was composed of sawmill wood processing residues (sawdust, wood chips and bark shavings) from untreated Sitka spruce (*Picea sitchensis*) predominantly harvested in the south-west of Ireland and burned at 700-800°C (Chapter 3). Further samples for chemical monitoring of bottom and fly ash (Table 4) from this sawmill were taken in May 2012 and 2013 (Table 1).

Table 1: Source and outline of presented data

	Data on waste ash composites provided by plant operator		Data generated on bottom and fly ash by this study		
	WAC compliance requirements				
	Case site	Case site	Case site	Case site	5 other sites
Period	2007-2013	2010-2013	2011	2012-2013	2013
Datasets	13	6	1	2	5
Repl.	1	1	3	1	1
Scope	Mineral oil, BTEX and PCB in solids, WAC elements in leachate	PAH in solids	elemental solid and leachate composition, PCB and PCDD/F in solids, PAH in leachate	elemental solid and leachate composition, PAH in leachate	elemental solid and leachate composition, PAH in leachate

'Case site' refers to the site of the case study, Replications (Repl.)

Five further wood energy operations

Separate sampling of bottom and fly ashes to test for spatial variability of ash composition in 2013 (Tables 5, 6) was possible at five of the ten sites represented in Chapter 2. Bottom and fly ash were taken from the respective conveying systems before the ash entered the holding facility. The boilers varied in age (2-30 years) and size (<2-12 MW thermal yield) but all worked with a form of moving grate technology. Untreated wood fuel types were processing residues in the form of sawdust, wood and bark chips. The identity of the boilers and plant owners were made anonymous.

Wood ash composition and corresponding leachates

Prior to analysis of solids and leachates, ash samples were dried at 30°C until weight remained constant. Particles greater than 4 mm were crushed until they passed through a 2 mm sieve. Standard waste leachates were generated from dry ash according to BS EN 12457-2 (CEN 2002) with distilled water (10 l/kg). Simple aqueous leaching tests with various wastes including coal and biomass ashes are considered suitable for both chemical and biological testing (Schultz et al. 2002; Tsiridis and Samaras 2006; Barbosa et al. 2013). Bottom and fly ash leachates were examined for 28 dissolved elements (chapter 2). Chemical analyses of the ash solids (including PCB and PCDD/F) and corresponding aqueous extracts were performed by National Laboratory Service (Leeds, UK; UKAS #0754) as described in Chapters 2 and 3. PCDD/F and PCB analysis was done as 'snapshots' for three sub-samples collected in 2011 (Table 1). Analytes

included Cd, Pb, mercury (Hg) and nickel (Ni) from the European Priority Substance List (2455/2001/EC, Parliament and Council of the European Union 2001), Cd, Pb and Hg and their compounds are classified as priority hazardous substances. Mobile concentrations of 16 PAH indicators, some of which are also priority substances were analysed in leachate to avoid solid sample analysis bias frequent with wood ashes (chapter 2). Furthermore, leachates were examined for the elements As, barium (Ba), chrome (Cr), copper (Cu), molybdenum (Mo), antimony (Sb), Se and Zn, which are listed in WAC (2003/33/EC, Council of the European Union 2003).

Data management and statistics

Pre-existing WAC compliance analyses (leachate, semi-annual, n=13) of the wood ash waste composite, as disposed at the case study site, were summarized (Table 3). Quartile coefficient of dispersion (QCOD) was used as additional measure of variation with these pre-existing leaching data because the sample population was relatively large. For correlation analysis (Pearson's, two-tailed p-values, df=11), leachate concentrations were transformed into standard scores. The standard score (z) is the fold value of the standard deviation (σ) describing the distance of the measured concentration of an element (x) to the respective mean of that element across the population of all 13 samples (μ).

$$z = \frac{x - \mu}{\sigma}$$

Results below detection limit were excluded from correlation analysis. PAH concentrations from wood ash solid waste analyses (2010 to 2013, n=6), provided by the plant operator, were corrected for their respective surrogate recovery (chapter 2, Nollet and Gelder 2013). ITEQ conversion of PCDD/F measurements (2011 samples) was provided by the laboratory and applied older Toxic Equivalence Factors from 1998 (WHO and International Programme on Chemical Safety 2005). For the case study site, variability of bottom and fly ash elemental composition as a function of time was calculated from average concentrations of a quadruplicate ash sample analysis (Chapter 3) in 2011 and two single sample analyses for the subsequent years of 2012 and 2013. Averages are given together with standard deviation. Frequency of detection (FOD) shows the ratio of samples with confirmed element presence (successful detections) out

of the total number of analyses in the respective aqueous or solid matrix. Element contents were determined after ionisation via mass spectrometry (Chapters 2, 3), thus no information on the original compounds and chemical speciation they occurred in was available. Statistical analyses were performed with Graph Pad Prism (Graph Pad Software, La Jolla, USA).

Results

Site record on organics in composite wood energy ash waste

Pre-existing WAC compliance analyses of composite wood ash waste, the mixture of bottom and fly ash as disposed from the case study site (2007-2013), stated an average mineral oil (>C10-C40) burden of 664 ± 1450 mg/kg (FOD 0.69). Median concentration was 101 mg/kg, ranging from 28 to 4230 mg/kg including an extreme outlier. When this outlier was excluded, the maximum value was 550 mg/kg. Petroleum derivate associated compound (BTEX) analysis revealed toluene and o-xylene detectable in the range of 4-7 µg/kg in very few samples (FOD 0.08). Consequently, the sum of BTEX was, between 2007 and 2013, reported as <24 µg/kg in pre-existing analyses. Further in pre-existing WAC compliance analyses, seven polychlorinated biphenyls (PCB) congeners (28, 52, 101, 118, 138, 153 and 180) were not detected (<3 $\mu g \cdot kg^{-1}$), thus the sum of 7 PCP species was consistently <21 µg/kg. No data were available for polychlorinated dibenzo p-dioxins and furans (PCDD/F) in the composite wood ash waste for the period.

Six pre-existing polycyclic aromatic hydrocarbons (PAH) sample analyses were obtained for the case study site (2010-2013, data not tabularized). Across the five surrogate compounds the average recovery was low (29.3%). On average 46.4 and 55.5% of naphthalene-d8 and acenaphthene-d10 respectively were recovered, phenanthrene-d10 surrogate recovery was 27%. Of added chrysene-d12 as well as perylene-d12 surrogates, less than 10% could be found again. The presence of all 16 PAH indicators at a total of 23.3 and 24.8 mg/kg was confirmed in two out of six waste ash samples. Here, average recovery across all deuterium marked surrogates was 52 and 57% respectively. Naphthalene was the only compound detected in all waste ash samples, up to 2.5 mg/kg. Considering

all six samples, the average sum of 16 PAH was 10.9 ± 10.8 mg/kg in wood ash waste from the site. The organic carbon remainder (TOC) in ash wastes from the record was 19 ± 13.6% of the ash dry weight.

Organic contaminants in bottom and fly ash

Triplicate analysis of the separate bottom and fly ash sample from the case study site (2011) revealed that polychlorinated biphenyls were present. In bottom ash, four PCB congeners (18, 47, 49 and 52) to a total 92 ng/kg were detected. In contrast, fly ash contained about 3-fold more PCB (252 ng/kg, congeners 18, 28, 47, 49 and 52). PCB congeners above number 52 were not detectable in either solid bottom or fly ash, average limit of detection was 3 ± 1 ng/kg.

Polychlorinated dibenzo p-dioxin and furan (PCDD/F) presence in the same bottom and fly ash samples (2011) from the case study site were confirmed with good precision (Table 2). Concentrations of dioxins (sum of isomers) were 12 times greater in fly ash than in bottom ash. Similarly, the sum of furan isomers was 7.8-fold higher (Table 2) in fly ash compared to bottom ash. In bottom ash, the most toxic 2,3,7,8 chlorinated dioxins accounted for 8.3 International Toxic Equivalents (ITEQ). The largest single compound contribution (4.7 ITEQ) was 9.4 ng/kg 1,2,3,7,8-PeCDD. Only tetra and penta chloride substituted (involving positions 2,3,7,8) furan compounds were detected in bottom ash and account for 3.5 ITEQ. In fly ash, 49.4 ITEQ were determined for PCDDs. 1,2,3,7,8-PeCDD was again the largest contributor (25 ITEQ from 49.9 ng/kg). PCDFs accounted for 21.9 ITEQ in fly ash, the total toxic burden in PCDD/F is 6-fold larger than in bottom ash.

Mobility of PAH in water (data not tabulated) was monitored from 2011 to 2013. Of the 16 indicator PAH, only naphthalene was detected in the mobile phase. Naphthalene was present in bottom ash leachate of the initial 2011 sample only (0.013 $\mu g \cdot l^{-1}$). The frequency of its detection (FOD) was 0.75 in 2011. In the subsequent two years of chemical monitoring no PAH were detected in aqueous leachates of bottom or fly ash.

Table 2: p-Dioxin and furan compounds chlorinated in positions 2,3,7 and 8 with ITEQ and sum of isomers detected for tetra (T), penta (Pe), hexa (Hx) and hepta (Hp) chlorodibenzo (CD) p-dioxins (D) and furans (F) in bottom and fly ash solids from untreated wood fuel, as ng/kg, n=3

	Bottom ash				Fly ash			
p-Dioxins	Average		SD	%CV	ITEQ	Average	SD	%CV	ITEQ
2,3,7,8-TCDD	1.78	±	0.40	23	1.780	13.9	±	2.56	18	13.900
1,2,3,7,8-PeCDD	9.36	±	1.33	14	4.657	49.9	±	1.72	3	25.000
1,2,3,4,7,8-HxCDD	5.40	±	1.06	20	0.540	26.3	±	2.84	11	2.633
1,2,3,6,7,8-HxCDD	7.87	±	0.99	13	0.787	39.7	±	2.64	7	3.970
1,2,3,7,8,9-HxCDD	4.21	±	0.06	2	0.421	25.5	±	2.95	12	2.550
1,2,3,4,6,7,8-HpCDD	13.6	±	1.40	10	0.136	125	±	27.6	22	1.257
OCDD	6.96	±	1.63	23	0.007	59.9	±	11.7	19	0.060
Sum of isomers									
TCDD	257	±	94.4	37		6527	±	864	13	
PeCDD	410	±	52.4	13		3080	±	174	6	
HxCDD	176	±	34.0	19		1663	±	207	12	
HpCDD	143	±	29.1	20		608	±	190	31	
Furans	Average		SD	%CV	ITEQ	Average	SD	%CV	ITEQ
2,3,7,8-TCDF	10.3	±	1.08	10	1.028	73.6	±	11.6	16	7.4
1,2,3,7,8-PeCDF	1.75	±	0.31	17	0.087	51.1	±	5.37	11	2.6
2,3,4,7,8-PeCDF	4.75	±	0.21	4	2.377	16.2	±	2.66	16	8.1
1,2,3,4,7,8-HxCDF	<0.7				<0.07	7.12	±	1.11	16	0.7
1,2,3,6,7,8-HxCDF	<0.4				<0.04	16.0	±	2.05	13	1.6
2,3,4,6,7,8-HxCDF	<2				<0.2	13.4	±	1.17	9	1.3
1,2,3,7,8,9-HxCDF	<0.8				<0.08	<0.8				<0.08
1,2,3,4,6,7,8-HpCDF	<2				<0.02	15.7	±	1.03	7	0.2
1,2,3,4,7,8,9-HpCDF	<0.9				<0.008	6.66	±	1.17	18	0.1
OCDF	<3				<0.004	36.9	±	2.60	7	0.0
Sum of isomers									
TCDF	313	±	150	48		2793	±	45.1	2	
PeCDF	75.5	±	7.37	10		401	±	66.1	16	
HxCDF	43.2	±	2.61	6		167	±	12.2	7	
HpCDF	10.0	±	0.77	8		50.8	±	5.37	11	
Total ITEQ					11.8					71.3

Site record on elemental contaminants in composite wood energy ash waste

The summary of 13 historical waste leaching tests commissioned by the operating company (Table 3) showed mean mobile concentrations of chromium (Cr), molybdenum (Mo), lead (Pb), antimony (Sb), selenium (Se), chloride (Cl⁻), sulphate (SO_4^{2-}), dissolved organic carbon (DOC) and total dissolved solids (TDS) in excess of allowable limits for inert waste.

Table 3: Inert and non-hazardous waste leaching limit values and leachable WAC metal and metalloid elements, halogens, carbon and total dissolved solids from ash waste between 2007 and 2013; BS EN 12457-2 leachate (10 L·kg^{-1}), in mg·kg^{-1}; Average ± Standard Deviation (SD) with frequency of detection (FOD, n = 13), Median and Quartile Coefficient of Dispersion (QCOD)

| | Limits (2003/33/EC) | | Waste ash: admixed furnace grate bottom ash (BA) and flue cleaning residues (FA), as disposed | | | | | |
	Inert waste	Non-hazardous waste	Average	±	SD	FOD	Median	QCOD
As	0.5	2	0.108	±	0.053	1	0.11	0.27
Ba	20	100	2.750	±	1.549	1	2.02	0.31
Cd	0.04	1	0.004	±	0.002	0.54	0.00393	0.40
Cr	0.5	10	0.900	±	0.709	1	0.785	0.53
Cu	2	50	0.123	±	0.131	1	0.0603	0.51
Hg	0.01	0.2	< 0.0001			0		
Mo	0.5	10	1.313	±	0.830	1	0.903	0.41
Ni	0.4	10	0.044	±	0.041	1	0.03	0.75
Pb	0.5	10	2.410	±	5.231	0.92	0.03805	0.95
Sb	0.06	0.7	0.094	±	0.129	0.69	0.0642	0.83
Se	0.1	0.5	0.672	±	0.483	1	0.64	0.33
Zn	4	50	2.735	±	4.462	1	0.55	0.90
Cl$^-$	800	15000	6534	±	4389	1	6372	0.42
F$^-$	10	150	6.8	±	3.704	0.23		
SO$_4^{2-}$	1000	20000	11919	±	7408	1	10800	0.32
DOC	500	800	1606	±	2232	1	433	0.66
TDS	4000	60000	54138	±	22258	1	57200	0.27

Non-hazardous waste limits were only surpassed by average Se and DOC concentrations. Median DOC concentration did not exceed the threshold. Both average and median TDS concentrations only just remained below the allowable limits for non-hazardous waste. Fluoride (F$^-$), Cd, Sb and Pb were not consistently detected (FOD <1) in standard waste leachate. The largest absolute range (minimum to maximum value) was found for mobile zinc (Zn) and Pb (>15 mg/kg), and the largest interquartile ranges (Q1 to Q3) were found for mobile Mo, barium (Ba) and Zn (1.02, 1.6 and 2.48 mg/kg). Across the metal and metalloid WAC elements As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn (Hg was excluded because it was not detected), the mean CV of detected average leachate concentrations was 99.6%. Average pH of waste leachates was 12.3 ± 0.18, mean electrical conductivity (ElC) was 4.89 ± 1.8 mS/cm.

Correlation of mobile WAC elements and leachate parameters

Within WAC data on composite wood ash for the period 2007-2013, the pH was negatively correlated (all coefficients below -0.7) with concentrations of the elements arsenic (As, p=0.067), Cd (p=0.019), copper (Cu, p=0.039), nickel (Ni, p=0.032), Sb (p=0.102) as well as DOC (p=0.013). In contrast, pH positively

correlated with TDS (p=0.006) and ElC (p=0.009). It has to be noted that the pH range in (generally alkaline) composite ash waste leachates was rather small (8.98 to 12.4). TDS concentrations positively correlated with Cl^- and SO_4^{2-}, coefficients were 0.79 and 0.7 with p-values of 0.004 and 0.016 respectively. A negative correlation between TDS and Cd was found (coefficient was -0.85, p=0.015). ElC was positively correlated with TDS (coefficient was 0.98, p=8.8·10^{-5}) and total Cr (coefficient was 0.85, p=0.015) but negatively correlated with Cd (coefficient was -0.87, p=0.024). DOC positively correlated with Ni and Sb (coefficients were 0.74 and 0.83, with p=0.009 and p=0.006 respectively). Salt forming sulphate further correlated positively with Se and Cl^- (coefficients were 0.96 and 0.73, with p=1.1·10^{-7} and p=0.005 respectively). Among metal and metalloid elements, Zn and Pb (coefficient was 0.91, p=4.4·10^{-5}), Sb and Ni (coefficient was 0.76, p=0.018) as well as Mo and Cr (coefficient was 0.86, p=1.5·10^{-4}) all exhibited positive correlations.

Elements in separated bottom and fly ash over 3 years

Over a three year monitoring period, elemental solid content (*aqua regia* extractable) of bottom and fly ash (Table 4) exhibits an average global CV (across all analytes) of 22 and 48% respectively. In bottom ash solids, the highest temporal variability, expressed as the coefficient of variation (CV), occurs for cobald (Co, 74%), As (48%), nitrogen (N, 41%) and Cr (38%) solid content. Most element concentrations in bottom ash solids exhibit a CV between 10 and 30% while particularly small CV were found for Se, Ni, boron (B), tin (Sn) and Zn (8, 6, 4, 3 and 2% respectively). In fly ash solids, Ba, As and Cu exhibit the largest CV over the three year monitoring period (Table 4), 132, 117 and 104% respectively. Least variable solid concentrations were found for Sb (CV 16%) while the gross of ash constituting elements varies at CV between 30 and 50%.

Table 4: Average concentrations of elements in bottom (BA) and fly ash (FA) solids ($_S$) and corresponding leachates ($_l$) over a three year monitoring period.

	BA$_s$ 3yr [mg/kg]				BA$_l$ 3yr [µg/l]				FA$_s$ 3yr [mg/kg]				FA$_l$ 3yr [µg/l]			
	Mean		SD	CV	Mean		SD	CV	Mean		SD	CV	Mean		SD	CV
Carbon	149000	±	24042	16%	n.d.				271000	±	205993	76%	n.d.			
Nitrogen	465	±	193	41%	n.d.				1166	±	642	55%	n.d.			
Aluminium	16483	±	3525	21%	748	±	872	117%	13979	±	6594	47%	3059	±	3114	102%
Antimony	1.30	±	0.34	26%	4.03	±	1.55	39%	1.55	±	0.24	16%	17			
Arsenic	4.03	±	1.94	48%	20.3	±	4.45	22%	23.2	±	27.2	117%	15.8	±	19.4	123%
Barium	1001	±	199	20%	65.4	±	76.7	117%	236	±	313	132%	247			
Beryllium	0.40	±	0.06	15%	<1				0.33	±	0.15	45%	<20			
Boron	102	±	3.85	4%	1388	±	887	64%	196	±	83.6	43%	1327	±	458	35%
Cadmium	1.39	±	0.22	16%	0.15	±	0.03	18%	10.1	±	7.25	72%	0.62	±	0.59	95%
Calcium	90392	±	23604	26%	32080	±	34745	108%	88944	±	31042	35%	273108	±	163665	60%
Chromium	27.2	±	10.3	38%	52.1	±	26.2	50%	25.2	±	11.7	46%	330	±	278	84%
Cobalt	16.7	±	12.3	74%	1.04				8.31	±	2.86	34%	<1			
Copper	79.1	±	15.4	19%	4.69	±	3.64	78%	149	±	156	104%	3.52	±	0.68	19%
Iron	13342	±	2027	15%	<0.03				9491	±	3663	39%	<0.3			
Lead	11.8	±	3.00	25%	<2				38.0	±	18.2	48%	4.45			
Lithium	13.4	±	1.43	11%	n.d.				11.1	±	3.89	35%	n.d.			
Magnesium	13925	±	2222	16%	1647				15225	±	5004	33%	<3			
Manganese	9278	±	2338	25%	16.1				10723	±	4122	38%	<0.01			
Mercury	<0.2				<0.01				<0.2				<0.01			
Molybdenum	<1				68.0	±	32.0	47%	2.10	±	0.60	29%	257	±	99.2	39%
Nickel	18.2	±	1.17	6%	<1				16.1	±	5.27	33%	6.14			
Phosphorus	9355	±	2223	24%	712	±	1008	142%	11451	±	4701	41%	588	±	851	145%
Potassium	45525	±	10471	23%	698333	±	453437	65%	61675	±	17764	29%	4141250	±	2109883	51%
Selenium	2.92	±	0.24	8%	6.84	±	1.47	22%	5.48	±	2.05	37%	64.7	±	48.2	75%
Silver	<1				n.d.				2.04	±	0.70	34%	n.d.			
Sodium	3740	±	561	15%	57092	±	37062	65%	3671	±	1009	27%	180463	±	73075	40%
Strontium	603	±	185	31%	212	±	208	98%	650	±	191	29%	2573	±	1377	54%
Thallium	3.08	±	0.82	27%	<1				4.48	±	1.12	25%	<10			
Tin	1.41	±	0.04	3%	<2				3.00	±	1.47	49%	4.02			
Titanium	831	±	123	15%	5.16	±	4.24	82%	632	±	302	48%	54.2	±	32.9	61%
Vanadium	23.9	±	5.68	24%	107	±	83.3	78%	20.8	±	8.93	43%	75.9	±	71.9	95%
Zinc	323	±	5.86	2%	5.29				1669	±	847	51%	846	±	1634	193%

Elements in leachate of separated bottom and fly ash over 3 years

Biological oxygen demand (BOD) of bottom and fly ash 10 l/kg standard waste leachates was only detectable once (FOD 0.33, LOD <1.4 mg/l) at 5.58 and 4.03 mg/l respectively. Chemical oxygen demand of bottom and fly ash was 98.1 ± 28.2 and 58.4 ± 4.52 mg/l. Over three years and across all analytes, the leachates exhibit an average CV of 71% and 79% for bottom and fly ash respectively. The average CV across only metal and metalloid WAC elements (Section 3.2) in bottom and fly ash leachates in contrast were 49% and 90% respectively. In bottom ash leachate, on average 0.97 ± 0.48 g/l ash constituents, as sum of all analytes, are dissolved. Potassium (K) poses 69 ± 10%, Cl⁻ and $SO4^{2-}$ make up 7 ± 3% and 15 ± 9% of leachate load respectively. No infringement of WAC leaching limits was noted during the three year monitoring period. In bottom ash leachate (Table 4) all calculated average concentrations, apart from As, of hazardous elements considered in WAC are smaller than those reported for the composite energy ash waste (Table 3).

Fly ash leachate carried an almost 9-fold higher average of 8.6 ± 5.69 g/l dissolved analytes. The mean K contribution was 44 ± 3% while Cl⁻ and $SO4^{2-}$ on average make up 11 ± 2% and 41 ± 5% respectively of the total dissolved analytes. Leachable Se and $SO4^{2-}$ constantly surpass allowable limits set for non-hazardous waste (70 and 2000 μg/l). WAC elements (Sb, As, Cd, Cr, Mo and Zn) are, on average, more concentrated in fly ash leachate than in extracts of the composite waste. Substantial differences were found between average and median concentrations of Pb and Zn in composite wood energy waste leachates (Table 3). Over the three year monitoring period however Pb was only detected in fly ash leachates once (Table 4) and the measured concentration was close to the median level determined from the composite waste. Zn was found leachable from bottom ash in only one sample (FOD 0.33, LOD 5 μg/L). In contrast, Zn was found mobile in all fly ash leachates (FOD 1) and associated with a very high CV (193%). Cd and Sb, not consistently detectable (FOD <1) in composite ash waste leachate between 2007 and 2013 (Table 3), were also not detected in every sample during the three year chemical monitoring period (Table 4). In bottom and fly ash the frequency of detection for Cd was 1 and 0.67, respectively, while Sb was detectable with FOD 0.67 and 0.33 respectively.

Variability of bottom ashes from five Irish wood boilers

Five other, non-case study wood energy plants (Section 2.1.1) also fired untreated wooden biomass. Operators stated that most of the fuel was derived from Irish grown *Picea sitchensis*. The global CV (over all analytes) of element concentrations in solid bottom ash from these five other wood energy operations (Table 5) was 75% and thus 3-4 times larger than the over-time variability of bottom ash solids from the case study site (22%, Table 4). Across the five ash sources, highest spatial variability (by CV) was found for Pb (202%), Sn (190%), Sb (158%), Ni (108%) and carbon (C, 101%). Most elements in bottom ash solids exhibited a spatial variability of CV 50-100% while Zn, strontium (Sr), magnesium (Mg), vanadium (V), B, Mo, lithium (Li), calcium (Ca) and K solid concentrations are, in order of decreasing CV, least variable between bottom ashes from different boilers. Discrepancies in average and median bottom ash solid content were found for Pb, Sn and Sb where the average is 56, 16 and 4-fold larger than the respective median. Other than for these three elements, concentration averages are 1.32 ± 0.27 times larger than the respective medians (Table 5). For Pb, Sn and Sb maximum values detected were 868, 130 and 32-fold larger than the smallest measured concentration. Lesser absolute concentration ranges were found for Ni, sodium (Na), Ba, iron (Fe), Co and Cr where the largest measured bottom ash solid concentration was still up to 20-fold higher than the minimum.

In contrast to solid content determination where FOD is seldom <1, only Al, Cr, K and Na were found in leachate of all five bottom ashes. The global CV of leachable components in bottom ash leachate from five boilers was 92% (Table 5), slightly larger than in leachate from a single source over a three year period (71%). Mo, B and As leachate concentrations were least variable (17, 15 and 13% CV) across wood boilers. By average bottom ash leachate concentrations of two elements (Ba and Cr) surpass allowable limits for non-hazardous waste materials 12 and 6-fold respectively, by median concentration in leachate, only Cr violates this threshold. Se and Sb leachate concentration averages reach 72 and 50% of the allowed WAC threshold for non-hazardous waste, median leachate concentrations account for 33 and 50%.

Table 5: Bottom ash from five other Irish sites (n=5), with coefficient of variation (CV) and frequency of detection (FOD)

Analyte	*Aqua regia* extractable solid concentration [mg/kg]					Aqueous leachate concentration [mg/L]				
	Average	CV	(FOD)	Median	Range	Average	CV	(FOD)	Median	Range
Carbon (C)	33026	101%	(1)	22200	3610 .. 78200			n.d.		
Nitrogen (N)	1750		(0.2)	1750	<200 .. 1750			n.d.		
Aluminium (Al)	12028	62%	(1)	10500	5220 .. 23100	3.10	118%	(1)	1.30	0.36 .. 9.13
Antimony (Sb)	9.64	158%	(1)	2.63	1.13 .. 36.6	0.04	53%	(0.4)	0.04	0.02 .. 0.05
Arsenic (As)	3.80	62%	(0.8)	3.55	1.53 .. 6.56	0.03	13%	(0.4)	0.03	0.03 .. 0.03
Barium (Ba)	2001	77%	(1)	1400	244 .. 3860	12.0	191%	(0.8)	0.78	0.13 .. 46.3
Beryllium (Be)	0.46	60%	(0.6)	0.374	0.242 .. 0.775			(0)		<0.002 .. <0.02
Boron (B)	218	39%	(1)	183	160 .. 363	3.34	15%	(0.6)	3.30	2.86 .. 3.86
Cadmium (Cd)	2.16	92%	(0.6)	1.28	0.777 .. 4.43			(0)		<0.0001 .. <0.001
Calcium (Ca)	222600	30%	(1)	198000	151000 .. 320000	341	91%	(0.8)	290	21.2 .. 763
Chromium (Cr)	217	87%	(1)	130	38.3 .. 453	6.36	151%	(1)	3.06	0.12 .. 23.1
Cobalt (Co)	12.3	95%	(1)	7.55	2.41 .. 31.9			(0)		<0.001 .. <0.02
Copper (Cu)	275	71%	(1)	229	72.8 .. 593	0.02	109%	(0.8)	0.01	0.005 .. 0.04
Iron (Fe)	28574	96%	(1)	16400	4870 .. 74500			(0)		<0.00003 .. <0.0006
Lead (Pb)	328	202%	(1)	5.91	1.74 .. 1510	0.01	136%	(0.6)	0.003	0.003 .. 0.03
Lithium (Li)	18.8	32%	(1)	16.7	11.4 .. 25.1			n.d.		
Magnesium (Mg)	30500	44%	(1)	25900	15400 .. 47500			(0)		<0.0003 .. <0.006
Manganese (Mn)	17746	87%	(1)	11500	8240 .. 45000	0.01		(0.2)	0.01	<0.0001 .. 0.01
Mercury (Hg)			(0)	<0.2	<0.2			(0)		<0.00001 .. <0.00002
Molybdenum (Mo)	2.08	36%	(0.8)	2.215	1.06 .. 2.84	0.17	17%	(0.8)	0.17	0.13 .. 0.20
Nickel (Ni)	65.5	108%	(1)	39.2	9.7 .. 188	0.03		(0.2)	0.03	<0.001 .. 0.03
Phosphorus (P)	15700	66%	(1)	13900	4300 .. 32700	0.22	83%	(0.6)	0.14	0.09 .. 0.42
Potassium (K)	72760	25%	(1)	71500	45000 .. 94900	3178	82%	(1)	2000	1550 .. 7780
Selenium (Se)	6.59	69%	(1)	3.88	3.45 .. 14	0.04	130%	(0.6)	0.02	0.002 .. 0.09
Silver (Ag)	3.16	56%	(1)	2.68	1.61 .. 6.18			n.d.		
Sodium (Na)	10516	98%	(1)	8220	1760 .. 28200	379	110%	(1.0)	287	56.2 .. 1100
Strontium (Sr)	1537.6	48%	(1)	1570	696 .. 2340	6.94	105%	(0.8)	5.43	0.20 .. 16.7
Thallium (Tl)	7.27	67%	(1)	4.33	3.51 .. 14.9			(0)		<0.004 .. <0.02
Tin (Sn)	65.0	190%	(0.8)	4.065	1.93 .. 250	0.01		(0.2)	0.01	<0.002 .. 0.01
Titanium (Ti)	588	76%	(1)	383	200 .. 1180			(0)		<0.004 .. <0.04
Vanadium (V)	18.0	40%	(1)	15.7	9.32 .. 28.3	0.39	104%	(0.6)	0.17	0.15 .. 0.86
Zinc (Zn)	264	49%	(1)	297	43.7 .. 377	0.05	53%	(0.8)	0.06	0.02 .. 0.08

Variability of fly ashes from five Irish wood boilers

The average CV (over all analytes) of fly ash solid composition (*aqua regia* extractable) from five other wood boilers was 82% (Table 6), nearly twice as large as the temporal variability of fly ash from the case study site (48%, Table 4). Spatially most variable in fly ash are the elements Sn (205%), manganese (Mn, 121%), Zn (120%), K and C (both 116%), Na (110%) and titanium (Ti, 102%). Less than 50% CV was found for As (41%), B (31%) and Mo (9%).

Average and median discrepancy, stark difference between mean and median, was less pronounced in fly ash than in bottom ash as only Sn, Na and C exhibit 13, 3 and 3-fold difference respectively. The range of concentrations measured in the different fly ashes appeared larger though, fold difference between maximum and minimum solid concentrations of Sn, C, Ti, Al, Fe, Mn and Zn are, in decreasing order, between 123 and 21-fold. Between 20 and 10-fold differences are found for Co (19-fold), Na, V, Ba and silver (Ag, 11-fold). The global CV of leachable components in fly ash leachate from five boilers is 115% (Table 6), larger than in fly ash leachate from a single source over a three year period (79%). Mo, V, Zn and Ba concentrations in fly ash leachate were least variable (52, 57, 62 and 69% CV) across wood boilers. On average, leachate concentrations of two elements (Cr and Se) surpass allowable limits for non-hazardous waste materials by 6 and 2-fold respectively, when median concentration in leachate is compared to the limits, this is not the case. Sb and As average leachate concentrations account for 63 and 32% of acceptable WAC limits, median leachate concentrations are lower and reach only 35 and 16% of said limit values.

	Aqua regia extractable solid concentration [mg/kg]						Aqueous leachate concentration [mg/L]					
Analyte	Average	CV	(FOD)	Median	Range		Averag	CV	(FOD)	Median	Range	
Carbon	220444	116%	(1)	67200	7720 ..	534000			n.d.			
Nitrogen (N)	1883	56%	(0.8)	1795	710 ..	3230			n.d.			
Aluminium (Al)	8518	94%	(1)	6120	679 ..	20500	5.67	197%	(1)	0.692	0.019 ..	25.6
Antimony (Sb)	2.60	83%	(1)	1.72	1.42 ..	6.44	0.04	106%	(0.6)	0.024	0.011 ..	0.0974
Arsenic (As)	3.56	41%	(1)	2.96	2.78 ..	6.19	0.06	122%	(0.6)	0.032	0.007 ..	0.152
Barium (Ba)	197	93%	(1)	142	41.6 ..	509	0.24	69%	(0.6)	0.203	0.094 ..	0.416
Beryllium (Be)	0.33	78%	(0.6)	0.249	0.128 ..	0.626			(0)		<0.002 ..	<0.02
Boron (B)	174	31%	(1)	161	130 ..	266	3.68	127%	(0.6)	1.79	0.24 ..	9
Cadmium (Cd)	17.4	62%	(1)	14.3	4.35 ..	32.6	0.001	71%	(0.4)	0.001	0.0005 ..	0.00154
Calcium (Ca)	121460	64%	(1)	104000	50500 ..	253000	484	86%	(0.6)	717	1.98 ..	733
Chromium (Cr)	110	90%	(1)	61.8	46 ..	284	6.54	202%	(1)	0.623	0.47 ..	30.2
Cobalt (Co)	7.62	79%	(1)	6.72	0.782 ..	14.9			(0)		<0.001 ..	<0.02
Copper (Cu)	200	40%	(1)	189	105 ..	302	0.02	115%	(1)	0.004	0.003 ..	0.0551
Iron (Fe)	9926	74%	(1)	7700	841 ..	19700			(0)		<0.00003 ..	<0.0006
Lead (Pb)	27.5	77%	(1)	19.8	6.66 ..	62	0.08	122%	(0.6)	0.029	0.019 ..	0.195
Lithium (Li)	14.6	60%	(1)	12.7	5.45 ..	26.8			n.d.			
Magnesium (Mg)	19260	67%	(1)	12900	10800 ..	41800	0.007		(0.2)	0.007	<0.0003 ..	0.00665
Manganese (Mn)	13102	121%	(1)	6700	1910 ..	41000			(0)		<0.00001 ..	<0.0002
Mercury (Hg)			(0)	<0.2	<0.2				(0)		<0.00001 ..	<0.00002
Molybdenum (Mo)	2.77	9%	(0.6)	2.75	2.55 ..	3.02	0.21	52%	(1)	0.147	0.11 ..	0.357
Nickel (Ni)	21.7	60%	(1)	29	4.42 ..	34.2			(0)		<0.001 ..	<0.01
Phosphorus (P)	11874	97%	(1)	6850	4310 ..	31900	8.59	86%	(0.6)	12.3	0.077 ..	13.4
Potassium (K)	106620	116%	(1)	58400	36700 ..	326000	8600	142%	(1)	3110	1760 ..	30300
Selenium (Se)	6.24	71%	(1)	4.15	3.24 ..	14	0.11	162%	(1)	0.036	0.006 ..	0.409
Silver (Ag)	5.38	83%	(1)	3.91	1.14 ..	12.9			n.d.			
Sodium (Na)	13450	110%	(1)	3960	1830 ..	33200	819	168%	(1)	211	95 ..	3270
Strontium (Sr)	937	57%	(1)	841	456 ..	1840	1.63	123%	(0.6)	0.88	0.11 ..	3.9
Thallium (Tl)	6.06	77%	(1)	4.27	3.42 ..	14.4	0.11		(0.2)	0.11	<0.004 ..	0.112
Tin (Sn)	29.5	205%	(1)	2.19	1.12 ..	138	0.04		(0.2)	0.042	<0.002 ..	0.0423
Titanium (Ti)	395	102%	(1)	341	21.6 ..	1070	0.04		(0.2)	0.042	<0.002 ..	0.0417
Vanadium (V)	12.6	85%	(1)	7.71	1.36 ..	24	0.030	57%	(0.6)	0.028	0.015 ..	0.0489
Zinc (Zn)	1619	120%	(1)	975	234 ..	4980	0.69	62%	(0.8)	0.85	0.064 ..	0.995

Discussion

In this study, six years of historic WAC data on ash waste from the case study site, the 'composite' of bottom and fly ash, are summarized. This study reports on the compositional consistency of wood ash, an important aspect in the consideration of wood ash re-use and/or disposal. This study distinguishes bottom and fly ashes from untreated wood fuel, based on their chemical composition. This is the first such study on the two types of wood ash for Ireland. The following sections on organic and elemental composition are each initiated with an assessment of the ash waste and then substantiated with the separate examination of the constituting bottom and fly ash variability. This 'all available data' approach is superior to 'snapshot' analyses. Elemental composition analysis is then extended by further bottom and fly ashes from five Irish, non-case study site, wood energy operations.

Organic contaminants in waste ash from the case study site

The waste record for the case study wood energy operation, describes the composite ash material over six years. The analysis of waste ashes provides initial knowledge on presence and variability of the chemical burden over time and potential environmental hazards (Chapter 2).

BTEX are known to be generated and released during wood and biofuel combustion (Rey-Salgueiro et al. 2016). Reference values from 15 Spanish biomass boilers, generating ash or biochar, outlined sum concentrations of BTEX up to 30 mg/kg (Rey-Salgueiro et al. 2016). PCB concentrations in wood ash are generally considered low or even non-detectable (Pitman 2006). Yet, a small amount of 3.4 µg/kg was reported in a study by Bundt et al. (2001). In this study, neither BTEX (<24 µg/kg) nor PCB (<21 µg/kg) contamination is recorded for the ash solid waste from the case study site between 2007 and 2013. This is in accord with the low abundance of these compounds described for Irish wood energy wastes (Chapter 2). Based on pre-existing WAC data, the waste ash from the case study site is thus, in regard of BTEX and PCB, considered non-contaminated and compositionally consistent.

A substantial, but variable, mineral oil load (Hydrocarbon Index, CV 218%) was found in the waste ash of the case study site. The average Hydrocarbon Index (n-decane, C10 to n-tetracontane, C40) in waste ash from the case study site exceeded the average value common in Ireland (Chapter 2). The respective median mineral oil concentration, in contrast, remains below the average of the ten samples analysed in Chapter 2. Incidental spill of lubricants (C14-C50) or machine oils are possible sources of mineral oils but no conclusive information could be obtained for outlier samples. The consistent detection and presence of mineral oils, at least in traces, also suggests an alternate origin. For example, incomplete valorization during the burning, and transformation products from the energy conversion, similar to pyrolysis oils (Zhang et al. 2007). Origin and character of detected mineral oil loads were not further analysed. However, the C10-C40 oils can be considered a complex mixture of aromatic and aliphatic hydrocarbons (RIVM and Verbruggen 2004). Further investigation of the quality of this mineral oil phase in ash, for example potential freight of other organic contaminants such as PAH therein, is necessary but its presence and variability already suggest caution.

The record of waste analyses from the case study site shows that only structurally simple PAH compounds, such as naphthalene, could be extracted and surrogates recovered at acceptable ratios (Section 3.1). Surrogates of PAH with higher molecular mass largely remained in the sample. The low PAH surrogate recovery rates coincided with high TOC abundance. However, more than one third of analyses detected all 16 PAH indicators to a recovery corrected sum of 23-25 mg/kg. A relationship between the presence of organic contaminants such as PAH in ash or biochar and abundance of charred fuel substances (residual organic matter, assessed by LOI), more specifically the degree of aromatization/ carbonization of charred biofuel compounds has been proposed by others (Kloss et al. 2012; Rey-Salgueiro et al. 2016). Reference concentrations in the literature vary, Rey-Salgueiro et al. (2016) as well as Straka and Havelcová (2012) found PAH concentrations in ash >1 mg/kg while other authors stated much (20 to 200-fold) higher concentrations (Bundt et al. 2001; Masto et al. 2015). While unburned matter in ash may hint at the presence of complex reaction products with PAH it may also lower or entirely prevent the compounds' extractability for

analysis (Rey-Salgueiro et al. 2004) or transfer into water. Limited by the quality of analyses on record, general PAH presence, based on the few available valid analyses, may be assumed but no statement on the consistency of PAH abundance in the waste ash of the case study site can be made.

Organic contaminants in separate bottom and fly ash

Existing data on polychlorinated dibenzo-p-dioxins and furans (PCDD/F) in wood ash waste from Ireland (Chapter 2) were limited to few sites (sum of ITEQ 2.7-6.4 ng/kg). No baseline data for PCDD/F existed for the case study site. Fly ash is clearly more heavily burdened, containing about 7-fold more ITEQ, when only the most toxic (2,3,7,8 chlorinated) compounds, are considered (Table 2). The solid PCDD/F burden in bottom ash from the case site is between 1.8 and 4.4-fold larger than for other wood boiler operations that routinely analyse for these compounds (Chapter 2). For fly ash, the difference is even larger and concentrations are between 11 and 26-fold higher. Further emphasizing the qualitative distinction between bottom and fly ash, was the fact that higher chloride substituted (hexa and hepta) dibenzo furans were not detectable in bottom ash. Reference PCDD/F content in ash from untreated wood was expected to be below 10 ng/kg (Wunderli et al. 2000), bottom ash from the case study site thus confirms this value while fly ash exceeds the expected concentration 7-fold. Wood fuel from saltwater soaked logs produced PCDD/F during burning (Preto et al. 2005), thus coastal climate might also impact on and possibly increase PCDD/F burden in European wood ash (Pitman 2006). Quality and quantity of PCDD/F burden of wood bottom and fly ash from the case study site are thus distinct.

Polychlorinated biphenyls (PCB) were below detection limit in pre-existing composite ash analyses from the waste record of the case study site (Section 4.1). However, the class of compounds was found in analyses of initial bottom and fly ash samples (2011). Higher PCB burden in fly ash than in bottom ash, was demonstrated but sum concentrations, are in fact very small, in the range of 100 and 250 ng/kg in bottom and fly ash respectively. PCDD/F and PCB burdens were only analysed once, while this prevents an assessment of their variability over time the strong enrichment of PCDD/F in fly ash is nonetheless striking. The presence of PCDD/F, persistent organic pollutants in ashes from untreated

wood fuel in Ireland indicates the need for further investigation, optimization of the combustion regime and a heightened awareness. It is also a strong argument for the segregation of bottom and fly ash, even from untreated wood fuel.

Elemental composition of composite waste ash leachate from the case study site

The average CV of 91% over all dissolved WAC elements over six years (Table 3) was only slightly smaller than the average variability of the same set of elements among ten Irish wood energy ash leachates (118%, Chapter 2). This shows that waste ash leachates from a single site can exhibit almost as much compositional variability as was found among the waste ashes of ten distinct wood boilers in Ireland. Particularly variable over six years were Pb, Zn and Sb concentrations (CV of 217, 163, and 137%) in the ash waste leachate from the case study site. In fact these elements exceeded the variation observed in measurements of wood ash from ten sites in Ireland (Chapter 2) emphasising that wood ash from a single source may release a highly variable leachate.

Correlation analysis of leachate concentrations from the composite wood energy ash wastes (2007-2013) suggested the co-abundance of some metals however. Positive correlations between metal element pairs (Zn and Pb, Sb and Ni, Mo and Cr) in leachate may point at complex minerals or salts in ash, in which they occur together, or be related to the formation of oxyanionic species (Sb, Mo and Cr). Relative to other elements, oxyanion forming elements (As, B, Cr, F, Mo, Sb, Se, V and W), some potentially hazardous, are commonly leached in higher proportions from alkaline biomass ashes (Vassilev et al. 2013). Among physico-chemical leachate parameters, the strong correlation of pH, TDS and ElC in the leachates likely depicted the alkaline nature of the parent waste ash materials, facilitated by oxides and hydroxides contained therein (Ludwig et al. 2005; Vassilev et al. 2010; Barbosa et al. 2013). The waste hazard relevant element selenium may leach from sulphate or chloride salts as their ions correlated positively and their association was reported before (Izquierdo and Querol 2012).

Thus, unsurprisingly, some regularity existed for the composition of wood energy ash waste leachates from a single site. Closer investigation of the correlated and highly variable Pb and Zn concentration in leachate seemed

pertinent. Overall variability of the case study site waste ash leachate could potentially be lowered by the identification of the Pb and Zn source. Also Se leaching, identified as commonly in excess of acceptable WAC limits among Irish wood energy wastes (Chapter 2), and associated with the mobility controlling chloride and sulphate provided an indication to be followed up in the separate ash types.

Elemental composition of bottom and fly ash and corresponding leachates from the case study site over the three year monitoring period

The three year separate chemical monitoring of bottom and fly ash demonstrated greater compositional consistency of bottom ash compared to fly ash solids. Least variation of content in bottom ash was shown for Se, Ni, B, Sn and Zn, suggesting these elements to commonly occur in the measured concentration. In contrast, arsenic (As) is among the most variable elements in both bottom and fly ash, but the solid concentration CV was still more than 2-fold larger in fly ash. Average CV over all analytes in bottom and fly ash solids (22 and 48% respectively) also differs by a factor of 2. This is interesting since the quadruplicate analysis of the initial ash samples from 2011 (Chapter 3) exhibited better precision (lower CV) of the fly ash analysis. As bottom ash contains glass-like clinker particles, their presence in subsamples from 2011 may have skewed said initial analyses, particularly relative to fly ash samples that are much more homogenous (well sorted material) when particle size distributions are concerned. It may thus be concluded, that while single time point, 'snapshot' analyses can capture the composition of a fly ash sample, the results are unlikely to be directly informative about the composition of fly ash from that particular site in general.

According to WAC, solid bottom ashes from the case study site contain no hazardous substances in mobile concentrations exceeding what is admissible as non-hazardous waste. The resulting leachate concentrations of WAC elements, apart from As, are also less than for the composite waste. From fly ash, selenium and sulphate leaching mark the material non-compliant with non-hazardous waste limit concentrations. Thus it was concluded that bottom and fly ash carry

distinct chemical waste hazard potential. The sum of dissolved analytes, pH, and ElC proved higher total dissolution of elements out of fly ash than out of bottom ash initial 2011 samples (Chapter 3). This observation is confirmed over the three year monitoring period. When all analytes are considered, bottom and fly ash leachate actually display very similar average CV of element concentrations (71% and 79% respectively). The consistency of bottom and fly ash leachate composition from a single site over time may thus be considered similar. However, the variability (average CV) of metal and metalloid WAC elements in leachate of bottom ash from the case site over three years (49%) is markedly lower than fly ash leachates (90%) or composite waste ash leachates (99.6%) from the case site over three and six years respectively. While supporting distinct hazard character of bottom and fly ash solids as well as their corresponding leachates this also supposes fly ash a likely source for composite waste ash leachate variability.

When comparing pre-existing hazardous element mobility of the composite waste from the case study site with the two separate ash types constituting said waste it can further be concluded that Pb and Zn as well as Se and SO_4^{2-} originate from the fly ash parts. This matches with earlier observations of metal enrichment in fly ash solids (Narodoslawsky and Obernberger 1996). As the WAC elements seem relatively more concentrated in fly ash in general, composite ash hazard through mobile elements was strongly impacted, if not governed, by the presence of the flue gas cleaning residue as part of the composite.

In fly ash leachate, the elements Al, Ba, Ca, Cr, Pb, Mo, K, Se, Na, Sr, Ti and Zn are present in higher concentrations than in bottom ash leachate. In bottom ash leachates, As, B, Cu, Mg, Mn, P and V are more concentrated (Chapter 3). The confirmed presence of specific elements in leachate from bottom and fly ash differs. Among macro elements (occurring in mg/L range, and important for plant growth) P, Mg and Mn transfer out of bottom ash into the leachate in concentrations of 1.87, 1.65 and 0.02 mg/L which corresponds to at least 23.4, 5.5 and 2-fold of the respective higher values than in fly ash. The trace elements Co, Cd and Sb are confirmed in bottom ash, but not fly ash leachate. Noteworthy here is, that detection limits in fly ash leachate were higher, thus Co, Cd and Sb

could still be present in 19.2, 10.5 and 3.9-fold concentrations in fly ash leachate. In contrast, the trace element Pb is confirmed in fly ash leachate in a concentration of 4.45 µg/L, which is at least 2.3-fold more than in bottom ash leachate. Thus, the bottom and fly ash leachates are qualitatively and quantitatively different in composition.

Bottom ash elemental consistency of composition

Average solid concentrations for bottom ashes from different boilers (Table 5) seem less reliable because of greater underlying variation; the global CV is 3-4 times larger than in bottom ash solids from a single source over three years (Table 4). A comparison of average element concentrations between single and multiple source bottom ashes is, because of the variation identified among the five other wood ashes, of only limited informative value. Still, 72% of all analytes (including WAC relevant elements Sb, Ba, Cd, Cr, Cu, Pb, Mo, Ni and Se) were observed in higher average solid concentration within the five non-case-study site bottom ash samples than in the single source bottom ash over three years. The hazard potential arising from the solid concentrations of these elements in a single source bottom ash over time could thus be expected lower and more consistent than the more generic average of the larger bottom ash sample population.

Discrepancies between average and median solid contents for Pb, Sn and Sb in the five non-case site bottom ashes though, point at skewed, non-normal distributions with large outliers as a source of the variation (Table 5). Particular caution thus is advised, as very high maximum concentrations of these elements (i.e. Pb 1.51 g/kg ash, Sn 0.25 g/kg ash, Sb 0.04 g/kg ash) can occur in wood ash from untreated fuel in Ireland. Comparison to the geometric mean appeared more prudent and exhibited the medians of most elements in the five non-case site ashes to be smaller than their respective averages but still larger than average concentrations of bottom ash from the case study site. Solid concentrations in case site bottom ash over three years can thus be assumed in the lower half (quartiles 1 and 2) of the respective elements' distributions across 5 ashes from other Irish wood energy operations. Noteworthy, the median Pb concentration in five Irish wood ashes from untreated fuel was in fact less than the average case

study site Pb concentration over three years. Also As and Cd median concentrations in the in five Irish wood bottom ashes were rather similar to average content of bottom ash over three years. Labelling the case study site bottom ash non-contaminated in comparison would thus still be an overstatement.

Pb, Sn, Sb, Ni and C show the highest variability in these Irish solid bottom ashes from different sites. In case site bottom ashes these elements did not display the same high variability over three years, Sb, Pb and C (CV of 26%, 25% and 16% respectively) rather matched the global CV over all analytes (22%) in bottom ash solids. Ni and Sn average concentrations in case site bottom ashes over three years were in contrast determined with very low underlying variability (CV 6% and 3% respectively). For these elements in particular, the wood bottom ash summary (Table 5) and average or median concentrations therein should not be used to predict a generic Irish bottom ash. Some elements however display high consistency across the five solid bottom ashes examined. The variability of Zn>Sr>Mg>V>B>Mo>Li>Ca>K in the five ash solids is lowest.

With the exception of carbon, all element concentrations determined for bottom ash from the case study site fall within the large range of concentrations described from five other Irish wood bottom ashes. However, some elements such as Pb, Sn and Sb outliers from the five non-case site bottom ashes cannot be substantiated in the case site bottom ash analyses and do not apply. On the other hand, the least variable elements Ca and K show very similar CV in both the case site and five non-case site ashes. Thus some compositional consistency can be expected for single source bottom ash solids.

Al, Cr, K and Na were always mobile in leachate from all five non-case site bottom ashes examined The global CV over all analytes in five Irish bottom ash leachates (Table 5) was slightly larger than from case site bottom ash leachates over time (Table 4) as well as the solid concentrations of the five parent bottom ashes. We thus suspect less compositional consistency of the leachates in general. A good prediction however seems possible for water dissolved Mo, B and As, as these elements exhibit the lowest CV across leachates from five, non-case study site bottom ashes. In contrast, for particularly variable Ba, Cr and Pb

in leachate no prediction of other ash concentrations should be attempted on the basis of the bottom ash summary (Table 5).

Fly ash elemental composition and consistency

Fly ash solids are spatially more variable than bottom ashes, just as fly ash was much more variable than bottom ash across time (case study site). Thus there is an even greater need for caution when assuming compositional consistency for fly ash. However, the difference between case study site solids over time and five different boiler fly ashes (global CV 82%) is, likely because of high variability of a single source fly ash (global CV 48%), not as pronounced as is the case with bottom ashes. Fly ash solids from five boilers (Table 6) exhibit highly variable contents of Sn, Mn, Zn, K, C, Na and Ti. These elements are thus associated with the highest uncertainty when attempting to extrapolate the composition of a generic fly ash. Apart from C, which was also highly variable in fly ash solids from the case site, said elements do not vary particularly strongly among single source fly ashes over time. Element variability across the larger fly ash samples from five sources is thus not directly informative about the individual compositional peculiarities of fly ashes that accrue from a single source. Among the particularly variable elements, Sn, Na and C show the largest differences between average and median, pointing at skewed, non-normal distribution of data on these elements. While carbon may not pose a hazard as an element, the presence of C outliers and likely association with incomplete combustion and thus organic contaminants (Section 4.1) still warrants caution. In general, average and median discrepancy points at outliers and may thus hint at specific problems occurring at individual sites. In fly ash Mo, As and B, in contrast, occur most consistently, here a generalization appears reliable. The very large element concentration ranges in Irish fly ash solids from untreated wood fuel further clearly emphasize the need for site specific characterization.

The global CV of elemental components of fly ash leachate (115%) from five ash sources is larger than for leachates of bottom ashes from the same five sources (92%) and fly ash leachates from the case site over three years (79%). Mean element concentrations are thus on average associated with a standard deviation of at least equal size. As mobile concentrations are applied to determine chemical

waste hazard before disposal, it is not feasible to characterize a generic Irish fly ash hazard potential. Still, Cr and Se certainly pose a hazard in the concentrations they occur. Less certain in comparison are hazards from Sb and As.

Clean, non-contaminated wood ash

Sustainability considerations and economic interests can converge in the recycling of waste residue from biomass fired power plants, particularly ash from untreated fuels. In this study it was demonstrated that fly ash contains more PCB, more PCDD/F and more hazardous elements, that its compositional variability is higher than for bottom ash of a single site as well as from multiple source. Thus, it might be considered precautionary to avoid fly ash distribution in the natural environment. Indeed, for recycling purposes, blending of the two ash types has been stated a medium-term option only (Narodoslawsky and Obernberger 1996). The use of composite ashes (blends) in agriculture or forestry, though practical, is deemed a missed opportunity to segregate potential pollutants (Narodoslawsky and Obernberger 1996). Based on the data generated in this study, it is recommended that bottom and fly ash, even from untreated wood fuel, need to be kept separate, and distinct after use pathways need to be developed.

In this study it was demonstrated that both fly ash and bottom ash from a single source vary over time. *Aqua regia* extractable solid content of single source bottom or fly ash over time displayed the smallest variations and thus suggests some degree of compositional consistency for the ash solids. Leachates, in contrast, always displayed much more variation and over-time consistency of their composition thus seems less likely. This raises the question whether snapshot analyses, to our knowledge the bulk of data published on wood ash, is sufficient to depict the character of single source ash materials.

Compositional variation complicates regulatory overview. Enabling further use and marketing, the European Chemical Agency (ECHA) has regulated a number of ashes. Hazardous components of these ashes, in the example of plant ashes (CAS # 93333-79-0), presumably a mixed composite sample, is given as a sum, below 0.1%. The ECHA regulations acknowledge the need to classify waste materials targeted for recovery or recycling, but there may be a risk of overestimation of compositional consistency.

This study shows the substantial variation in compositional make-up of wood ash from clean, untreated wood, and emphasises the need for comprehensive analysis (over-time) of compositional variability.

Distinct chemical composition of bottom and fly ashes mean different hazard properties. Thus, rather than the misleading concept of "clean wood ash", there is a need for precision selection of wood ashes for different after-uses, depending on their burden of hazardous elements.

Acknowledgements

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Chapter 5
Ashes from untreated wood fuel: Waste hazard and potential toxicity

Abstract

No data are available on the biological hazards of ash from untreated wood fuels in Ireland. This investigation applied standard tools from chemical risk assessment with aquatic species to describe such hazards from pH neutralized leachates, as is required for appropriate disposal of the current waste material. Extended with pH native leachate testing, ash hazards are characterised to inform potential re-use in the environment.

Waste leachate toxicity using five common bioassays distinguished hazard potentials of wood bottom and fly ash clearly. Neutralized aqueous extracts, as required for standard test validity, almost consistently incur less toxicity than their native, alkaline pH precursors. Test populations of *Aliivibrio fischeri* (Microtox[®]) and *Pseudokirchneriella subspicata* (micro algae) seem equally sensitive to native extracts (EC_{50} is 5% leachate). In *Lemna minor, Daphnia magna* and *Oncorhynchus mykiss* (rainbow trout) the disparity in bottom and fly ash toxicity is independent of pH adjustment.

The combination of native and neutralized leachate toxicity testing broadens the scope of a standard waste hazard assessment towards ecosystem impacts, especially where alternatives to disposal are sought and alkalinity is a material property intended to be exploited in recycling.

Introduction

Endeavours to increase fuel efficiency in general and endorsement of renewable, potentially carbon neutral energy both further the advance on sustainable resource use. Combined heat and power (CHP) technologies improve energy conversion efficiency relative to other heat generating boilers and their application, not only in the bioenergy sector is increasing. To date, the development of combustion based renewable energies, has not been matched by solutions on how to deal with the accruing waste (Chapter 1). The various types of energy ash constitute one of the world's largest solid waste streams today and pose a considerable management challenge (Reijnders 2005). Based on operation of origin, the European Waste Catalogue (EWC, 2000/532/EC, European Commission 2000) classifies energy ashes in chapters 10 and 19, from power stations and waste management facilities respectively. Therein absolute and mirror categories, in part based on parent fuel type, refine the distinction of non-hazardous and hazardous waste materials and govern disposal. However, more than one category may apply. In chapter 10 of European waste catalogue entitled 'Fly ash from coal' and 'fly ash from peat or untreated wood' are absolute non-hazardous entries while 'wastes from gas cleaning containing dangerous substances' is a mirror entry, potentially hazardous and as relevant for said fly ashes. Mistaken waste identity may result in differing hazard or even risk analysis and subsequently inadequate handling and disposal. Thus, chemical limit criteria for waste acceptance on sites designated for inert, non-hazardous or hazardous waste (WAC, 2003/33/EC, Council of the European Union 2003) warrant appropriate disposal. Effects of chemical mixtures present in ash waste are, however, hard to predict and elude chemical classification. Ashes from coal, peat or untreated wood may, while classified as non-hazardous in EWC and compliant to respective limits, still pose a threat to biota in cases where they get released.

Classification as hazardous waste in EWC is based on fifteen criteria (2008/98/EC, European Parliament and Council 2008), one is H14 'ecotoxic' encompassing materials 'which present or may present immediate or delayed risks for one or more sectors of the environment'. Biological hazard analyses to this end have been undertaken for a range of ash type wastes such as from coal

fired power plants (Jenner and Janssen-Mommen 1993; Karuppiah and Gupta 1997; Tsiridis and Samaras 2006) and also for chapter 19 ashes such as from municipal or industrial solid waste incinerators (Hidehiro 1996; Lapa et al. 2002; Römbke et al. 2009; Stiernström et al. 2013; Stiernström et al. 2014). However, laboratory toxicity test data on ashes from wood fuels (Aronsson and Ekelund 2005; Aronsson and Ekelund 2006; Stiernström et al. 2011; Barbosa et al. 2013) and particularly untreated wood fuels are still scarce. Given the attention renewable, potentially carbon neutral fuels have attracted, this lack of data is surprising. Among energy ashes, wood combustion residues still accrue in comparably low volumes, most are a-priori classified as non-hazardous and the bulk is landfilled (Reijnders 2005). Ease of disposal, as non-hazardous waste, facilitates the use of renewable fuels such as wood. Yet, doubt has been cast by more recent findings of some heavily contaminated biofuel ashes (Pöykiö et al. 2009; Vassilev et al. 2010; Chapters 1 and 4). Further to this, a biofuel fly ash takes up a middling rather than low biological hazard rank among municipal and industrial waste incinerator ashes (Stiernström et al. 2011). Other biomass ashes from a pulp and paper industry boiler were even classified ecotoxic (Barbosa et al. 2013). Caution is thus advised in dealing (disposal or preparation for after-use) with supposedly 'clean' biomass energy ashes, even from untreated wood fuels, as they may bear some hazardous properties (Reijnders 2005; Vassilev et al. 2010; Vassilev et al. 2013, Chapter 4).

Waste prevention, followed by preparation for re-use (recovery) are the top priorities set in the revised European Waste Framework Directive (WFD, European Parliament and Council 2008). Instrumental to these aims are By-product (Article 5) and End-of-waste criteria (EoW, Article 6) respectively (Chapter 2). In case by-product criteria are fulfilled, a material ceases to be waste entirely, the latter introduces a pathway for a waste to become a by-product under a distinct set of criteria. The most striking difference between both these sets reflects regards applicability, and thus level of precaution. That is either direct, without further processing, in case of by-products, or only after passing a recovery operation for materials via EoW. The four fundamental EoW criteria (Chapter 2) laid down in WFD have been further specified for a few antecedence waste streams (various metal scraps and glass cullet) used as feedstock in

industrial processes only. These follow 'a pathway that most often controls the risks of health and environmental damage via industrial permits' (Villanueva et al. 2010). Ashes and slags, in contrast, are regarded under 'streams used in applications that imply direct exposure to the environment'. For ashes EoW criteria are yet to be specified further and are expected to involve limit values for pollutant content or leaching (Villanueva et al. 2010). Premise to efforts of waste preparation for re-use (via EoW) is that the material composition is known, that the waste is clean and with low potential risk of environmental and health damage (Villanueva et al. 2010).

Biological effect analysis in addition to physico-chemical data, particularly regarding unknown compounds and mixtures in current waste materials, is widely acknowledged and advocated (Moser and Römbke 2009; Römbke et al. 2009). Already for some time, test batteries designed to represent several trophic levels and, therein, species which depict connections in a model food web, are common in waste and biomaterial ecotoxicity assessment (Chassé et al. 2006; Moser and Römbke 2009; Stiernström et al. 2011). Simple aqueous leaching tests with various wastes including coal and biomass ash are considered suitable for both chemical and biological testing (Schultz et al. 2002; Tsiridis and Samaras 2006; Barbosa et al. 2013). Wood combustion residues are very alkaline (Etitgni and Campbell 1991; Someshwar 1996) and this presents a difficulty for biological assessment (Aronsson and Ekelund 2005; Aronsson and Ekelund 2006; Barbosa et al. 2013; Chapter 3). Ideally, test organism homeostasis should not be affected by the conditions of the test (stresses) other than the substance(s) under investigation. Adjustment of test solution pH is often required to match the respective organism's tolerance range as to obtain valid results according to OECD or ISO toxicity testing standards. It has been shown that waste inherent speciation of metals changes with pH (Wadge and Hutton 1987; Hansen et al. 2001) and that measureable toxicity is affected by these changes (Lapa et al. 2002; Barbosa et al. 2013; Chapter 3). Toxicity testing at the margins or even outside of a model organism's tolerance range can only result in a severe response. In contrast, results from phototrophic organisms exposed to wood ashes (Aronsson and Ekelund 2006; Chapter 3) have demonstrated that growth may be sustained at pH values normally deemed too high for plant survival. We

argue that neither approach, testing using pH adjusted or native samples, is able to comprehensively depict a test substances hazard potential. The former is appropriate in the context of 'safe' disposal on landfills where waste materials are managed according to their properties (e.g. alkaline substances deposited in dedicated cells or neutralized), while the latter depicts waste inherent hazard potential such as is relevant in case of spills or inappropriate release.

Recovery and after-use of current waste, if precaution-oriented, may aid the protection of natural resources, lead to the closure of element and material cycles as well as, eventually, have economic benefits (Römbke et al. 2009). However, storage, transport and disposal of wood ashes, subject to waste management, already entail environmental hazards (Reijnders 2005). Existing limit concentrations for acceptance on landfills (WAC) and hazard criteria are defined for waste and, again, based on the presumption of safe disposal, as separated from the environment as possible. Consequently, the limit values expected to specify the four basic EoW criteria for ashes and slags to cease being waste, will likely depict a high level of precaution. Even greater scrutiny of toxicity (hazard to biota) should be applied when alternative pathways for the current waste material are considered. The question is whether the standard tools for hazard assessment are sensitive enough to assess potentially valuable and supposedly 'clean' materials like wood ash from untreated fuel.

It was argued before that when chemical composition and leaching potential are assessed, all available data should be taken into consideration (Chapter 4). Particularly for ashes intended for spreading as fertilizing or liming agent (direct exposure to the environment), over-time variability of a current waste material should be known as well. With relative wood fuel homogeneity in Ireland (Chapters 2 and 4), particular attention was given to stable toxicants such as heavy metals originating from the fuel exclusively. It was demonstrated at the case study site of this study that the mixture of bottom and fly ashes into the composite wood ash waste increased the leaching potential of elements like Pb, Zn and Se and thus potentially its chemical waste hazard (Chapter 4). The separation of bottom and fly ashes was thus strongly suggested for after-uses that may come in direct contact with the environment. Here, data are presented on the effects of leachates from separate bottom and fly ash using a range of standard

aquatic toxicity model species. We compare the effects on biota from pH adjusted as well as pH native leachates.

We hypotheses that (i) biological hazards from pH native and neutralized ash extracts are different, and that (ii) thus waste hazard characterization required for adequate disposal does not sufficiently reflect the damage incurred if non-hazardous wastes such as wood ash from untreated fuels should enter the environment.

Materials and methods

Wood energy ashes, leachates and test solutions

The test substances (wood bottom and fly ash) for biological assessment were collected in May 2011 from a 3.8 thermal MW rotating grate CHP wood energy boiler. The parent fuel was sawmill wood processing residues (sawdust, wood chips and bark shavings) from untreated Sitka spruce (*Picea sitchensis*) harvested in the south-west of Ireland and burned at 700-800°C (Chapters 3, 4). Bottom and fly ash were collected from the solid residue conveyors serving the water pool below the firing grate and the electrostatic precipitator respectively.

Ash samples were dried at 30°C until weight remained constant and particles larger than 4 mm were excluded. Standard waste leachates were generated from dried ash according to BS EN 12457-2 (CEN 2002) with distilled water (10 L/kg, 24 h contact time) followed by qualitative filtering (Fisherbrand, FB 59031). Chemical analysis of the aqueous extracts was performed by National Laboratory Service (Leeds, UK; UKAS #0754). Bottom and fly ash leachates were examined for 28 dissolved elemental analytes including their mobility from the parent ash material (chapters 3 and 4). Analytes include the four elements Cd, Pb, Hg and Ni from the first European Priority Substance List (2455/2001/EC, Parliament and Council of the European Union 2001) three of which, apart from Ni, are classified as priority hazardous substances. Furthermore, leachates were examined for the elements As, Ba, Cr, Cu, Mo, Sb, Se and Zn, as well as the ions Cl^- and SO_4^{2-} which are listed in WAC (2003/33/EC, Council of the European Union 2003). Results of the quadruplicate solid and leachate analyses (Chapter 3) and over time variability of the ashes from the case study site (Chapter 4) were

reported earlier. As the test substances to this study (leachates from the 2011 samples) were not assessed for their WAC compliance in pervious chapters, we repeat this type of analysis for the specific leachates under investigation. The extracts served as stock solutions for ecotoxicological testing. Test solutions were prepared as dilutions of (pH) native or neutralized fresh leachate (100 g aeq/L; chapter 3). Leachate volumes were deducted from distilled water requirement in respective standard media. Concentrated (1M) sulphuric acid (for *Lemna minor* and *Daphnia magna* assays) or hydrochloric acid (for tests with Microtox, *Pseudokirchneriella subspicata* and *Oncorhynchus mykiss*) were used to pH adjust ash leachates via titration.

Test battery

A set of simple, whole organism bioassays used for the assessment of wood ash leachate toxicity included two single cell and three higher model organisms (Table 1). Exposure durations varied from 30 min to 21 days to cover potential acute and chronic toxicity. Models were chosen from ISO and OECD aquatic standard tests to represent all trophic levels of an aquatic ecosystem and provide for optimal comparability and reproducibility.

Table 1: Test battery for the waste hazard assessment of wood ash; Trophic levels with selected representing aquatic species, standardization reference, duration of the assays and main endpoint

Trophic level	Model species	Test reference	Duration	Endpoints
Biodegradant destruents	MICROTOX (*Aliivibrio fischeri*)	ISO 11348-3	30 min	Bioluminescence
Primary producers	Green algae (*Pseudokirchneriella subspicata*)	OECD 201	72 h	Growth
	Aquatic macrophyte (*Lemna minor "5500"*)	OECD 221	7 d	Growth
Primary consumers	Water flea (*Daphnia magna*)	OECD 202	48 h	Immobility
Secondary consumers	Rainbow trout (*Oncorhynchus mykiss*)	OECD 203	96 h 21 d	Mortality

Inhibition of bacterial bioluminescence assay (Microtox®)

The Microtox assay utilizes *Aliivibrio fischeri* (Gamma Proteobacteria, Vibrionales, Vibrionaceae), formerly classified in the Vibrio Genus. The bacterium occurs as free floating cells in marine and some freshwater habitats but can also be found in the bacteriome of higher organisms. The test system is adapted for pH 5-8. Inhibition of bioluminescence was the endpoint in standard toxicity testing (EN ISO 11348-3, CEN 2008). The tests were conducted at

Shannon Aquatic Toxicology Laboratories (SATL, Shannon, Ireland) with the M500 analyser (Modern Water, Guildford, UK). Microtox tests were conducted with bacterial populations from freeze dried batches and according to ISO 11348-3. Sensitivity was validated with potassium dichromate ($K_2Cr_2O_7$), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) and 3,5-dichlorophenol ($C_6H_4OCl_2$). Inhibition of bioluminescence in the range of 20-80% after 30 min contact time was achieved by potassium dichromate at 52.9 mg/L, zinc sulfate at 2.2 mg/L and 3,5-dichlorophenol at 3.4 mg/L.

Algal growth inhibition test (Pseudokirchneriella subspicata)

Pseudokirchneriella subspicata (KORSHIKOV) HINDÁK (Chlorophyceae, Sphaeropleales, Selenastraceae), synonymous with *Selenastrum capricornutum* PRINTZ and *Raphidocelis subcapitata* is a crescent-shaped, single celled, non-motile microalga with ubiquitous distribution in oligotrophic to eutrophic freshwater ecosystems. Algae are primary producers and an important food source for higher organisms feeding on plankton, making them a highly relevant model in aquatic toxicity testing. Most cultured algae species exhibit a pH tolerance between 6.5 and 9, while optimum growth is generally achieved between pH 8.2 – 8.7 (Lavens and Sorgeloos 1996). *P. subspicata* algal strain (CCAP 278/4, Culture Collection of Algae and Protozoa, Argyll, UK) was used in the tests (OECD 2011). Tests were conducted in IOI400.XX2.C incubators (Gallenkamp, UK) at SATL, growth was assessed microscopically (cell counts) and via chlorophyll fluorescence. Sensitivity with was validated with potassium dichromate (EC_{50} is 0.8 mg/L, 95% CI: 0.64 to 1.02 mg/L) and 3,5-dichlorophenol (EC_{50} is 1.85 mg/L, 95% CI: 0.64 to 5.96 mg/L).

Macrophyte growth inhibition test (*Lemna minor*)

Lemna minor LINNAEUS (Asimatales, Araceae) is an aquatic macrophyte with wide distribution in temperate regions and is commonly used in single substance phytotoxicity tests (OECD 2006) as well as water quality assessment (chapter 3). The discoid stems (fronds) of the vascular plant *L. minor* are floating on the water surface and the thin root emanates from a central location on the lower surface of the frond (Landolt and Kandeler 1987). The pH optimum of *L. minor* growth is 6.2, the species tolerates conditions between pH 3-4 and 10.5 (McLay 1976). Plant material for testing originated from cultures kept at School for

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Biological, Earth and Environmental Sciences, UCC. The strain (#5500) originated in Blarney, Ireland. Exposure duration was 7 days at 20 ± 2 °C with 16/8 hour simulated day and night cycle (Chapter 3).

Invertebrate acute immobility test (*Daphnia magna*)

The freshwater crustacean *Daphnia magna* Straus (Branchiopoda, Cladocera) is among the most widely used aquatic test organisms. The 48 h acute toxicity test (OECD 2004) exposes (neonates, age < 24 h) to a range of concentrations of a water borne test substance. Endpoint of this standard test is immobility which is assessed after 24 and 48 h. The pH range tolerance of *D. magna* in regard of their mobility spans pH 5.5 to pH 10 where they remain unaffected while pH values lower than 4 and higher than 11.5 cause total immobilization in a test population (Seco et al. 2003). A culture of *D. magna* was obtained from Shannon Aquatic Toxicity Laboratories (Shannon, IE), sensitivity of the test was validated with potassium dichromate (EC_{50} was 1.21 mg/L, 95% CI: 1.03 to 2.1 mg/L).

Fish acute and prolonged survival test (*Oncorhynchus mykiss*)

The rainbow trout, *Oncorhynchus mykiss* Walbaum (Salmoniformes, Salmonidae) is a common test organism used with OECD Guideline 203 (OECD 1992). During the 96 h duration acute and 21 d prolonged exposure survival tests, mortality of the test organisms is recorded every 24 h. Both were conducted at SATL and based on the OECD guideline. Depending on the weight of the test organisms up to seven fish may be exposed to a solution of the test substance per 20 L tank in static and semi-static exposure systems respectively. Large amounts of leachate were required for medium changes during the prolonged exposure and required a deviation from the leaching protocol, water accommodated fractions (WAF) were generated by mechanical stirring of ash (10 L/kg) in glass basins.

Calculations and statistics

Leachate concentrations were expressed as gram ash equivalents per liter (g aeq/L). As leachates were prepared from 100 g of ash extracted with 1 L of water, the numerical value in g aeq/L was synonymous with % leachate as expression of dilution (e.g. 20 g aeq/L = 20% leachate proportion of the test solution). Elemental compositions of leachates were reported before (Chapter 3)

and represent full, undiluted 100 g aeq/L or 100% leachate. The ratio at which an analyte was detectable out of four ash sample analyses (Chapter 3) was given as frequency of detection (FOD). Relative mobility is defined as the proportion of an element in leachate relative to the elements solid concentration (Chapter 3). The global coefficient of variation (CV) is calculated as the average of all individual element CV.

Raw data from each bioassay replication were normalized with the average response of the respective pure medium control (n=2 per independent replication). EC_{50} was calculated using the pooled normalized data from all replications for non-linear regression (variable slope). Statistical analyses were performed with Graph Pad Prism (Version 5, Graph Pad Software, La Jolla, USA).

Table 2: Acute toxicity classification

Toxic units	Description
<3	Non Toxic
3 – 10	Slightly Toxic
10 – 50	Toxic
50 – 100	Very Toxic
>100	Extremely Toxic

Toxic units (TU), as a more intuitive representation of toxicity than EC_{50} as increasing numbers signify higher toxicity. TU were calculated as $TU = 100/EC_{50}$. Toxicity classification (Table 2) was based on the standard operation procedure (SOP) of SATL (Shannon Aquatic Toxicity Laboratory 2012).

Results

Distinction of the test substances (bottom and fly ash leachates)

Leachates of bottom and fly ash were clearly distinguished from each other (Chapter 3). Higher pH and electrical conductivity were found in fly ash leachates (FAL) than in bottom ash extracts. Among WAC or priority hazardous elements only As and Cu were enriched in bottom ash leachate (BAL) while a much larger number of these potentially harmful elements (Zn, Ba, Se, Cr, Mo and Pb) were relatively more concentrated in FAL. Among plant nutrient

elements, BAL was richer in P, Mg and B while fly ash leachate carried more K, and Ca. Orthophosphate was only detected in BAL while the sum concentration of nitrate and nitrite (Total oxidized nitrogen) was 6 fold larger in FAL than in BAL. Biological oxygen demand was not detected in either of the ash type leachates while the chemical oxygen demand was on average the same but associated with much larger variation in BAL than in FAL. Out of the 16 polycyclic aromatic hydrocarbons (PAH), only naphthalene was detected, it was present in bottom ash leachate only, at 0.013 µg·l^{-1} (FOD 0.75).

Leachates from bottom ash contained an average sum of 1.74 g/L dissolved elements (including sulfates), mainly potassium (K, 69.8% of total dissolved elements), Cl$^-$ (17.1%), SO$_4^{2-}$ (6.4%), sodium (Na, 5.7%) and calcium (Ca, 0.68%). Boron, phosphorus and magnesium together represented 0.32% and were present in the range of 1-2 mg/L with a residual of 0.04% for the other confirmed analytes, mainly trace elements. By rank of concentration (200-0.2 µg/L, median at Mn 16 µg/L), the metal elements vanadium (V), molybdenum (Mo), Cr, strontium (Sr), aluminium (Al), the metalloid arsenic (As), barium (Ba), manganese (Mn), Cu, selenium (Se), titanium (Ti), Zn, the metalloid antimony (Sb), cobald (Co) and Cd were detected in bottom ash leachate.

Fly ash leachate carried the 6.6-fold amount (11.5 g/L) of dissolved elements (including sulfate) constituted from 47.2% K out of 11.5 g/L total dissolved elements, 36% Cl$^-$, 10.8% SO$_4^{2-}$, 1.85% Na and 3.81% Ca as well as zinc (Zn, 0.03%). Aluminium and Strontium (Al, Sr, both 0.02%) were present in the range of singe mg/L, other dissolved trace elements made up a proportion of the same size in (0.02%). In decreasing order of abundance (800-4.3 µg/L, median at Ti 78 µg/L), the elements B, Cr, Ba, Mo, Se, Ti, P, V, As, Pb and Cu were detected in fly ash leachate (Chapter 3).

The quadruplicate analyses of bottom and fly ash leachates from 2011 exhibited a global (over all elemental analytes) coefficient of variation (CV) of 25 and 26% respectively. When only WAC relevant elements are considered, the CV of BAL was 26% while fly ash only displayed 20% coefficient of variation.

Toxicity to aquatic model species

Leachate toxicity assessment with five ecologically relevant model species was performed adopting OECD or ISO standards (Table 1). The ranges of test concentrations in the bioassays were chosen to determine the 50% effect concentrations (EC_{50}) and for the two types of wood ashes accruing on site. Threshold concentrations for biological effects, such as the EC_{10} were determined from the same datasets.

Inhibition of bacterial bioluminescence assay (MICROTOX®)

The inhibition of bioluminescence of *Aliivibrio fischeri* due to exposure to native wood bottom and fly ash leachates (Figure 1, full symbols) followed a sigmoidal dose-response curve. The EC_{50} for native fly ash leachate was 3.6 g aeq/L (95% CI: 2.74 to 4.74 g aeq/L) while native bottom ash leachate exhibited a marginally higher EC_{50} of 4.84 g aeq/L (95% CI: 4.1 to 5.7 g aeq/L). Within the tested concentrations the steepness of the dose-response curve and measurement value dispersion around the mean for native fly ash leachate (slope at EC_{50} is 3.89, SD at 4.5 g aeq/L is 38.3%) were higher than for native bottom ash leachate (slope at EC_{50} is 2.6, SD at 4.5 g aeq/L is 20%).

Neutralized ash samples (Figure 1, open symbols) were tested at concentrations exceeding the EC_{50} of the native samples (5.625 to 45 g aeq/L) and displayed little effect on the bioluminescence in concentrations up to 11.25 g aeq/L. While bottom ash only exhibited a minor impact and small variability in the light output of the bacteria in 22.5 g aeq/L, the effect of fly ash at this concentration was about twice as high and varied strongly between independent replications. The derived EC_{50} values were similar but exhibited a large, error margin, the EC_{50} for neutralized bottom ash was 43 g aeq/L (95% CI: 24.4 to 75.6 g aeq/L) and fly ash EC_{50} was 39 g aeq/L (95% CI: 8 to 189 g aeq/L). Neutralized bottom ash leachates showed a 9-fold higher EC_{50} than their native counterparts. For fly ash the difference between native and pH neutralized leachate EC_{50} was smaller, still the EC_{50} is 5 times larger than with native extracts.
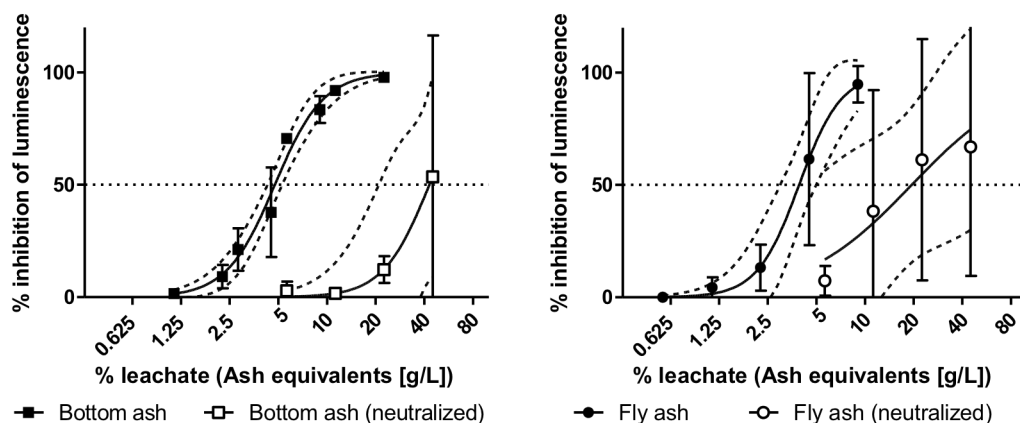
Figure 1: Dose-response relation of native and neutralized wood bottom and fly ash leachates in the MICROTOX assay (*Aliivibrio fischeri* bioluminescence) after 30 min relative to the pure medium control with 95% CI limits, native leachate (filled symbols) and neutralized leachate (open symbols); (A) Bottom ash, (B) Fly ash; Average ± SD, n = 3

Algal growth inhibition test

The inhibition of *P. subspicata* growth due to exposure to dilutions of either native bottom or fly ash leachate (Figure 2, full symbols) resulted in similar dose-response relations. The IC_{50} obtained for native bottom ash leachate was 3.73 g aeq/L (95% CI: 1.72 to 8.07 g aeq/L) and 1.88 g aeq/L for native fly ash leachate (95% CI: 1.03 to 3.44 g aeq/L).

Figure 2: Dose-response relation of native and neutralized wood bottom and fly ash leachates to *Pseudokirchneriella subspicata* biomass growth after 72 h, normalized with average growth in the controls of each replication, native leachate (filled symbols) and neutralized leachate (open symbols); (A) Bottom ash, (B) Fly ash; Average ± SD, n = 4

The slope (± SE) of the dose-response curve at the IC_{50} is -0.94 ± 0.3 for bottom ash and slightly steeper (-1.38 ± 0.48) for fly ash. The dose-response curves of neutralized bottom and fly ash leachates (Figure 2, open symbols) were particularly different from each other. There was little effect caused by neutralized bottom ash leachate (up to concentrations of 10%). In contrast, neutralization of fly ash leachate seemed to affect the test organism in concentrations as little as 0.32% and did not change the dose response. The IC_{50} calculated for neutralized bottom ash leachate was 38.6 g aeq/L (95% CI: 25.3 to 58.7 g aeq/L), the neutralized fly ash leachate IC_{50} is 2.09 g aeq/L (95% CI: 1.31 to 3.32 g aeq/L). The slope of the best-fit dose-response curve, measured in the IC_{50} was steeper for bottom ash (-4.48 ± 3.99) than for fly ash (-0.95 ± 0.19). In *P. subspicata* tests, the neutralized bottom ash leachate showed a 6 fold larger EC_{50} than native BAL. Again, the difference between neutralized FAL and native fly ash leachate was less pronounced, the fold difference was 1.3.

Macrophyte growth inhibition test

Frond growth rates for *L. minor* exposed to dilutions of neutralized and pH native ash leachates followed a sigmoidal dose-response curve (Figure 4). While growth rates stayed on the level of the control up to 10 g aeq/L in pH native bottom ash leachate and declined to the EC_{50} at 36.9 g aeq/L (95% CI: 29.7 to 45. g aeq/L), plants in 80% leachate (80 g aeq/L) were dead. A dose dependent decrease only became evident in neutralized bottom ash leachates at 40 g aeq/L and the calculated EC_{50} was extrapolated outside the range of tested concentrations at 112 g aeq/L (95% CI: 45 to 279 g aeq/L). While frond growth rate averages per test concentration were incidentally found above the control value in bottom ash leachate, this was not the case with fly ash leachates (Chapter 3). In the test with pH native leachates, frond growth rates declined when exposed to concentrations higher than 5 g aeq/L, a similar decline in neutralized fly ash leachates was only found between 20 and 40 g aeq/L.
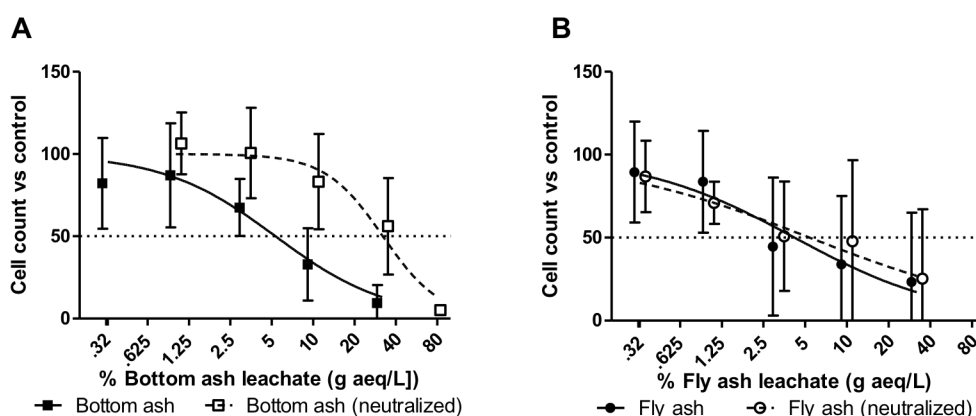
Figure 3: Dose-response relation of native and neutralized wood bottom and fly ash leachates to *Lemna minor* frond number, normalized with average growth in the controls of each replication, native leachate (filled symbols) and neutralized leachate (open symbols); (A) Bottom ash, (B) Fly ash; Average ± SD, n = 5

Fly ash leachate exhibited an EC_{50} of 19.6 g aeq/L (95% CI: 14.1 to 27.2 g aeq/L) while neutralized fly ash leachate inflicted 50% effect on the frond growth rate at 57.8 g aeq/L (95% CI: 32.4 to 103 g aeq/L). A 1.5-fold difference was estimated between the EC_{50} values for neutralized BAL toxicity and native bottom ash leachate. With fly ash the difference was larger, EC_{50} of neutralized FAL in the *L. minor* assay was 2.5-fold larger than for native FAL.

Invertebrate acute immobility test (*Daphnia magna*)

In acute *D. magna* immobility assays, the EC_{50} was found for bottom ash leachate at 55.5 g aeq/L (95% CI: 51.3 to 60 g aeq/L). For neutralized leachate no immobilization of more than 50% of the test population could be obtained within the range of possible leachate dilutions, EC_{50} is thus assumed >80 g aeq/L (highest test concentration). Fly ash leachate immobilized 50% of the *D. magna* neonates at concentrations of 3.46 g aeq/L (95% CI: 3.17 to 3.81 g aeq/L), neutralized fly ash leachates were associated with an EC_{50} of 8.15 g aeq/L (95% CI: 7.46 to 8.92 g aeq/L).
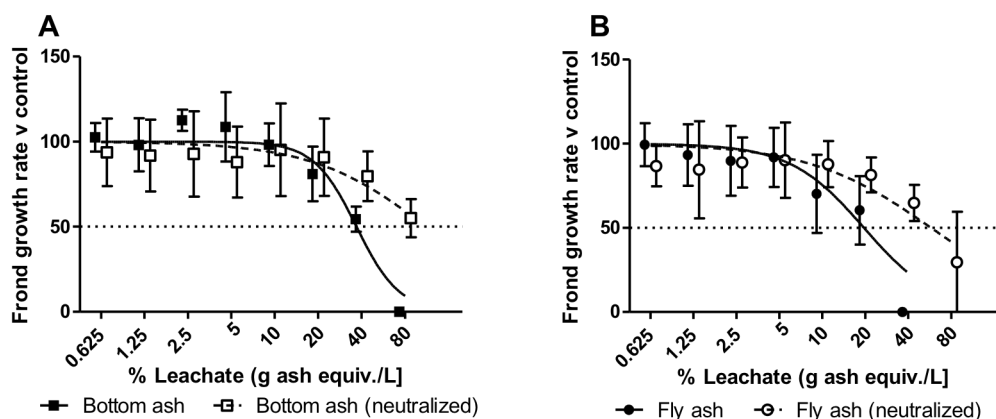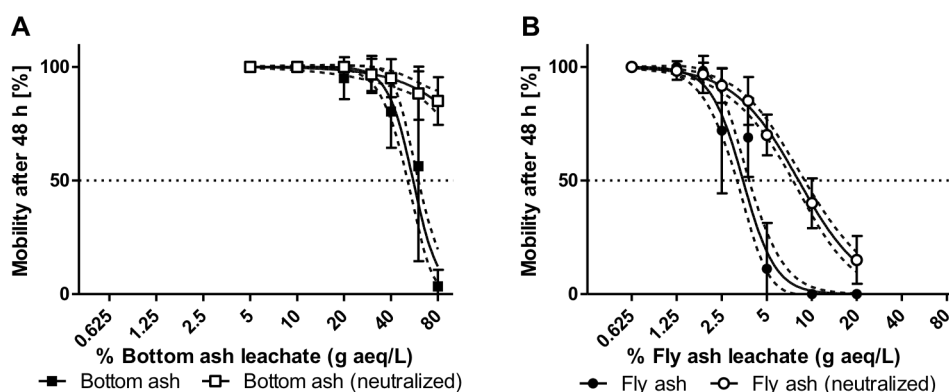
Figure 4: Dose-response relation of native and neutralized wood bottom and fly ash leachates to *Daphnia magna* **mobility, normalized with average growth in the controls of each replication, native leachate (filled symbols) and neutralized leachate (open symbols); (A) Bottom ash, (B) Fly ash; Average ± SD, n = 6**

The fold-difference between neutralized and native BAL EC_{50} in tests with *D. magna* was >1.4, for fly ash leachate the difference can be described with a fold-value of 2.4.

Fish acute and prolonged survival test (*Oncorhynchus mykiss*)

Concentrations of 1 to 56 g aeq/L native bottom ash water accommodated fraction (WAF) did not have an effect on the survival of juvenile rainbow trout. However, in the three replicates for 100 g aeq/L survival was 57, 28 and 0%. No mortality occurred in the range of 3.2 to 100 g aeq/L neutralized bottom ash water accommodated fraction. In one test replicate with 3.2 g aeq/L fly ash water accommodated fraction, one out of 7 animals died while at 10 g aeq/L no mortality was found. At 32 g aeq/L fly ash WAF only two animals survived in one out of three replicates, survival was thus below 10%. Survival in 32% neutralized fly ash water accommodated fraction in contrast was 81%. As EC_{50} for neutralized water accommodated fractions from bottom and fly ash were outside the tested concentration range, no reliable factor between response to neutralized and native water accommodated fractions could be calculated for the acute fish mortality test.

During 21 d prolonged exposure (results not plotted) to both pH native and pH neutralized bottom ash water accommodated fractions (10, 32 and 56 g aeq/L) juvenile Rainbow trout showed 100% survival. Neither was mortality found in

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the 21 d prolonged exposure to native or pH adjusted fly ash water accommodated fraction (1, 3.2 and 10 g aeq./L).
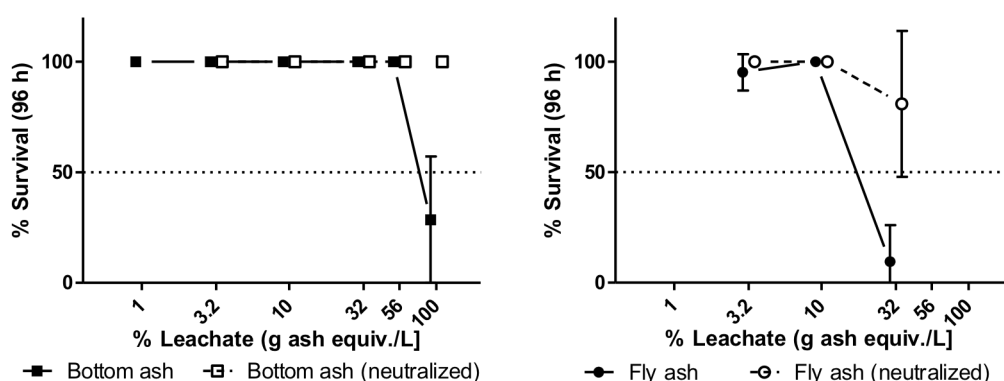
Figure 5: Dose-response relation of native and neutralized wood bottom and fly ash leachates to *Oncorhynchus mykiss* **in 96 h acute toxicity assay, normalized to pure water control value, native water accommodated fraction (filled symbols) and neutralized water accommodated fraction (open symbols); (A) Bottom ash, (B) Fly ash; Average ± SD, n = 3)**

Discussion

Wood ash leachates

The alkaline pH of wood ashes (Ludwig et al. 2005; Aronsson and Ekelund 2006; Vassilev et al. 2013; Barbosa et al. 2013) causes reduced mobility of the water soluble element fraction in the material. Supposedly similar to coal ashes, the solubility of a large number of elements is pH sensitive (Izquierdo and Querol 2012). Increased leaching (inter alia, of Al, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sn Ti, Zn) is expected with a lowering of the pH. The applied leaching procedure (EN 12457-2) however reflects waste inherent pH status as distilled water is used as eluent (Tsiridis and Samaras 2006). Thus oxyanionic trace elements (As, B, Cr, F, Mo, Sb, Se, V and W), some potentially hazardous, are leached in at increased proportions from alkaline wood ashes (Vassilev et al. 2013).

FAL carries about 7 times more dissolved elements than BAL. While, for example, the per cent proportion of the saliferous and thus likely mobility controlling chloride and sulphate are twice as large in FAL as in BAL, the absolute concentrations in the leachates differ more than 10-fold (Chapter 3). Fly

ash leachate accordingly exhibits higher pH and electrical conductivity and can be assumed very salt-laden in comparison to BAL. Qualitative disparity is concluded as only FAL contains Pb and only BAL contains Mg and Mn. The presence of trace elements Co, Cd and Sb is confirmed only for bottom ash leachate. Noteworthy here is that detection limits in fly ash leachate were higher, thus Co, Cd and Sb was still be present in 19.2, 10.5 and 3.9-fold concentrations in fly ash leachate. In decreasing order (in parentheses when calculated ratio involved a limit of detection (LOD) smaller than the comparative value), the relative mobility of P in the bottom ash sample is 25-fold as high as in fly ash, also the elements As, (Mg), B, V and Cu are between 6 and 2-fold and (potentially Pb and Mn around 1.5-fold) more soluble from a bottom ash matrix than from a fly ash matrix. In contrast, from fly ash Ba, Al and Zn are 217, 123 and 111-fold more soluble than in bottom ash respectively. Ca, Sr and Ti are still between 42 and 24-fold more mobile in fly ash while for Se, Cr, K, Na and (Fe) the factor ranges between 8 to 2-fold (Chapter 3). Thus, qualitative and quantitative distinction of BAL and FAL (Chapters 3 and 4) is also confirmed for the single time point ash samples. The solubility of the elements Cd, Sb, Tl, Ni, Co, Be and Sn cannot be compared because of differing LOD.

The overall compositional variability of BAL and FAL (as global CV, from quadruplicate analysis, 25 and 26% respectively) is very similar (Chapter 3). Thus the single sample leachate analysis reliability and precision are clearly distinguished from (better than) over-time variability of BAL and FAL on the site (Chapter 4). In fact, three year chemical variability over all analytes in the BAL and FAL (71 and 79%, Chapter 4) is, with a factor of 2-3 fold larger than the test substances BAL and FAL in this study.

Assessment according to waste regulations

Acceptable element leaching limits for non-hazardous waste (Council of the European Union 2003) are defined for five oxyanion-forming elements (As, Cr, Mo, Se and Sb). The mobile fraction of those elements in bottom ash is below the respective acceptable limits (only represents between 10 and 20%). The mobile oxyanion-forming species fractions, except for As, are higher in fly ash: Se violates the limit by factor 2, Cr and Mo are in range of 25% of the respective

limits, arsenic leaching represents 4% of acceptable amounts and while leachable Sb was not detected in quantities over 200 μg/kg in fly ash leachate, this could still account for up to 29% of the acceptable leaching limit. Among elements less soluble at alkaline pH, leachable Zn represents 66% while others (Ba > Cd > Ni > Pb > Cu > Hg) range below 2.5% of the acceptable leaching limit. Total amounts of chloride leachable from fly ash are in the range of 83% of the limit while leachable sulphate exceeds the limits by more than factor 2. Thus, the parent fly ash of the leachates tested here exhibits mobility (as defined in WAC) of potentially hazardous elements and compounds and may not be considered non-hazardous waste.

Test solutions

OECD recommendations for limit testing of single chemicals state 100 mg/L. In comparison, biological effect assessment for ECHA registered plant ashes (CAS # 93333-79-0) was performed with water accommodated fractions from 100 mg ash per litre. The complex composition of ash materials is acknowledged as 'Substance of Unknown or Variable composition, Complex reaction products or Biological materials' (UVCB), and synergistic, antagonistic and/or additive interactions of compounds therein are thus likely. The application of maximum concentrations equivalent to those from mono-substance limit testing thus appears almost negligent when 'direct application in the environment', such as with biomass ashes, is intended. The concentrations tested in this study are much higher and derived from the standard waste leachate protocol (100 g ash per litre). Based on the sum of dissolved analytes, 5.75 g aeq/L bottom ash and 0.87 g aeq/L fly ash dilutions contain 100 mg/L dissolved ash constituents. When nominal ash amounts extracted in leachate generation are applied, 100 mg/L could be assumed at 0.1 g aeq/L already.

High Ca concentrations in both ash leachates suggest considerable transfer of hardness into the solutions for biological testing. Mitigation of toxic effects from heavy metals through hard water is well documented. Calcium, dissolved in ash leachates may, up to a threshold concentration, reduce the toxicity of certain metal ions like Zn in daphnids but in high concentrations, such as measured in fly ash leachate, can interfere with reproduction of Daphnia (Komjarova and

Blust 2009). Water hardness, pH, dissolved organic carbon as well as alkalinity can affect the chemical speciation, bioavailability and thus toxicity of dissolved metals.

Test battery

OECD and ISO standards always state a pH range for which the respective test system response is reliable. These ranges are set in respect to the tolerance of the given test organism. Thus, most hazard characterizations employ pH adjusted extracts (Hidehiro 1996; Tsiridis and Samaras 2006; Stiernström et al. 2014). Also pre-existing composite waste ash leachate compliance testing for the case site, subject to this study, was conducted with pH adjusted extracts and consistently reported <2.2 TU. Other investigations have avoided neutralizing ash leachates to avoid potential changes in speciation of dissolved ash components (Barbosa et al. 2013). To our knowledge, few studies have considered both pH native and neutralized extracts (Lapa et al. 2002). However, changes in element speciation also happen when leachates are diluted in standard test media, especially with high dilution factors for small test concentrations. The inherent buffer capacity and set pH of standard media would, at least to some extent, cause these changes. In this study, native as well as neutralized ash leachates were assessed by means of whole organism toxicity tests. Toxicity is classified as Toxic Units according to a SOP widely used in aquatic toxicity testing of industrial effluents and solid waste leachates in Ireland (Table 2, Shannon Aquatic Toxicity Laboratory 2012).

Inhibition of bacterial bioluminescence assay (MICROTOX®)

Toxicity of native ash leachates in the *A. fischeri* model is only marginally different for bottom and fly ash. EC_{50} are found in a close range between 4 and 5 g aeq/L ash (21 and 25.6 TU, toxic), confidence intervals being as low as 3.1 g aeq/L for fly ash leachate and up to 5.3 g aeq/L for bottom ash leachate. The dose response curve for bottom ash leachate appears to be more gradual (lower slope, Figure 1) than for native fly ash and that may relate to the much higher dissolved ash component freight in fly ash. Due to the high pH of the leachates the results are *a priori* obtained outside the margins for validated MICROTOX toxicity tests. However, the results are relevant for integrating the

waste materials inherent pH in the toxicity assessment. Further to this, the observed results are similar to native wood ash extract toxicity described in Barbosa et al. (2013). In contrast, the effects of neutralized ash leachates on *A. fischeri* appear clearly smaller and distinct from their native counterparts. Vasseur et al. (1986) suggested reduced bioavailability due to the complexation of metal ions into hydroxide forms at slightly alkaline pH. The strong reduction of measurable effect due to neutralization in this study may thus suggest that metals are not the principal cause of the observed toxicity. In contrast, Lapa et al. (2002) showed decreased solubility for Pb and Cr as well as possibly Cu and Zn when ash extract pH is lowered from 12 to MICROTOX suitable pH 6-8. Also observed in that study, was significantly diminished toxicity from neutralized municipal solid waste incinerator ash extracts in comparison with native leachates. Thus, these data imply an impact of metals on measured toxicity to bacteria. Concentrations of up to 22.5 g aeq/L neutralized bottom ash leachate have a consistently low impact on the endpoint in this study, while 45 g aeq/L incurs with considerable variation an average effect of slightly over 50% inhibition (2.2 TU, non-toxic). With neutralized fly ash leachates the underlying variation in the average response is even more pronounced, linking the determined EC_{50} of 19.4 g aeq/L (5.2 TU, slightly toxic) to a wide 95% CI. While the difference in EC_{50} and corresponding TU between neutralized bottom and fly ash leachates is not substantial and the wide confidence intervals are overlapping, the results may still, with large uncertainty, reflect higher pH independent toxic action (e.g. from metals) from fly ash leachate than from bottom ash. However, alkaline substances such as ash are used to increase a sludge or biomaterial pH to >9 for sanitation purposes (Winblad and Simpson-Hebert 2004). This suggests that the observed toxicity of native ash extracts to bacteria is also pH driven. It was also reported by Tsiridis and Samaras (2006) that the pH status of the solid parent material of ash leachates greatly influences the observable aqueous extract toxicity. The factor separating bacterial response to native and pH neutralized leachates is the largest among all test systems in this study. Thus emphasised is a severe discrepancy between waste hazard assessment and spill or inappropriate release scenarios.

Algal growth inhibition test (*Pseudokirchneriella subspicata*)

Algal assays, despite their short duration are acknowledged as chronic tests since multiple generations of the model organism arise within 72 h. Micro algae toxicity tests are common for initial, rapid toxicity assessment of wastes. In tests with native ash leachates, only little difference in toxicity of bottom and fly ash was observed with EC_{50} at 4.2 and 5.3 g aeq/L (23.8 and 18.9 TU, toxic) respectively. The confidence intervals (not shown) are, as in MICROTOX, narrower for bottom ash leachates than for fly ash leachates. Deviation from the control growth was found in the lowest test concentration (0.32 g aeq/L) for both native bottom and fly ash leachates indicating some toxic action at even lower concentrations. EC_{20} determined for native ash leachates with the same algal species (Barbosa et al. 2013) lie within the 95% CI range of the EC_{50} in this study. The effect of leachate neutralization is very different for the dose response characteristic of the two ashes. Neutralized bottom ash causes no growth inhibiting effect in concentrations up to 3.2 g aeq/L and EC_{50} is shifted towards higher concentrations (32.2 g aeq/L, 3.1 TU, slightly toxic). In contrast only marginal difference in biological response of *P. subspicata* is found for neutralized fly ash leachates when compared to the native leachate (EC_{50} is 5.4 g aeq/L, 18.5 TU, toxic). The impact of alkaline pH values may be limited for the growth inhibition due to fly ash leachate, again pointing in the direction of dissolved elements and compounds for the explanation of the effect.

Macrophyte growth inhibition test (*Lemna minor*)

Lemnaceae are described as pioneer species in ash settling ponds (Dorman et al. 2010) indicating their high tolerance towards ash-borne toxicants. The growth inhibition assay with *L. minor* (Figure 3) shows that the species is indeed less sensitive to ash leachates but clearly distinguishes toxic concentrations of native bottom and fly ash leachate (respective 95% CI do not overlap). While bottom ash leachate EC_{50} is found at 37% (2.7 TU, non-toxic), fly ash inhibits the plant frond growth at EC_{50} 20% native leachate (5.1 TU, slightly toxic). The dose-response relations in native ash leachates are markedly different with a more abrupt decline in concentrations over 20% for bottom ash and a gradual growth inhibition effect apparent in fly ash leachates (concentrations above 5%) indicating sub-acute toxic action in fly ash, but not bottom ash leachates.

Neutralization of ash leachates shifts the dose-response towards higher concentrations, neutralized bottom ash leachate EC_{50} is estimated above the range of test concentrations at 112 g/L (<1 TU, non-toxic) while neutralized fly ash inhibits *L. minor* growth to half the control average at 57.8% (1.7 TU, non-toxic). Also, the decline in growth of the model organism due to exposure to neutralized ash leachates appears more gradual and is likely associated with dissolved toxicants. A study of wood ash effects with the freshwater moss *Fontinalis antipyretica* (Aronsson and Ekelund 2006), conducted in a concentration range between 1 and 10 g/L, found no inhibition of growth but reveals the influence of sudden pH rises to be detrimental for aquatic, photosynthetic organisms.

Invertebrate acute immobility test (*Daphnia magna*)

The widely applied immobilization test with daphnids clearly demonstrates differing toxicity potential of native bottom and fly ash leachates (Figure 4). Bottom ash leachates immobilize 50% of the test population at 56 g aeq/L (1.8 TU, non-toxic) while fly ash leachates produce the same effect already at 3.5 g aeq/L (28.8 TU, toxic). While the EC_{50} for fly ash is in the range of reported toxicity for a bulk sample (Barbosa et al. 2013), the bottom ash leachate in this study is considerably less toxic. This is surprising as alkaline conditions in the high concentrations of the acute test with BAL were expected to impact on the mobility of the neonates. In neutralized state, toxicity of BAL is not detecteable within the concentration range. The adjustment of pH in FAL also reduces toxicity of the extracts (12.3 TU, slightly toxic), but to a much lesser extent than observed for BAL.

Fish acute and prolonged survival test (*Oncorhynchus mykiss*)

The vertebrate (fish) acute 96 h survival test system shows the highest resilience/tolerance of a species against native bottom and fly ash water accommodated fractions (>1 TU, non toxic and 3.6 TU, slightly toxic respectively). Exposed tissues such as gill epithelial cells are the most likely point of effect from alkaline WAF of bottom and fly ash. Neither in neutralized bottom nor in fly ash water accommodated fractions of the same concentration range, mortality was found to exceed 50%. Detoxification of the ash extracts due to neutralization and possibly the connection of water pH and observed mortality

with native WAF may thus be assumed. The short duration of the acute fish survival test and the absence of more sensitive endpoints may have prevented the observation of effects. The 21 day prolonged survival test was conducted with bottom and fly ash WAF in concentrations up to 56 and 10 g aeq/L respectively but failed to observe any effect on survival of the juvenile trout. While in no regard comprehensive, the explorative testing of bottom and fly ash WAF indicates that secondary consumers like fish may (at least for a few days) survive shock effects immediately after ash application.

Biological effect summary

Bacteria (MICROTOX) and microalgae assays exhibit similar EC_{50} for bottom ash leachate (~5 g aeq/L), while the associated 95% CI are different (95% Confidence interval in *P. subspicata* test is larger, Figure 6, Table 1). EC_{50} values in sub-chronic *L. minor* < acute *D. magna* < acute *O. mykiss* tests are higher (37, 56 and 98 g aeq/L). Neutralized bottom ash leachates are consistently less toxic than their parent leachates (Figure 6).
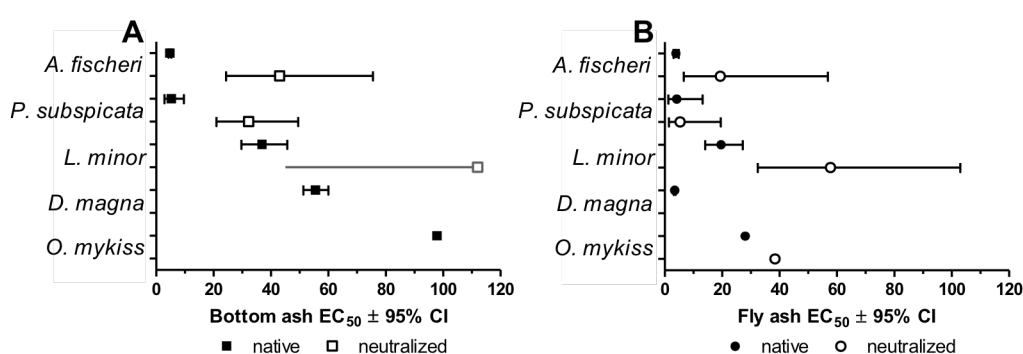
Figure 6: EC_{50} values determined for inhibition of bioluminescence in *Aliivibrio fischeri* (MICROTOX, acute), inhibition of growth in *Pseudokirchneriella subspicata* cells (chronic) and *Lemna minor* fronds (sub-chronic), immobilization in *Daphnia magna* (acute) and mortality in *Oncorhynchus mykiss* (acute); (A) Bottom and (B) Fly ash; grey empty square: EC_{50} outside of tested range > 80 g/L, upper 95% CI not shown; values as % leachate and g ash equivalents per litre.

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Table 1: Summary table of 10% and 50% effect concentrations (EC) relative to the respective pure medium control

	Endpoint		Bottom ash	(95% CI)	Neutralized bottom ash	(95% CI)	Fly ash	(95% CI)	Neutralized fly ash	(95% CI)
MICROTOX ® *Aliivibrio fischeri* (acute)	Inhibition of bioluminescence (30 min)	EC_{10}	2.36	(1.50 to 3.70)	21.1	*very wide*	2.18	(0.85 to 5.56)	4.31	*very wide*
		EC_{50}	**4.75**	(4.29 to 5.27)	**43.0**	(24.4 to 75.6)	**3.9**	(3.12 to 4.89)	**19.4**	(6.66 to 56.8)
Pseudokirchneriella subspicata (chronic)	Inhibition of growth (cell number, 4 d)	EC_{10}	1.85	(0.31 to 10.9)	11.0	(2.50 to 48.6)	~0.04	*very wide*	~0.003	*very wide*
		EC_{50}	**5.33**	(2.93 to 9.68)	**32.2**	(21.0 to 49.5)	**4.19**	(1.33 to 13.2)	**5.39**	(1.49 to 19.5)
	Inhibition of activity/growth (fluorescence, 4 d)	EC_{10}	5.58	(1.97 to 15.8)	18.8	(14.3 to 24.6)	1.52	(0.53 to 4.37)	7.37	(4.15 to 13.1)
		EC_{50}	**44.2**	(29.5 to 66.2)	**66.9**	(61.0 to 73.4)	**15.8**	(12.5 to 20.1)	**39.9**	(32.1 to 49.5)
Lemna minor (sub-chronic)	Inhibition of growth (frond number, 7 d)	EC_{10}	14.8	(9.82 to 22.2)	35.7	(12.8 to ~99.1)	8.33	(3.87 to 17.9)	24.8	(12.4 to 49.7)
		EC_{50}	**36.9**	(29.7 to 45.7)	**~112**	(45.0 to ~278)	**19.6**	(14.1 to 27.2)	**57.8**	(32.4 to 103)
	Inhibition of growth (biomass, 7 d)	EC_{10}	25	(8.18 to 76.6)	51.6	(27.7 to ~96.4)	6.92	(3.25 to 14.7)	26.7	(13.6 to 52.3)
		EC_{50}	**33.1**	(20.2 to 54.2)	**87.9**	(69.0 to ~112)	**17.8**	(13.2 to 24.1)	**61.6**	(48.9 to 84.5)
Daphnia magna (acute)	Immobilization (48 h)	EC_{10}	20.3	*very wide*	26.5	(12.4 to 56.8)	1.99	(1.54 to 2.58)	2.64	(1.98 to 3.52)
		EC_{50}	**55.5**	(51.3 to 60.0)	**>80**	*very wide*	**3.47**	(3.17 to 3.81)	**8.15**	(7.46 to 8.92)
Oncorhynchus mykiss (acute)	Mortality (4 d)	EC_{10}	n.d.		n.d.		n.d.		n.d.	
		EC_{50}	97.8	very wide	>100	none	28	very wide	38.4	very wide

The lower confidence limits of the 50% growth and bioluminescence inhibition effect in algae and bacteria are similar, 21 and 24 g aeq/L respectively. In contrast, EC_{50} is higher and 95% CI is wider in the bacterial test. The EC_{50} values determined for neutralized bottom ash leachate (>80 g aeq/L) are outside of the test concentration range in the *L. minor*, acute *D. magna* and *O. mykiss* tests. The 95% CI limits are in the range of 0.5 and 2-fold of the EC_{50} value for all test systems and considerably wider than in non-neutralized bottom ash leachates. The smallest bottom ash EC_{50} value in the battery is 2.9 g/L (lower 95% CI limit) in growth tests with *P. subspicata* while the highest EC_{50} were measured in fish and extrapolated for duckweed.

For fly ash leachates, EC_{50} values measured with bacteria and microalgae are very similar (full symbols, Figure 6B) and only marginally different from the values determined for bottom ash leachate. Also, results in the microalgae test are more variable than in MICROTOX. Fly ash leachates have a similarly small EC_{50} (~5 g aeq/L) in acute tests with *D. magna*. EC_{50} determined in common duckweed and rainbow trout are higher but not substantially different from each other (between 20 and 30 g aeq/L respectively). Lowest EC_{50} in neutralized fly ash leachate is found in the algae test (5.4 g aeq/L) and is as low as for the non-neutralized leachate. EC_{50} in bacterial and macrophyte tests are subsequently higher (19.4 and 57.8 g aeq/L respectively). As with bottom ash, neutralization of fly ash leachates also results in an increase in EC_{50}, however, in bacterial, algal and macrophyte assays, this effect is less substantial than observed in bottom ash leachates. Also, while neutralized bottom ash leachate (3.2-100 g aeq/L) did not have an effect on survival in the fish test, an EC_{50} of 38,4 g aeq/L for juvenile trout was determined for neutralized fly ash leachate. The highest EC_{50} measured for neutralized fly ash was 57.8 g/L in *L.minor*.

The factors between native and neutralized leachate toxicity is largest in MICROTOX tests, the discrepancy between waste hazard and potential hazard in case of release is thus largest for the commonly used, rapid toxicity screening test.

Potential risk scenarios

While ecotoxicological studies of municipal waste incineration ashes, coal ashes, ashes from treated materials and others are common, there are very few studies on the toxicity of ash materials at the supposedly less contaminated end. Waste testing in line with guideline and legislation demands neutralization of leachate samples and therein assumes only extracts close to pH 7 are received by water-bodies. Fresh, pH native leachates, straight from the parent material are relevant for heavy rain or flood scenarios deviating from normal operations.

Chemically, there are indications (exceedance of waste acceptance limits) that wood ash, even from untreated fuel, may not be considered entirely non-hazardous waste. PCDD/F in bottom and fly ash proves their presence in the composite waste material and also PAH are likely to be present, yet largely immobile (Chapter 4). Safe disposal on a landfill side is the final step. However, until then the methods of collection, intermediate storage and transport also bear release potential. Incidental spill, flooding, run-off or wind drift may release ash into the local environment potentially resulting in concentrations high enough to cause damage to biota. This may be due to immediately mobile constituents, intermediately due to compounds released in weathering or continuously due to persistent pollutants. Vicinity of water bodies is an additional reason for concern as transport may occur over longer distances. In lentic waters such as lakes or at slip-slopes in rivers locally confined deposition may occur and result in ash concentrations high enough to harm resident flora and fauna. Particularly with such uncontrolled or incidental release, the wood ash waste inherent alkalinity poses a threat and mandates the appraisal of associated risks. Toxicity of native ash extracts to bacteria and algae exhorts concern for both water and soil environments that may receive uncontrolled input. Eventual landfilling confines the waste solids and thereby limits release pathways of immobile contaminants and environmental exposure (Chapter 4). The principal risks arising from mobile constituents though remain. Management, as in balancing of pH in deposits on these sites, reduces the toxicity and potential environmental impact of aqueous effluents (e.g. run-off and leachate) greatly.

Controlled turnout of ashes as fertilizing or liming agents brings solid ash presence in the respective environment. Apart from dissolvable, mobile

constituents that may be transported from the site, more stable compounds containing hazardous trace elements, organic contaminants or even persistent compounds are released with the ash. Chemical assessment solely based on WAC requirements is thus inappropriate to evaluate land applicability as solid element concentrations are omitted (Chapters 2 and 4). The contamination of fly ash solids with higher amounts of hazardous trace elements and PCDD/F could have been missed. Toxicological tests show that microorganisms such as bacteria and algae are at relatively highest risk, both groups reside in both water and soil. Cautious management of applied ash amounts on soils with regard to pH though, should be able to avoid acute effects on these organism groups.

Conclusion

Rapid test systems employing single-celled model organisms like MICROTOX and algae growth inhibition assays, as well as the acute immobilization test with daphnids, are commonly used for waste toxicity screening (Moser and Römbke 2009) and have proven to be consistently sensitive. The standard tool set from waste hazard characterization is thus a good starting point for the development of biological criteria in EoW. However, we argue that the standard tool set should be extended with pH native testing, particularly when application in the environment (i.e. fertilization and/or liming) is considered. Chronic growth tests with algae may be the most relevant among the three since model organism reproduction is incorporated while endpoints in acute tests with *A. fischeri* and *D. magna* do not consider sub-acute effects. However, the effect may stem from simple cytotoxicity, chronic toxicity or from affecting the reproduction of the microalgae. More importantly, as primary producers, an effect on algae may easily issue a cascade of effects (such as food shortage in the immediately higher trophic tier).

Given the differing pH sensitivity of the model organisms in the test battery and native ash leachate dilutions exhibiting pH values above standardized test requirements (particularly with high test concentrations), results may strictly not reflect toxic action of dissolved contaminants but rather a risk scenario for ash release that integrates material inherent physico-chemical properties. Based on native leachates, sensitivity to wood ash in acute exposures decreases with the

model organism complexity. Among higher organisms, the invertebrate model proves more sensitive than the higher plant model, and the vertebrate model is least sensitive.

Acknowledgements

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Chapter 6
Physicochemical characteristics and toxicity of particle size fractions of ash from untreated wood

Abstract

Analysis of the water dissolved release from solid waste materials identifies components that may become mobile in run-off or percolate from weather exposed storage facilities or landfills. Thus, leachates are widely used to assess (i) the immediate chemical hazard of their parent waste materials and (ii) potential ecotoxicity in receiving aquatic environments. Granular refuses such as combustion residues are a variable mixture of gravel, sand, silt and smaller sized particles. Due to their large surface to volume ratio, small particle size fractions bear substantial pollution potential via leaching, while also being at risk of dispersal by wind. Chemical and ecotoxicological characteristics of wood energy bottom and fly ash particle size fractions were quantified to assist the development and risk minimization of sustainable recycling options for the current waste. Measurable toxicity as inhibition of luminescence in *Aliivibrio fischeri* (Microtox) and several growth parameters for *Lemna minor* decreases with increasing particle size for both bottom and fly ash.

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Introduction

The use of renewable solid biofuels, as a component of a sustainable energy mixture, is increasing. Apart from dedicated energy crops, harvest and process residues from agriculture and forestry are also increasingly exploited for their calorific value (Chapters 2, 3, 4; van den Broek et al., 2001; Vassilev et al., 2010). Sustainable power generation from such biofuels is attractive because of their renewable character and potential carbon neutrality. However, it is essential to consider the entire life-cycle of fuel biomass to achieve actual sustainability (Vassilev et al., 2010). Both issues related to the strain on fuel producing soils, as well as accruing waste, still need to be resolved. Soils of fuel producing agricultural or forest plots may become impoverished in nutrients due to extensive removal of biomass. Energy conversion, such as combustion, produces ash residues that retain a proportion of the nutrients originally assimilated by the growing biofuel plant (Someshwar, 1996; Steenari et al., 1999). At present, such ashes are largely disposed of on landfills. Thus, ash after-use for mineral and nutrient recycling, rather than disposal, seems self-evident. A common misconception though, is that ash from biofuels is 'clean' and environmentally innocuous (Chapter 2, 4; Vassilev et al., 2010). Disposal, after-use options and particularly the use of ash in the environment as ameliorant requires careful appraisal of each particular ash material.

The European Waste Catalogue (EWC, European Commission, 2000) classifies residues from thermal processes, such as combustion of untreated wood, as absolute non-hazardous waste materials. Intermediate storage, transport and disposal of ash waste materials are licensable under the European directive Integrated Pollution Prevention and Control (IPPC, 2008/1/EC). In order to dispose wood ash on landfill, compliance with chemical waste acceptance criteria (WAC, Council of the European Union, 2003) is required. Toxicity screening tests are commonly used to confirm non-hazardous status of wood ashes in case of limit value infringement. Concentrations of mobile contaminants from waste solids are analysed via bulk sample leachate (EN 12457-2, CEN, 2002). These and similar, usually pH adjusted extracts are then used to determine potential ecotoxicity of a waste by exposing aquatic species (Barbosa et al., 2013; Pöykiö et al., 2009; Schultz et al., 2002; Steenari and Karlfeldt Fedje,

2010). Strictly, this simple standard mobility scenario depicts risks of 'safe' disposal on an appropriate landfill. The characteristics of bulk ashes, parent materials of the test substances (ash fractions) in this study, have been chemically and ecotoxicologically assessed as waste (Chapters 2, 4, 5) but also as a potential fertilizing agent (Chapter 3). Disposal of materials with fertilizing or liming potential as waste contradicts sustainable resource use (Chapter 2). However, the after-use potential of these ash residues may be off-set by their contaminant burden and potential toxicity (Chapter 2, 3). The high content in alkali and alkaline earth metal oxide hydrates in ash may cause burns on tissues, while high levels of soluble salts in bulk ashes may cause osmotic damage to organisms (Aronsson and Ekelund, 2002; Steenari et al., 1999). Release of ash in the environment may be intentional or incidental. The current handling of ash (storage, loading and transport until disposal) involves a range of release opportunities on site and en route (Reijnders, 2005). One major release pathway is via run-off or percolation waters. Wind, rain and flooding may facilitate the spillage of waste solids or dissolvable components. It may be argued that the smallest ash particles contribute a significant part in overall incidental release. The environment may thus receive a sub-fraction of ash, or its dissolved components, for which the bulk sample is not necessarily representative.

Particle size distribution (PSD) of ash is relevant for ecotoxicological testing, the handling of the material on site and subsequent disposal or after-use. According to leaching standard (CEN, 2002), granular waste materials shall not contain particles larger than 4 mm. Furthermore sample homogenization is considered crucial for reliant characterization of waste, including granular materials (Moser and Römbke, 2009). Wood ashes, as thermally valorised materials, usually contain 80% of their mass as particles <1 mm (Demeyer et al., 2001). Particle size fractions (PSF) that are very fine are known to cause dust problems (Dahl et al., 2010; Steenari et al., 1999). The highest concentrations of metals and metalloids is demonstrated within the finer PSF of bottom and fly ash (Barbosa et al., 2013). Arsenic and Chrome minerals (Lundholm et al., 2007) have been shown to be particularly present in fine ash fractions from treated wood. Cadmium is reported to occur more frequently in fine PSF (Aronsson and Ekelund, 2002) and fine ash fractions absorb PAH more efficiently than larger

PSF (Pérez-Gregorio et al., 2010). Certain PSF also contain unburned organic matter that still bears residual energy (Demeyer et al., 2001; James et al., 2012). Re-burning, mechanized recovery, after-use in construction or possibly as soil treatment thus require knowledge of ash PSD and profit from compositional distinction of PSF (James et al., 2012) and their toxicity.

Apart from particle size, the pH of wood ash and the difference between solid ash and ash leachates (Chapter 3) need to be considered when assessing the potential after-use of wood ash. Data available on the parent bulk samples suggests that wood ashes from untreated fuel cause toxicity (Chapter 5). Native extracts are almost consistently associated with lower Effect Concentration (EC) values than pH adjusted leachates. Microtox, bacterial (*Aliivibrio fischeri*) luminescence, and algal growth inhibition tests proved to be most sensitive and may delineate the lower limit of the ash leachate toxicity interval (5% native leachate, corresponding to 5 g/L ash equivalents in EN 12457-2 leachate, Chapter 5). Aquatic environments are thus likely beginning to suffer damage at ash concentrations of *A. fischeri* EC values. The effect on decomposers (bacteria) or unicellular primary producers may issue a cascade effect on other tropic levels but only 'incipient' damage can be proven by the assay. The aquatic macrophyte growth inhibition assay with *Lemna minor* (Chapters 3 and 5) shows the vascular plant model to be among the least sensitive species. The additional use of a particularly resilient test model is uncommon in environmental risk assessment but received EC values delineate a worst case scenario. *L. minor* is, as a primary producer, somewhat independent of the functioning of other trophic levels. EC values of the plant thus point at critical ash concentrations at which a whole aquatic ecosystem suffers 'terminal' damage.

Bottom and fly ash have been shown to produce stimulation of growth (Chapter 3) in *L. minor* at low concentrations of up to 5% leachate (corresponding to 5 g/L ash equivalents in EN 12457-2 leachate). In principal, environmental concentrations sufficiently below this threshold may be acceptable to allow exploitation of liming and nutritional properties of ash while avoiding incipient damage to the ecosystem. A further outcome of that study (Chapter 3) was that solid ash suspensions facilitate the onset of growth inhibitory effects at lower concentrations than leachates. The use of 'native pH' ash suspensions, instead of

pH adjusted ash leachates, thus provides the basis for a highly conservative risk assessment for the range of PSF contained in wood ash.

The aims of this study were to determine chemical properties and ecotoxicological characteristics of up to five particle size fractions (ranging between <0.125 and >6.3 mm) of wood ash and corresponding leachate. An effect concentration interval from most to least sensitive model organism was used to delineate 'incipient' to 'terminal' type effects in aquatic systems from distinct ash PSF.

Materials and methods

Bulk wood ashes

Bottom and fly ash samples originated from a commercial, combined heat and power (CHP) wood boiler in County Cork, Ireland (Chapters 3, 4, 5). Untreated Sitka spruce (*Picea sitchensis*) sawmill residues (sawdust, wood chips and bark shavings, secondary wood fuels according to the Unified Bioenergy Terminology, FAO, 2004), accrued on-site and utilized for energy recovery. The furnace setup collects bottom ash in a water basin below moving grates and the fly ash was collected using an electrostatically charged vortex filter cleaning the flue. Physico-chemical composition of original bulk samples and their toxicity to a range of model organisms, including *A. fischeri* and *L. minor* applied here, were characterized (Chapters 3, 5).

Ash fractions and chemical analysis

Fractionation by dry sieving was performed by the UCC Sedimentology Laboratory. A sieve cascade with bottom pan (collecting <0.125 mm fraction), assembled from standard analytical sieves (ISO 3310) was applied and shaken on a tumbler (AS 200, Retsch) for 30 min at 40% amplitude. Sieve mesh diameters were 0.125, 0.5, 2 and 6.3 mm. Three samples were sieved to generate sufficient amounts of ash for exposure tests and the sub-samples of each fraction were then gently homogenized by hand. Loss on ignition analysis (500 °C) was performed with 1 g samples of the ash fractions until weight remained constant. Chemical analyses of the solid ash fractions using *aqua regia* extraction and of water extractable components (EN 12457-2; CEN, 2002) were processed as single

samples by a certified laboratory (UKAS #0754). These analyses were performed applying mass spectrometry (Chapter 3) where element content of ash solids or corresponding leachates is ionized for measurement. Thus, the analysis did not distinguish chemical speciation; detected concentrations were likely constituted by a range of compounds containing a given element. Leachate analyses were used in this study for the evaluation of mobile ash constituents. It was assumed, that supernatant from ash 'sediment' suspensions qualitatively, and likely also quantitatively, contained similar compounds (Chapter 3).

Bioassays

Aquatic toxicity was assessed with a bacterial (*A. fischeri,* Microtox) and a vascular plant (*L. minor*) assay. Microtox 30 min screening tests (Reagent lot #12K4130) were performed with pH native ash suspension supernatant using two replicates and an M500 analyser with MicrotoxOmni software (Modern Water, Guildford, UK) at SATL. The sensitivity of the test system was validated with potassium dichromate, zinc sulfate heptahydrate and 3,5-dichlorophenol (Chapter 5). Growth inhibition tests using *Lemna minor* adopted OECD guideline 221 methodology (OECD, 2006), and were conducted as sediment test modification (Chapter 3). *L. minor* specimen (Blarney Plants cultivar, Serial #1007, ID #5500) originated from UCC stock laboratory culture. Test solutions were Hutner's medium (Lahive et al., 2011) with suspended solids as 'ash sediment' without pH adjustment. The pH was measured at the start (day 0) of the test and afterwards (day 7), electrical conductivity (ElC) was measured on day 7.

Statistics

To validate the single sample analysis of bottom and fly ash PSF, a comparison with the parent ash solid was conducted. To this end, element concentrations from solid ash fraction analysis (Table 1) were corrected with their respective average weight ratio (of the original parent solid, Figure 1) and summarized. Element data (Table 1) was presented by enrichment factors (EF$_S$, Chapter 3) in ash parent bulk solids. EF <1 signified higher concentration in fly ash, conversely EF >1 meant higher concentrations found in bottom ash. The coefficient of variation (CV, data not shown) served as a measure of element content dispersion across the PSF of an ash and was calculated from bottom

(n=5) and fly ash (n=3) PSF solids. Liming potential of the PSF was calculated based on a Na, Mg, K and Ca solid content model (Zhang et al., 2002).

Leachate properties and element data (Table 2, 3) are shown in order of enrichment factors in bulk leachate (EF_L) from the parent solids (Chapter 3). Mobility (Table 3) was presented as EN 12457-2 leachate concentrations (per litre, after 10 l/kg extraction) to clearly distinguish water concentrations from solid content analysis. The term mobility was used as in WAC (Council of the European Union, 2003), where limits are set in mg/kg. The ten-fold value of results (in mg/L, Table 3) can thus be compared to these limits. Mobility profiles were based on leachate concentrations. Relative mobility was calculated as percentage of the *aqua regia* extractable solid content that was leachable in 10 litres of water (Chapter 3).

In biological assays, calculation of EC_{50} values was based on non-linear regression and performed with Graph Pad Prism 5 (La Jolla, USA). Toxicity was classified by Toxic Units according to a standard operating procedure (SOP) widely used in aquatic toxicity testing of industrial effluents and solid waste leachates in Ireland (Chapter 5, Shannon Aquatic Toxicity Laboratory, 2012). Toxic units (TU) were calculated as $TU = 100/EC_{50}$ (Barbosa et al., 2013; Horvat et al., 2007). They additionally inform about the dilution factor necessary to hypothetically decrease measurable toxicity of dissolved ash components in standard leachate to 1 TU (corresponding to an EC_{50} of 100% leachate, or 100g/L ash equivalents).

Results

Particle size, appearance and residual combustible matter

The particle size distribution of bulk bottom ash was rather homogeneous across the range from <0.063 through to >6.3 mm (Figure 1A). On a per weight basis, the average bottom ash particle dimension (D_{50}) was 0.29 mm. The five bottom ash fractions obtained for biological and chemical analysis were, by weight ratio, also evenly distributed. Fly ash (Figure 1B) in contrast, contained no particles larger than 2 mm equivalence diameter, 80% of its mass was posed by particles smaller than 0.5 mm. D_{50} was 0.08 mm.
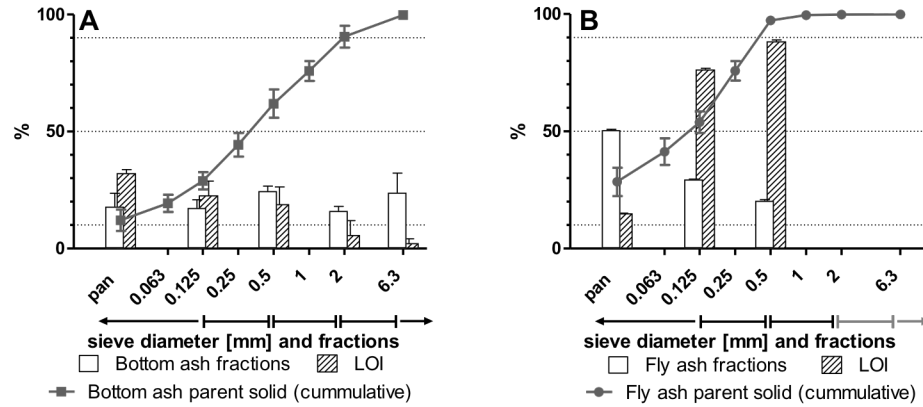
Figure 1: Cumulative particle size distributions of bulk bottom and fly ash (grey symbols with connecting lines, Average ± SD, n=7) and weight percentage of five selected fractions <0.125, 0.125-0.5, 0.5-2, 2-6.3 and >6.3 mm (white bars) with respective percentage loss on ignition (LOI, striped bars); Average ± SD, n=3

Particles >6.3 mm accounted for 23.9% of the bottom ash parent sample mass (Figure 1A). These were irregularly shaped clinker particles with a metallic glint and their average mass proportion of the bulk showed the largest standard deviation (SD 14.4%). The particle fraction 2-6.3 mm made up 16.1 ± 3.24% of the bulk bottom ash sample, and contained smaller clinker bits, rod shaped char and a few unburned wood splinters. Size fractions 0.5-2, 0.125-0.5 and <0.125 mm of bottom ash constituted 24.5 ± 3.57% (low density fraction with high char content), 17.3 ± 6.09% (seemingly less char than larger fractions and increasing ratio of matt grey ash) and 17.9 ± 9.95% (predominantly grey ash particles, also contained black char pieces) of the bulk sample respectively. Loss on ignition (LOI) decreased with larger particle sizes and corresponded well with the visual char and unburned matter observations. Four fractions of fly ash were segregated (Figure 1B), 2-6.3 mm, 0.5-2 mm, 0.125-0.5 mm and <0.125 mm which accounted for 0.37 ± 0.01% (rod shaped char with a few splinters of unburned wood, not further analysed), 20.3 ± 0.98% (mostly rod and discoid shaped char particles), 29.5 ± 0.29% (dark grey ash particles with char pieces) and 50.6 ± 0.49% (light grey fraction, few char pieces appearing as dispersed black points) of the bulk fly ash sample respectively. LOI analysis unveiled lowest residual combustible matter amount (14.8 ± 0.27%) in the smallest fly ash PSF (<0.125 mm) and showed that the larger fly ash PSF were almost entirely composed of charred fuel remains (Figure 1B).

Chemical composition

The sum of weight ratio corrected fraction composition (calculated bulk sample composition, not shown) was compared to the actual parent bulk solid analysis (Table 1). Three elements Cu, Sn and Pb exhibited 5.3, 3.5 and 2.3 fold higher concentrations in the calculated bottom ash composition than the parent, original bulk sample (Chapter 3). Apart from these three elements, the average deviation from the parent solid value was 16.8%. When Cu, Sn and Pb were included, the overall average deviation from the bulk solid sample was 44.5%. In fly ash deviations were smaller, Ag, Se, Cu and Tl weight ratio corrected fraction composition showed 2.3, 1.6, 1.4 and 1.4 fold higher concentrations than the parent solid fly ash and overall average deviation was 17%.

Presented by enrichment factor between bulk parent ashes (Chapter 3), elemental composition (Table 1) demonstrated a slight enrichment tendency of Ni and the elements Cr and Co (EF_S 1.32 – 1.4) as well as strong enrichment of Ba (EF_S 16.8) in bottom ash bulk samples. Based on detection limits, no enrichment of Sb and Hg in an ash type relative to the other could be found. Fly ash was in contrast rich in the priority hazardous elements Cd and Pb (EF_S 0.17 and 0.3) as well as the WAC elements Zn, As, Mo and Se.

A comparison of element content across the different ash fractions showed that bottom ash was characterised by a less uniform dispersion pattern of element content (increasing, decreasing or u-shaped pattern of concentrations along the particle size gradient) than fly ash (Table 1). Across all fractions of bottom ash coefficients of variation (CV) were higher than 50%; Cu, Cd, Sn, Zn, N, C and Pb exhibited the largest range of concentrations. Cd and C, like most elements, displayed a continuously decreasing content in bottom ash from small to larger particle sizes. In contrast, the decrease for Zn with increasing fraction particle size resembled an asymptotic curve. Similarly, Cu, Sn, N and Pb exhibited u-shaped distribution curves with highest concentrations in the smallest (<0.125 mm) but also the largest (>6.3 mm) particle size fractions.

Table 1: *Aqua regia* extractable solid concentrations of bulk bottom and fly ash from untreated wood (Chapter 2, mg/kg dry weight ± SD, n=4), sorted by EF_S with separated PSF (particle size in mm, mg/kg dry weight, single determination); Carbon content determined by LOI analysis; Priority substances in Annex II of Directive 2008/105/EC in bold, WAC relevant elements in bold and italic

Analyte	EF_S	Bottom ash (BA)						Fly ash (FA)			
		bulk	<0.125	0.125 - 0.5	0.5 - 2	2 - 6.3	>6.3	bulk	<0.125	0.125 - 0.5	0.5 - 2
Cadmium (Cd)	**0.17**	**1.62 ± 0.13**	**5.52**	**1.8**	**1.39**	**1.92**	**1.17**	**9.67 ± 0.25**	**16.2**	**7.72**	**2.96**
Zinc (Zn)	***0.18***	***325 ± 25.2***	***964***	***392***	***298***	***344***	***381***	***1832 ± 57.95***	***2850***	***1390***	***479***
Carbon (C, LOI)	0.25	118000	195000	117000	143000	69900	37800	479000	124000	505000	696000
Lead (Pb)	**0.3**	**11.5 ± 1.53**	**49.8**	**20.1**	**16.4**	**15.5**	**29.1**	**38.5 ± 0.9**	**57**	**32.8**	**15.1**
Nitrogen (as N)	0.38	655 ± 237	1110	560	580	260	1310	1715 ± 183	780	2030	2550
Arsenic (As)	***0.49***	***2.66 ± 0.15***	***5.79***	***2.91***	***2.4***	***3.27***	***2.66***	***5.44 ± 0.05***	***9.1***	***4.55***	***1.77***
Boron (B)	0.55	105 ± 6.28	216	124	109	119	78.7	191.8 ± 1.71	289	167	128
Molybdenum (Mo)	***0.6****	***<1***	***1.84***	***1.13***	***1.29***	***1.14***	***<1***	***1.68***	***3.54***	***<1***	***<1***
Silver (Ag)	0.71*	<1	3.84	3.24	2.72	2.87	2.63	1.41	5.15	2.09	<1
Selenium (Se)	***0.72***	***3 ± 0.68***	***7.08***	***5.83***	***5.01***	***5.35***	***4.83***	***4.18 ± 0.75***	***9.34***	***4.48***	***2.13***
Potassium (K)	0.8	57175 ± 9726	43000	58400	56300	49800	36700	71100 ± 3477	95900	56900	37900
Tin (Sn)	0.84	1.45	11.4	3.85	1.68	2.81	6.02	1.72	2.96	1.27	<1
Thallium (Tl)	0.93	3.95	8.06	7.06	6.05	6.38	5.77	4.23	8.7	3.86	1.58
Phosphorus (P)	0.95	11815 ± 1344	16500	13400	10700	11300	10800	12375 ± 486	21900	7470	2510
Antimony (Sb)	***1****	***<1***	***<1***	***<1***	***<1***	***<1***	***<1***	***0***	***1.09***	***<1***	***<1***
Mercury (Hg)	**1***	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**	**<0.2**
Magnesium (Mg)	1.05	16475 ± 1859	21000	19400	15600	15700	14400	15700 ± 668	27100	9890	3220
Copper (Cu)	***1.1***	***84 ± 26***	***856***	***165***	***119***	***110***	***921***	***76.5 ± 1.29***	***154***	***74.1***	***33.1***
Strontium (Sr)	1.13	816 ± 83.5	1170	933	780	825	721	724 ± 83.6	1130	477	172
Manganese (Mn)	1.14	11875 ± 1274	12500	11400	9660	10100	9350	10450 ± 436	13000	5520	2070
Calcium (Ca)	1.16	113475 ± 11523	162000	123000	105000	114000	111000	97975 ± 5261	173000	57800	18500
Sodium (Na)	1.17	4320 ± 538	3890	4810	4830	4550	4410	3695 ± 59	4410	3610	3010
Nickel (Ni)	**1.32**	**17 ± 1.26**	**26.1**	**22.7**	**19.6**	**19.6**	**21.2**	**12.9 ± 0.21**	**22.6**	**10.1**	**3.7**
Chromium (Cr)	***1.36***	***19 ± 1.91***	***29.8***	***24.2***	***21.8***	***22.4***	***19.6***	***14 ± 0.6***	***23.5***	***10.9***	***3.97***
Cobalt (Co)	***1.4***	***8.75 ± 0.59***	***11.3***	***12.7***	***12***	***10.4***	***10.9***	***6.24 ± 0.17***	***10.7***	***4.44***	***1.41***
Lithium (Li)	1.64	12.1 ± 1.1	13	14.2	13.2	13.1	16.2	7.4 ± 0.31	11.5	5.5	2.77
Vanadium (V)	1.71	18.6 ± 1.49	17	22.2	20.9	20.5	19.7	10.9 ± 0.24	19.2	7.39	1.83
Aluminium (Al)	2.11	13350 ± 1609	11400	16300	15600	14900	16000	6315 ± 134	11700	4250	934
Iron (Fe)	2.2	11125 ± 971	9840	14300	12200	12000	13600	5052 ± 102	8830	3260	758
Beryllium (Be)	2.24	0.35 ± 0.03	0.283	0.429	0.409	0.367	0.374	0.16 ± 0.02	0.275	0.108	<0.1
Titanium (Ti)	2.48	719 ± 49.5	481	925	843	750	775	290 ± 24.6	633	198	43.3
Barium (Ba)	***16.8***	***1227 ± 64***	***244***	***1020***	***1150***	***1080***	***1160***	***72.9 ± 12***	***38***	***51.1***	***227***
Modelled liming potential (CaO%)			28.3	22.6	19.3	20.6	19.6		32	11.4	4.2

* Calculated with at least one detection limit (arbitrary); ** Calculated according to model in Zhang et al. (2002); Solid lines frame elements with equal enrichment in bottom and fly ash (EF_S = 1), dashed lines frame elements with moderate enrichment tendencies (EF_S > 0.8 and <1.2)

Al, Ba and Li were the only elements whose content increased along with particle size of fly ash. Sb and Hg were not detected in any of the five bottom ash particle size classes (<1 and <0.2 mg/kg respectively).

The three analysed PSF of fly ash were more variable than bottom ash PSF as only the elements Na, B and K were associated with a CV (across all fractions) below 50%. Fly ash fractions displayed a clear pattern of elemental composition (Table 1) as nearly all metal and metalloid elements occurred in higher concentrations within the smallest particle size class (<0.125 mm) tested. Only C, N and Ba were enriched within the largest particles (0.5-2 mm). Hg was not detected (<0.2 mg/kg) in any of the three fly ash PSF.

Mobile components

A comparison of leachate showed an effect of particle size on pH. The pH increases from 11.6 to 12.2 with increasing bottom ash particle size. In the case of fly ash, the pH was instead constant over all PSF (Table 2). Electrical conductivity (ElC) of both bottom and fly ash PSF leachates decreased with larger particle diameter. Though, in the PSF with the largest fly ash particles the ElC was still about twice as large as in the PSF with the smallest bottom ash particles. Chloride was equally mobile from all fly ash PSF (1410 ± 75.5 mg/L). In the smallest bottom ash PSF 278 mg/L chloride were detected, leachable concentrations declined with increasing particle size to about a tenth of this value in the largest PSF (Table 2). Sulphate concentrations in both bottom and fly ash PSF leachates declined with increasing particle diameter. In the smallest PSF (<0.125 mm) of fly ash the SO_4^{2-} concentration was 7-larger than in the bottom ash PSF of the same size.

Biological oxygen demand (BOD) and chemical oxygen demand (COD) were highest in small PSF of bottom ash (Table 2) In fly ash BOD was near the detection limit (<3 mg/kg) while COD increased from smallest to larger PSF. No ammoniacal N (<0.5 mg/L) was detected in any of the ash PSF aqueous leachates. Nitrite, total organic nitrogen (TON) and orthophosphate concentrations in leachate increased with particle size of fly ash PSF. Nitrogen compounds from bottom ash were detected in the smallest PSF leachate only, also mobile orthophosphate concentrations declined with larger particles.

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Table 2: Leachate (EN 12457-2, 10 l/kg, 24 h contact time) properties electrical conductivity and pH, oxygen depletion potential, mobility controlling saliferous ions and plant available nutrient compounds from bottom (BA) and fly ash (FA) bulk parent solids (Chapter 2, average ± SD, n=4) as well as distinct PSF (particle size in mm)

	EF_L		Bottom ash (BA) bulk			<0.125	0.125 - 0.5	0.5 - 2	2 - 6.3	>6.3	Fly ash (FA) bulk			<0.125	0.125 - 0.5	0.5 - 2
Sulphate (SO_4^{2-})	0.07	mg/l	297	±	12.4	1120	573	671	418	<100	4133	±	92.4	7870	4170	1420
Chloride (Cl^-)	0.09	mg/l	111	±	41.3	278	173	165	121	24.1	1243	±	20.8	1330	1420	1480
Total Oxidised Nitrogen (TON)	0.14*	mg/l	<1			1.33	<1.00	<1.00	<1.00	<1.00	6.98	±	0.19	3.22	9.83	15.7
Nitrite (NO_2-N)	0.16*	mg/l	<0.1			0.103	<0.1	<0.1	<0.1	<0.1	0.63	±	0.01	0.38	0.7	0.91
Conductivity at 20 °C (EIC)	0.28	µS/cm	3560	±	2300	6250	4620	4320	2970	958	12700	±	6430	18700	14600	10000
pH at 20 °C	0.92		10.61	±	0.18	11.6	11.6	11.6	11.9	12.2	11.52	±	0.11	12.4	12.2	12.3
Chemical Oxygen Demand (COD)	0.93	mg/l	46.2	±	19.6	226	131	156	76.3	11	49.7	±	1.26	34.5	62.5	75.8
Ammoniacal Nitrogen (NH_3-N)	1*	mg/l	<0.5			<0.5	<0.5	<0.5	<0.5	<0.5	<0.5			<0.5	<0.5	<0.5
Biological Oxygen Demand (BOD)	1*	mg/l	<1.40			93.4	43.5	44.9	7.86	<3.68	<1.40			<2.33	<2.80	<2.92
Orthophosphate (PO_4^{3-}-P)	4.37*	mg/l	2.19	±	0.22	6.06	2.02	3.21	1.42	<0.5	<0.5			<0.5	0.649	4.17

* EF_L Calculated with at least one detection limit; Solid lines frame elements with equal enrichment in bottom and fly ash leachates ($EF_L = 1$)

Of the 16 US-EPA PAH indicators, none were detected (<0.02 µg/L) in either of the ash types' PSF leachates (data not shown). WAC and European priority elements, but not As and Cu, tended to be more concentrated in leachate from fly ash solids (Table 3). EF_L and thus enrichment in leachates was often based on at least one detection limit. Some discrepancies between concentrations in bulk sample leachate and the leachates of corresponding PSF were observed for Zn and Cu.

In aqueous leachate from any ash PSF, neither the macro elements Fe, Mg and Mn nor the trace elements Be, Co, Pb and Tl were detected. The sum of all analytes in the five bottom ash PSF, in order of increasing equivalence diameter, was 3.66, 1.96, 2.34, 1.55 and 0.28 g/L. In the case of fly ash, much more of its constituents were mobile, with the sum of all analytes adding up to 17.5, 10.9 and 6.37 g/L. Leachable Ba and Sr were exclusive to the smallest PSF (<0.125 mm) of fly ash (Table 3). Conversely, Sn and Hg were only mobile from the largest (>6.3 mm) and smallest PSF (<0.125 mm) of bottom ash respectively. From bottom ash, elements were generally most mobile in small PSF. The mobility profiles across PSF only deviated for the elements Cu (u-shaped), Zn (increasing with particle size), Ti (irregular) and Ca which was only detectable in leachate of the largest size fraction. In fly ash leachate, As, P, Na, Sb and Cd were found in the highest concentrations leachable from the largest particle class (0.5 mm to <1 mm). Conversely, the elements Al, Ba, B, Ca, K, Sr, Mo, Zn and Se were most concentrated in leachate from the smallest fly ash size fraction. Concentrations of V and Ni described an inverted-v shape being most abundant in leachate from particles of the size >0.125 mm and <0.5 mm while Cr and Cu are least present in leachate from this particle size class.

When considering relative mobility (Table 3), Molybdenum (Mo) was most complete and readily dissolved (76-95% from bottom ash PSF). While only 62% of Mo was mobile in the smallest fly ash PSF. Potassium (K) poses the most completely leached element in all fly ash PSF (84-86% mobility). While relative mobility seemed to decrease with larger particle sizes in bottom ash for most elements, an increase of relative mobility was observed in a range of elements from fly ash (Al, B, P, Na, As, Cr, Se, V and Zn).

Table 3: BS EN 12457-2 (10 L·kg^{-1}) leachate concentrations from wood bottom (BA) and fly ash (FA) bulk parent material (average ± SD, n=4) and particle size fractions (PSF) from a single determination; Relative mobility (%) based on solid content in parentheses, for bulk materials the calculation was performed with average leachate concentrations. Priority substances in Annex II of Directive 2008/105/EC in bold, additional WAC relevant elements in bold and italic), elements with supposedly small impact on toxicity and non-nutrient elements in grey

Fraction	EF$_L$	mm	Bottom ash leachate (BAL) Bulk	<0.125	0.125 - 0.5	0.5 - 2	2 - 6.3	>6.3	Fly ash leachate (FAL) Bulk	<0.125	0.125 - 0.5	0.5 - 2
Zinc (Zn)	*0.00*	µg/l	*5.29 (0.02%)*	*42.7 (0.04%)*	*46.3 (0.12%)*	*79.7 (0.27%)*	*49 (0.14%)*	*85.9 (0.23%)*	*3296 ± 2191 (1.8%)*	*109 (0.04%)*	*45.1 (0.03%)*	*51.5 (0.11%)*
Aluminium (Al)	0.02	mg/l	0.03 ± 0.03 (0.003%)	0.723 (0.06%)	0.834 (0.05%)	0.19 (0.01%)	0.157 (0.01%)	1.08 (0.07%)	1.96 (0.31%)	2.19 (0.19%)	0.998 (0.23%)	0.909 (0.97%)
Calcium (Ca)	0.03	mg/l	11.9 ± 4.46 (0.11%)	<20 (0.12%)	<10 (0.08%)	<10 (0.1%)	<10 (0.09%)	15 (0.14%)	437 ± 280 (4.46%)	81.2 (0.47%)	<20 (0.35%)	<20 (1.08%)
Strontium (Sr)	0.04	mg/l	0.07 ± 0.02 (0.09%)	<0.4 (0.34%)	<0.2 (0.21%)	<0.2 (0.26%)	<0.2 (0.24%)	<0.2 (0.28%)	1.86 ± 1.01 (2.56%)	0.918 (0.81%)	<0.4 (0.84%)	<0.4 (2.33%)
Cobalt (Co)	*0.05**	µg/l	*1.04 (0.12%)*	*<1 (0.09%)*	*<1 (0.08%)*	*<1 (0.08%)*	*<1 (0.1%)*	*<1 (0.09%)*	*<20 (0.32%)*	*<1 (0.09%)*	*<1 (0.23%)*	*<1 (0.71%)*
Tin (Sn)	0.05*	µg/l	<2 (1.38%)	<4 (0.35%)	<4 (1.04%)	<4 (2.38%)	<4 (1.42%)	4.47 (0.74%)	<40 (23.3%)	<4 (1.35%)	<4 (3.15%)	<4 (n.a.)
Barium (Ba)	*0.08*	mg/l	*0.02 ± 0.004 (0.02%)*	*<0.2 (0.82%)*	*<0.1 (0.1%)*	*<0.1 (0.09%)*	*<0.1 (0.09%)*	*<0.1 (0.09%)*	*0.25 ± 0.12 (3.39%)*	*0.209 (5.5%)*	*<0.2 (3.91%)*	*<0.2 (0.88%)*
Selenium (Se)	*0.09*	µg/l	*8.53 (2.84%)*	*33 (4.66%)*	*17.6 (3.02%)*	*19.6 (3.91%)*	*14.4 (2.69%)*	*2.91 (0.6%)*	*99.5 (23.8%)*	*141 (15.1%)*	*117 (26.1%)*	*86.5 (40.6%)*
Cadmium (Cd)	**0.1***	µg/l	**0.19 (0.11%)**	**0.115 (0.02%)**	**0.176 (0.1%)**	**0.24 (0.17%)**	**<0.1 (0.05%)**	**<0.1 (0.09%)**	**<2 (0.21%)**	**<0.1 (0.01%)**	**<0.1 (0.01%)**	**0.204 (0.07%)**
Nickel (Ni)	**0.1***	µg/l	**<1 (0.06%)**	**1.63 (0.06%)**	**1.46 (0.06%)**	**<1 (0.05%)**	**<1 (0.05%)**	**2.35 (0.11%)**	**<10 (0.77%)**	**<1 (0.04%)**	**1.5 (0.15%)**	**<1 (0.27%)**
Thallium (Tl)	0.1*	µg/l	<1 (0.25%)	<4 (0.5%)	<4 (0.57%)	<4 (0.66%)	<4 (0.63%)	<4 (0.69%)	<10 (2.36%)	<4 (0.46%)	<4 (1.04%)	<4 (2.53%)
Titanium (Ti)	0.1	µg/l	8.15 ± 1.03 (0.01%)	5.13 (0.01%)	12.5 (0.01%)	7.4 (0.01%)	<4 (0.01%)	4.57 (0.01%)	78.1 ± 12.5 (0.27%)	<4 (0.01%)	<4 (0.02%)	<4 (0.09%)
Potassium (K)	0.22	mg/l	1217 ± 306 (21.3%)	2060 (47.9%)	1110 (19%)	1380 (24.5%)	924 (18.6%)	217 (5.9%)	5445 ± 320 (76.6%)	8050 (83.9%)	5050 (88.8%)	3210 (84.7%)
Antimony (Sb)	*0.26*	µg/l	*5.12 ± 1.43 (n.a.)*	*5.92 (n.a.)*	*4.09 (n.a.)*	*3.63 (n.a.)*	*3.81 (n.a.)*	*2.27 (n.a.)*	*<20 (n.a.)*	*2.58 (2.37%)*	*6.68 (n.a.)*	*7.22 (n.a.)*
Chromium (Cr)	*0.32*	µg/l	*81.7 ± 17.4 (4.29%)*	*135 (4.53%)*	*93.8 (3.88%)*	*73.5 (3.37%)*	*53.4 (2.38%)*	*14.5 (0.74%)*	*254 ± 21 (18.2%)*	*354 (15.1%)*	*45.4 (4.17%)*	*144 (36.3%)*
Molybdenum (Mo)	*0.43*	µg/l	*104 ± 24.9 (104%)*	*163 (88.6%)*	*108 (95.6%)*	*107 (82.9%)*	*86.8 (76.1%)*	*34 (n.a.)*	*243 ± 43.5 (145%)*	*218 (61.6%)*	*150 (n.a.)*	*110 (n.a.)*
Lead (Pb)	**0.45***	µg/l	**<2 (0.17%)**	**<2 (0.04%)**	**<2 (0.1%)**	**<2 (0.12%)**	**<2 (0.13%)**	**<2 (0.07%)**	**4.45 ± 0.29 (0.12%)**	**<2 (0.04%)**	**<2 (0.06%)**	**<2 (0.13%)**
Sodium (Na)	0.47	mg/l	99.9 ± 16.6 (23.1%)	185 (47.6%)	95.6 (19.9%)	119 (24.6%)	80 (17.6%)	20.8 (4.7%)	212 ± 12.4 (57.4%)	165 (37.4%)	231 (64%)	230 (76.4%)
Iron (Fe)	1*	mg/l	<0.03 (0.003%)	<0.6 (0.06%)	<0.3 (0.02%)	<0.3 (0.02%)	<0.3 (0.03%)	<0.3 (0.02%)	<0.03 (0.006%)	<0.03 (0%)	<0.6 (0.18%)	<0.6 (0.79%)
Beryllium (Be)	1*	µg/l	<20 (56.7%)	<2 (7.07%)	<2 (4.66%)	<2 (4.89%)	<2 (5.45%)	<2 (5.35%)	<20 (128%)	<2 (7.27%)	<2 (18.5%)	<2 (n.a.)
Mercury (Hg)	**1***	µg/l	**<0.01 (0.05%)**	**0.0281 (n.a.)**	**<0.02 (n.a.)**	**<0.02 (n.a.)**	**<0.02 (n.a.)**	**<0.02 (n.a.)**	**<0.01 (0.05%)**	**<0.02 (n.a.)**	**<0.02 (n.a.)**	**<0.02 (n.a.)**
Manganese (Mn)	2*	mg/l	0.02 (0.001%)	<0.2 (0.02%)	<0.1 (0.01%)	<0.1 (0.01%)	<0.1 (0.01%)	<0.1 (0.01%)	<0.01 (0.001%)	<0.01 (0%)	<0.2 (0.04%)	<0.2 (0.1%)
Copper (Cu)	*2.09*	µg/l	*8.9 ± 3.89 (0.11%)*	*81.8 (0.1%)*	*24.4 (0.15%)*	*23.3 (0.2%)*	*16.9 (0.15%)*	*130 (0.14%)*	*4.26 ± 0.31 (0.06%)*	*3.14 (0.02%)*	*<1 (0.01%)*	*2.65 (0.08%)*
Boron (B)	2.56	mg/l	2.02 ± 0.43 (19.2%)	3.57 (16.5%)	1.86 (15%)	2.26 (20.7%)	1.59 (13.4%)	<1 (12.7%)	0.79 ± 0.9 (4.11%)	2.78 (9.62%)	2.06 (12.3%)	<2 (15.6%)
Arsenic (As)	*2.91*	µg/l	*23.4 (8.79%)*	*51.4 (8.88%)*	*32.3 (11.1%)*	*10 (4.17%)*	*19.3 (5.9%)*	*<3 (1.13%)*	*8.05 (1.48%)*	*6.58 (0.72%)*	*28.2 (6.2%)*	*33.3 (18.8%)*
Vanadium (V)	4.02	µg/l	183 ± 13.18 (9.85%)	427 (25.1%)	294 (13.2%)	234 (11.2%)	151 (7.37%)	46 (2.34%)	45.5 (4.19%)	51.3 (2.67%)	87.2 (11.8%)	54.9 (30%)
Magnesium (Mg)	5.5*	mg/l	1.65 ± 0.08 (0.1%)	<6 (0.29%)	<3 (0.15%)	<3 (0.19%)	<3 (0.19%)	<3 (0.21%)	<0.3 (0.02%)	<0.3 (0.01%)	<6 (0.61%)	<6 (1.86%)
Total phosphorus (P)	23.4	mg/l	1.87 ± 0.39 (0.16%)	6.15 (0.37%)	2.07 (0.15%)	3.42 (0.32%)	1.37 (0.12%)	0.045 (0%)	0.08 (0.006%)	0.043 (0%)	0.628 (0.08%)	3.93 (1.57%)

* Calculated with at least one detection limit; Where analyte was not detected, relative mobility calculation is based on the detection limit; Solid lines frame elements with equal enrichment in bottom and fly ash leachates (EF$_L$ = 1)

Biological response to ash PSF

Microtox assay

In the cases of both bottom and fly ash, toxicity screening using the Microtox assay (inhibition of bioluminescence, Figure 2A) yielded a number of staggered dose-response curves. There was a pattern with dose-responses curves for larger size particles shifting towards higher ash equivalent concentrations and thus EC. While curves suggested similar EC_{50} (4.78, 5.96 and 7.46 g/L) values for the three smaller bottom ash PSF (<1 mm), curves were situated further up the dose gradient for particles larger than 1 mm. No Microtox EC_{50} (>42.5 g/L) could be calculated for particles exceeding 6.3 mm equivalence diameter.
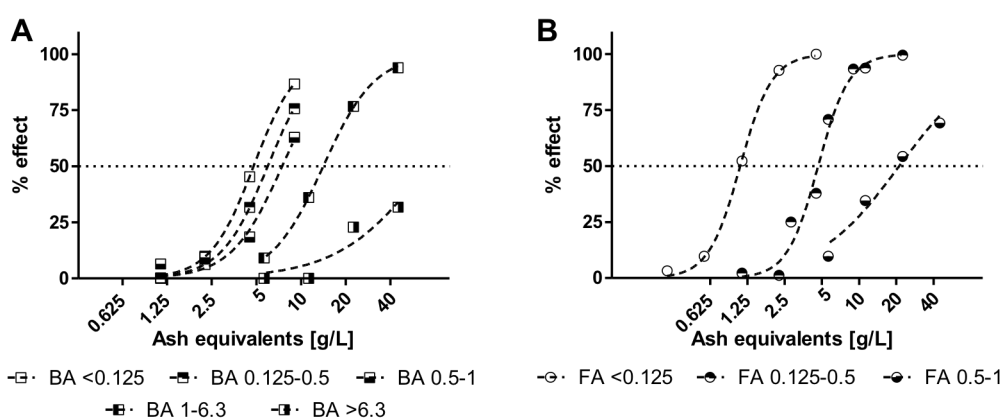

Figure 2: Inhibition of bioluminescence in *Aliivibrio fischeri* (Microtox) from size fractionated wood bottom (A) and fly (B) ash, Averages ± SD (SD very small, not visible), n=2

In ascending order of equivalence diameter 20.9, 16.8, 13.4, 7.09 and <1.41 toxic units (TU) were calculated from respective EC_{50} of bottom ash PSF. Fly ash PSF showed more distinct dose-response curves (Figure 2B), EC_{50} were 1.09 g/L, 4.67 g/L and 21.1 g/L for the size classes <0.125, 0.125-0.5 and >0.5 mm respectively (Table 4). These correspond to 91.7, 21.4 and 4.74 TU of the aqueous fly ash PSF extract.

Inhibition of growth assay with *Lemna minor*

The response of the vascular plant model to fractionated bottom and fly ash is similar to the bacterial response. Dose-effect curves are staggered in the same sequence, with the smallest PSF of both bottom and fly ash showing the lowest EC_{50} (Figure 3, Table 4). The range of pH in suspensions of bottom ash (smallest

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to largest PSF) at the lowest ash test concentration (10 g/L) was 8.84 to 6.69. ElC ranged from 2.49 to 2.06 mS/cm. At the highest test concentration of 160 g/L, the pH ranged from 10.5 for smallest bottom ash PSF (<0.125 mm) to 8.41 for the largest bottom ash PSF (>6.3 mm). At this high ash concentration the ElC range (smallest to largest PSF) was 14.9 to 2.31 mS/cm. ElC and pH conditions in the test concentrations framing the EC_{50} values are shown in Appendix Table 1. Frond growth rate of *L. minor* is reduced to 50% of the control value (EC_{50}) at 15.6 g/L (95% CI: 12.3 to 19.8 g/L) for the smallest PSF of bottom ash (<0.125 mm, Table 3). For the largest PSF, predominantly consisting of clinker, an EC_{50} could not be calculated and is assumed to be >160 g/L. Biomass growth EC_{50} of bottom ash PSF were consistently lower (Table 4), calculated with this more sensitive parameter are 19.2, 8, 5.78, 1.3 and <0.626 TU in the order of smallest to largest PSF.
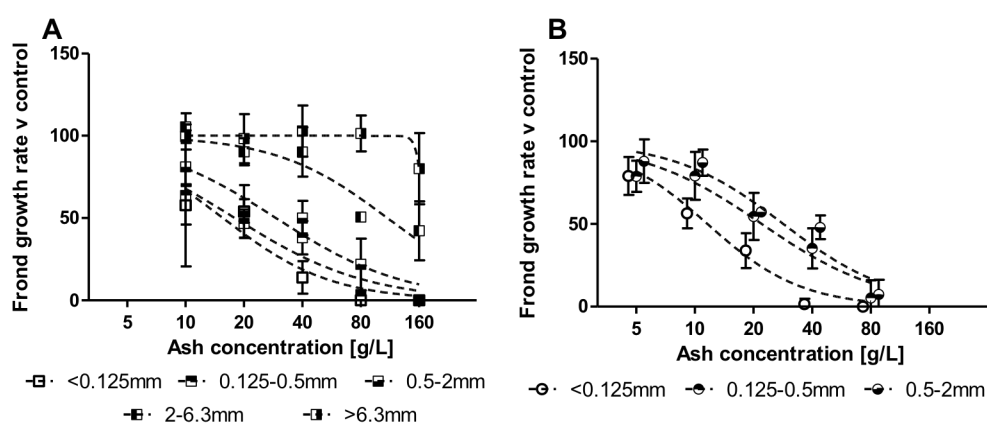

Figure 3: Relative frond growth rate of *Lemna minor* exposed to size fractionated wood bottom (A) and fly (B) ash, Averages ± SD, n=4

Water pH and ElC (data not shown) in fly ash suspensions of the lowest test concentration (5 g/L) ranged from pH 8.74 to 6.65 and 3.36 to 2.24 mS/cm for the smallest (<0.125 mm) to the largest PSF (>0.5 mm). At the largest fly ash test concentrations (80 g/L) pH ranged (smallest to largest PSF) from 11.3 to 9.85 while ElC ranged from 24.4 to 10.8 mS/cm. For the smallest PSF, fly ash exhibits a frond number growth rate based EC_{50} of 11.6 g/L (Figure 3), a smaller value than the bottom ash PSF of the same size. Fly ash PSF (0.125-0.5 mm) is marked by an EC_{50} of 22.1 g/L, slightly higher than the equivalent EC_{50} of bottom ash of the same PSF. The PSF with the largest fly ash particles yielded an EC_{50} of 28.4 g/L, similar to that yielded by the same size bottom ash PSF. EC_{50}

calculated from biomass growth response were smaller than those for frond growth rate, and it was calculated for biomass growth inhibition that 9.71, 6.21 and 7.23 TU were received.

Discussion

Ash particle size and pathways of unintentional dispersion

Cumulative particle size distribution curves of bottom and fly ash clearly demonstrate the disparity the ash nomenclature suggests, bottom ash appeared poorly sorted with all particle sizes (up to >6.3 mm) present while fly ash, in contrast, was well sorted and dominated by small, light-weight particles (Figure 1). Demeyer et al. (2001) stated that 80% of wood ash mass are particles <1 mm; bottom ash from grate firing in this study fits this general observation but fly ash contains the same weight proportion already in particles <0.5 mm. Bottom ashes from fluidized bed boilers such as investigated by Barbosa et al. (2013) and Dahl et al. (2010) may, for inclusion of boiler bed particles such as sand, be usually coarser than ashes from grate firing. However, ash melting and the formation of clinker also increase the average particle diameter (D_{50}) of bottom ash from boilers with grate technology. Bottom ash but also fly ash in this study (Figure 1) were finer than those detailed by Barbosa et al. (2013), fly ash showed half the D_{50} and bottom ash a third of D_{50}. The study by Dahl et al. (2010) on ash from a large fluidized bed boiler separated two stages of flue gas cleaning residue; the first, coarser cyclone fly ash from that study was found to have a similar PSD to the one reported here (Figure 1B). Larger particle dimensions within fly ash concurred with light-weight, rod-shaped char particles with a high LOI. The D_{50} of fly ash is thus likely connected to incomplete combustion and larger particles eligible for energy recovery (James et al., 2012). While the ashes from a grate fired boiler in this study appeared finer than some, they cannot, for the large range of particle sizes in ash (Demeyer et al., 2001; James et al., 2012) and similarity of fly ash to earlier descriptions (Dahl et al., 2010), be considered unusual.

The large proportion of small particles (<0.125 mm) in fly ash facilitates a high dust risk (turbulence, transport and re-deposition if the material should be

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exposed to wind or draught). Similarly, high proportions of relatively light char in the larger PSF of fly ash increase the chance of wind dispersal. In practice, mixture of fly ash to wet bottom ash on the site of production reduces the risk of dispersal by wind and also potential respiratory exposure of workers, thus seemingly increasing safety of storage and transport. At the same time, the introduced moisture may facilitate mobilization of ash components as leachate or percolate from the composite (bottom and fly ash) waste that accrues at storage facilities, similar to hardening processes described by Steenari et al. (1999). Even though admixture is in accordance with 'absolute non-hazardous waste' classification of bottom and fly ash from untreated fuel in EWC (codes 10 01 01 and 10 01 03 respectively), it conflicts with the possible separation of contaminants that are usually highly enriched in fly ash (Narodoslawsky and Obernberger, 1996). While indoor storage with drainage management largely covers dispersal risks by air and water on site, it may not always be feasible; additionally loading, transport and disposal on landfill create opportunities for unintentional release that favour small particles.

Elemental composition of ash PSF solids

Parent bulk (before fractionation, Table 1) bottom ash from clean biofuel, such as untreated wood (Chapter 3), is characterized by relatively higher compositional variability than fly ash. It is thus not surprising, that the same is found for the reconstructed ash element concentrations calculated from fraction element content and respective fraction weight proportion. Only small differences are observed between recalculated solid composition and actual parent ash. Thus it is concluded that the chemical analysis of the ash PSF solids is representative, even though it was only carried out in single replication.

Chemical disparity of bottom and fly ash, is well described for a range of wood fuel types (Dahl et al., 2010; Lundholm et al., 2007; Narodoslawsky and Obernberger, 1996; Park et al., 2012; Poykio et al., 2011). This disparity is reflected in EWC codes (European Commission, 2000) and further confirmed by the ashes analysed here (Table 1). Disparity of the ash types, even though resulting from the same thermal reaction is due to the valorisation/disaggregation of the fuel and volatilization of reaction products into aerosols. Fly ashes are

transported in the flue and get into contact with boiler condensate (Narodoslawsky and Obernberger, 1996; Serup et al., 2005). Both these aspects increase the chemical burden of fly ashes through adsorption of Cd, Pb, Zn and Hg. Bottom ashes in contrast are usually low in volatile compounds and may melt forming clinker deposits, immobilizing a proportion of the constituting elements therein. Furthermore the bottom ash in this study, as is widespread practice, is collected in a water bath below the firing grates, this may affect their pollutant load as compounds may leach out or, from already concentrated waters in the bottom drip pan, increase their load due to re-adsorption.

Bottom ash exhibits three distinct patterns of element distribution in PSF. Firstly, element concentrations may be decreasing with particle size (such as for As, B, Ca, Cd, C, Mg, Mn, P, Sr and Zn). Wind drift poses the highest dispersal risk for compounds concentrated in the finer PSF. The Cd predominance in the smallest PSF (<0.125 mm) unveiled here matches findings by Aronsson and Ekelund (2002). Secondly, elements with u-shaped distribution pattern (Cu, Sn, C and Pb, highest in silt and gravel sized particles) across bottom ash PSF are also at risk of wind or draught transport. Here, segregation of the clinker fraction (>6.3 mm) offers the chance to reduce total ash load of these elements. The third distribution pattern in bottom ash shows increasing concentrations (Ba, Li and Ti) in larger particles. Such elements are thus at low risk of being dispersed by air movement. Abundance of the plant nutrients P, Ca, Mg is slightly higher in the smallest PSF (<0.125 mm). Liming potential as CaO% (Table 1) is largest for the smallest bottom ash PSF (28.3%), the subsequently larger PSF exhibit rather similar liming potential between 22.6 and 19.3%. Segregation of bottom ash PSF will thus not greatly influence the liming potential.

In Fly ash only two element abundance patterns can be identified. The predominant amount of elements, including nutrients, is found in highest concentrations in the smallest PSF, concurrent with findings in Barbosa et al. (2013). A small number of elements, however, (C, N and Ba) are more concentrated in larger PSF. This matches with the char predominance in the two largest fly ash fractions, where these elements remain un-volatized. In fly ash, the smallest PSF displays notable liming potential (32% CaO, Table 1). The larger fly ash PSF only display between a third and a sixth of this liming value.

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Segregation of the smallest fly ash PSF, where undesired metal and metalloid elements are concentrated, would thus not only diminish the materials fertilizing but also liming potential.

Mobility from ash PSF

The salt load is much higher in fly ash than in bottom ash PSF leachates (Table 2). High mobility of chloride (Cl^-) and sulphate (SO_4^{2-}) such as described in Barbosa et al. (2013) was confirmed for the ashes in this study. As ligands, both are likely controlling species for chemical release into leachate (Barbosa et al., 2013). The two smaller fly ash PSF (<0.125 and 0.125-0.5 mm, Table 2) surpass SO_4^{2-} limits (2000 mg/L) according to European WAC (Council of the European Union, 2003). In all fly ash PSF leachates (Table 3), selenium (Se) concentrations exceed WAC non-hazardous waste limits (0.05 mg/L). Fly ash or any of its PSF thus cannot be considered non-hazardous under WAC. Research on coal fly ash found sulphate compounds of selenium highly mobile and prominent (Izquierdo and Querol, 2012). Additionally, the leachates of all fly ash PSF just remain below the allowable threshold for Cl^- (1500 mg/L). Sieving of fly ash and potential segregation of PSF is thus not an option to mitigate ash quality or lower potential environmental hazards regarding these elements and compounds.

In bottom ash, compound (Table 2) and element mobility profiles (Table 3) most commonly show decreasing leachate concentrations with increasing particle size, as expected from the larger total surface area of the smaller particles. This pattern may also be attributable to SO_4^{2-} as mobility controlling species (Barbosa et al., 2013). An exception is the Copper (Cu) mobility pattern which mirrors the PSF solid content and thus resembles a u-shaped mobility profile across PSF. Only Zn and Ca exhibit higher leachate concentrations from particles of larger size. Most elements show similar relative mobility (in parentheses, Table 3) over bottom ash PSF, suggesting similar compounds of the respective elements therein. In contrast, K, Na, As and V exhibit reduced relative mobility with increasing ash particle size. Lower concentrations in leachate from larger size bottom ash PSF are thus also result of reduced dissolvability of compounds containing these elements, which could point at different speciation in bottom ash PSF. In fly ash,

oxidized nitrogen compounds show higher concentrations in leachate from larger particles (Table 2). While nitrite exhibits only slightly increasing (with PSF size) leachate concentration values, nitrate concentrations in leachate of the largest fly ash PSF is 4 times higher than in the smallest PSF. The high char and unburned matter remainder in the larger size fly ash fractions are a likely cause. Also As, Al, P and Cd exhibit highest leachate concentrations from the largest particles (Table 3) suggesting a higher mobilization risk via leachate or percolate than due to wind or draught. In fly ash, copper again displays a u-shaped mobility profile across PSF. Most other elements display decreased concentrations of their compounds in leachate from larger PSF and thus correspond with the ash PSF solid content. Peculiar is, that the relative mobility of most elements in fly ash (in parentheses, Table 3) actually increases with PSF size.

In contrast to solid ash contents, which may be released by weathering over time, mobile components may immediately be released and transported in water. Compounds found in leachate are thus likely to contribute locally to water burdens at production and/or disposal site or diffusely to road side run-off during transport. Furthermore, if ash is used as ameliorant, mobile substances may migrate through soil profiles as percolate, and if not assimilated by biota or bound by the soil matrix, eventually transfer into ground or surface waters.

Toxicity assessment

The staggering of the dose-response curves (Figures 2, 3) clearly indicates differing hazard potentials of the wood ash PSF. Presented Microtox results for ashes from untreated wood fuel PSF show less toxicity than the coarser ashes from pulp mill biomass residues which were also tested in pH native state (Barbosa et al., 2013). Only the <0.125 mm fraction of fly ash was found to be as toxic (EC$_{50}$ 1.09 g/L, Table 4) in this study. According to Shannon Aquatic Toxicity Laboratory (2012) toxicity SOP (Chapter 5), said fly ash PSF (<0.125 mm) is considered 'very toxic' (91.7 TU). The next larger fly ash fraction (0.125-0.5 mm) as well as the three smallest bottom ash PSF are still considered 'toxic' to bacteria in pH native form. The 2-6.3 mm bottom ash fraction is deemed 'slightly toxic' (7.09 TU) while the largest bottom ash fraction (>6.3 mm) is considered 'non-toxic' (<2.36 TU). A large divergence between measurable

toxicity in Microtox tests with ash, depending on test solution neutralization, has been shown earlier (Chapter 5). Native pH test solutions may render the standardized test invalid, however they depict a scenario of unintentional release best and results are thus relevant for most conservative risk analysis.

The vascular plant growth inhibition assay showed that effect concentrations based on biomass are lower than those based on the number of developed fronds. This may be due to the higher resolution of weight measurements compared with integer value frond counts. Alternatively, the generation of new fronds, as to increase photosynthetic energy conversion potential could be favoured over biomass assimilation in face of toxicant stress. According to Shannon Aquatic Toxicity Laboratory (2012) toxicity SOP, all ash PSF apart from those containing particles larger than 2 mm are considered slightly toxic (3-10 TU) to *L. minor*. Ash particles larger than 2 mm are classified non-toxic.

The predominating tendency of element concentrations in ash PSF leachates to decrease with larger particle size of the parent solid (Table 3) corresponds with measurable toxicity. Singling out elements and their possible compounds that are likely to cause the observed staggered response (toxicity) is thus difficult. Enrichment factors in the leachates from the bulk solids (EF_L, Table 3) suggest the priority hazardous substances Cd, Ni and Pb and the potentially harmful WAC elements Zn, Co, Ba, Se, Sb, Cr and Mo to be relatively more abundant in fly ash leachates. Toxicity of those bulk fly ash leachates in Microtox and *Lemna minor* assays (Table 4) was consistently higher than bulk bottom ash toxicity (Chapter 5). Antipodal tendency of concentrations across PSF (increasing in leachates from larger particles) is found for Zn and possibly Ca from bottom ash and As, P, Na, Sb and Cd in leachates from fly ash PSF. These elements thus either mitigate measurable toxicity such as Ca in hard (high $CaCO_3$) waters, or alternatively may have ancillary effect on toxicity only.

Table 4: EC$_{50}$ (g ash equivalents per litre) summary for PSF of the bottom and fly ash in Microtox screens and *Lemna minor* growth inhibition assays

| | Bottom ash EC$_{50}$ | | | | | | Fly ash EC$_{50}$ | | | | | |
	A. fischeri	(95% CI)	L. minor (Fronds)	(95% CI)	L. minor (Biomass)	(95% CI)	A. fischeri	(95% CI)	L. minor (Fronds)	(95% CI)	L. minor (Biomass)	(95% CI)
Bulk sample (pH native leachate)	**4.75**	*(4.29 to 5.27)*	**36.9**	*(29.7 to 45.7)*	**33.1**	*(20.2 to 54.2)*	**3.9**	*(3.12 to 4.89)*	**19.6**	*(14.1 to 27.2)*	**17.8**	*(13.2 to 24.1)*
<0.125 mm	4.78	*(3.89 to 5.9)*	15.6	*(12.3 to 19.8)*	5.2	*(1.56 to 17.3)*	1.09	*(0.66 to 1.8)*	11.6	*(10 to 13.5)*	10.3	*(8.08 to 13.1)*
≥0.125 to <0.5 mm	5.96	*(5.37 to 6.61)*	18	*(11.4 to 28.3)*	12.5	*(8.67 to 18.1)*	4.67	*(4.12 to 5.28)*	22.1	*(17.3 to 28.2)*	16.11	*(11.9 to 21.7)*
≥0.5 to <2 mm	7.46	*(5.86 to 9.5)*	29.3	*(23.2 to 36.9)*	17.3	*(15.2 to 19.7)*	21.1	*(13.2 to 33.8)*	28.4	*(23.4 to 34.6)*	13.83	*(9.05 to 21.2)*
≥2 to <6.3 mm	14.1	*(12.5 to 15.9)*	110	*(83.9 to 143)*	77	*(57.4 to 103)*						
≥6.3 mm	>42.5		>160		>160							

Microtox results for the two smallest ash fraction extracts (<0.125 and 0.125-0.5 mm, representing 40 and 80% of bottom and fly ash bulk mass respectively) confirm earlier findings of higher fly ash toxicity relative to bottom ash (Chapter 5) as confidence intervals do not overlap (Table 4). In contrast, extract from the bottom ash 0.5-2 mm PSF exhibited higher toxicity than the extract of the same fly ash PSF (the fractions both represent up to 20% of the bulk ash mass). High residual organic matter in fly ash, increasing with particle dimensions, may be a factor mitigating toxicity through adsorption here.

Test solution pH, around the calculated EC_{50}, is consistently between pH 8.75 and 9.25 (Appendix Table 1). McLay (1976) reported a pH driven reduction in *L. minor* growth of 20-30% at these conditions. The measured ash PSF toxicity is thus at least partially related to the alkaline conditions brought about by the test substance (Chapter 3).

Conclusion

Sieve fractionation and potential segregation of small size PSF is an option to reduce ash chemical burden. With bottom ash this may selectively reduce the loads of Pb, Cu, Zn and Sn. The general enrichment of elements in the finest fraction of fly ash in contrast prevents a selective mitigation of the material by sieving. Segregation of fly ash PSF by sieving does not impact on the mobile undesirable element based hazard classification of the material according to WAC but would strongly reduce liming potential (CaO%).

EC_{50} values derived from Microtox and *Lemna minor* assays may capture the concentration interval that ranges from incipient environmental effects to most sensitive, likely single celled species such as bacteria and algae (that may issue cascade effects along the food web), to terminal damage to an ecosystem where only few most resilient species are able survive. This study showed that fine ash particles are more toxic than larger particles. Bacterial communities may, after exposure to ash, be adversely affected by relatively small amounts of ash introduced into an ecosystem (1-5 g/L of very fine fly and bottom ashes respectively). In the case of bottom ash, these fine fractions also contain the highest levels of several plant nutrients (P, K, Mg, Ca), thus creating a

conundrum between exploiting wood ash fertilising potential and avoiding its toxic properties.

Acknowledgements

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Appendix

Appendix Table 1: *Lemna minor* EC_{50} (g ash equivalents per litre) with pH and ElC in surrounding test concentrations

Particle size fraction (PSF)	Ash	Frond number growth rate EC_{50}	pH in test concentrations below and above of EC_{50}	ElC [mS/cm] in test concentrations below and above of EC_{50}	Biomass growth rate EC_{50}	pH in test concentrations below and above of EC_{50}	ElC [mS/cm] in test concentrations below and above of EC_{50}
<0.125 mm	BA	15.6	8.84 - 9.23	2.49 - 3.50	5.2	<8.84	<2.49
<0.125 mm	FA	11.6	8.74 - 9.24	4.52 - 7.27	10.3	8.74 - 9.24	4.52 - 7.27
≥0.125 to <0.5 mm	BA	18	8.96 - 9.3	2.44 - 2.64	12.5	8.84 - 9.23	2.49 - 3.50
≥0.125 to <0.5 mm	FA	22.1	9.03 - 9.49	3.84 - 6.43	16.1	8.74 - 9.24	4.52 - 7.27
≥0.5 to <2 mm	BA	29.3	8.96 - 9.36	2.65 - 3.10	17.3	8.84 - 9.23	2.49 - 3.50
≥0.5 to <2 mm	FA	28.4	8.38 - 9.04	3.29 - 5.05	13.8	8.74 - 9.24	4.52 - 7.27
≥2 to <6.3 mm	BA	110	9.22 - 9.37	2.58 - 3.30	77	8.35 - 9.16	2.21 - 2.58
≥6.3 mm	BA	>160	>8.41	>2.32	>160	>8.41	>2.32

Chapter 7
Conclusions

Rationale and status quo

Wood energy contributes to the European target of 20% demand coverage by renewable energy sources (European Parliament, 2009) by 2020. Wood energy is potentially carbon neutral. This is based on the assumption that growing wood stock takes up and assimilates the amounts of carbon dioxide released during the combustion process. Additionally, wood energy presents an opportunity for sustainable power generation. That is because the combustion residues are mineral resources that could be applied to maintain or even increase wood (fuel) production volumes through fertilization. In turn, augmented wood biomass production would increase carbon sequestration. The main barrier to the development of fertilization approaches using wood ash, and after-use of the material in general, is its current classification as waste.

Waste handling (storage, transport and disposal) is expensive, entails risks of unintentional release or spillage and landfill capacity is limited. Wood energy producers are thus confronted with increasing cost of ash waste handling and, at the same time, the facts that wood energy is currently neither proven to be sustainable nor carbon neutral. Basic physico-chemical analysis of wood ashes (Murphy suite) enables landfilling of the composite waste as non-hazardous material on landfills, yet the limited extent of analysis does not allow evaluation of potential after-use (Chapter 2).

Composite wood ashes

The first significant outcome of this study is the compilation of an Irish wood energy waste summary for ash solid and leachate composition (Chapter 2), using wood ash data from ten boilers. This compilation incorporates the standard parameters required in chemical waste hazard characterization (WAC) and is expanded with details on further metal and nutrient elements in, and mobile from the composite ash. The summary provides the first geographically relevant reference values for wood ash in Ireland and thus enables producers to benchmark the waste ash from their facility in light of these national descriptive statistics. Further to this, local wood energy waste can now be assessed by stakeholders interested in the ash as secondary raw material.

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Nutrient and base cation content clearly demonstrate the resource character of the current waste and at least some Irish composite wood energy ashes show properties suggesting application and recycling in the environment with beneficial outcome is possible (Chapter 2). This conclusion is based on the average element contents of composite wood ash wastes in comparison to wood ash application and sludge and bio-solid application guidelines in other European countries and European regulation respectively (Chapter 2). However, considerable variation in elemental composition of the composite wood waste ashes suggests properties like the liming capacity, fertilizer suitability and chemical hazard to be very diverse. In fact, 42% of all leaching analysis data from the 10 boilers compiled for chapter 2 exhibit infringement of WAC limits for water mobile selenium. Strictly, these composite ashes cannot be considered a non-hazardous waste. In absence of end-of-waste leaching limits (Chapter 5), the compliance with non-hazardous waste leaching limit concentrations may act as the first quality criterion for ashes which are intended to be recycled.

Additionally, organic contaminant load of composite wood ashes in Ireland is insufficiently characterized to date. For example, a large number of existing analyses of polycyclic aromatic hydrocarbons (PAH) are not valid (Chapter 2) according to the basic surrogate recovery criterion (60-120%). Persistent organic pollutants like polychlorinated dibenzo p-dioxins and furans (PCDD/F) are not routinely analysed in Ireland and the analysis of a fly ash sample from the case study site revealed 70 ng/kg International Toxic Equivalents (ITEQ) of 2,3,7,8-tetrachlorodibenzo p-dioxin (Chapter 4). This is considerably in excess of the 3-7 ng/kg of ITEQ that was thought to be present in Irish wood energy ash based on existing data (Chapter 2). Finally, mineral oils (as Hydrocarbon Index, C10-C40) are present in all wood waste ashes in Ireland (Chapter 2). This heterogeneous substance class is rarely reported upon in compositional investigations published to date. Due to its lipophilic nature, other organic contaminants may be enriched in this oil phase while the oils may also pose a hazard themselves.

These gaps in the knowledge of composite waste ashes pose considerable uncertainty of the innocuousness of the material. While some ashes exhibit a suitable elemental composition to be used as soil treatment agent, empirical

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biological data on hazards to biota would have to be generated for the waste ashes to ensure no environmental risk is ensued by their use in the environment.

Wood bottom and fly ash

The second important outcome of this work is the summary of elemental composition for Irish bottom and fly ashes for the first time (Chapter 4). Compared with the variability of elemental content in composite waste ashes solids from ten Irish boilers (Chapter 2), both bottom and fly ash from five boilers display less variation in their chemical make-up (Chapter 4). Greater compositional consistency, and thus a more reliable assessment of hazards and beneficial properties such as liming capacity and fertilizer suitability can be expected if bottom and fly ash were separated. Thus prediction of solid ash elemental composition from the respective summaries is most reliable in the order of bottom ash > fly ash > composite ash. In fact, a lot of the overall variation in hazardous elements in the composite waste ashes seems to stem from the inclusion of fly ash (Chapter 4). Variability in elemental composition of leachates from bottom and fly ash (Chapter 4) is also less than in leachates from the composite waste. In general, composition of ash leachates is much more variable than the parent ash solids. Given the variability of ashes, data on the composition of a specific wood ash solids and leachates cannot be extrapolated from the compiled summary of wood ashes from Ireland (Chapters 2 and 4).

Case study

The combined heat and power (CHP) wood energy plant which is the subject of the case study, was installed in 2006 as a model plant and thus features more recent technology than most other biomass power plants of the same size in the country. The separate ashes from the case study site were investigated for their compositional consistency as solid materials as well as corresponding leachates over time (Chapter 4). Growth promotion potential (Chapter 3) as well as hazard potentials to aquatic life (Chapter 5) were described. Finally, composition of solids and leachates as well as hazard potentials to biota were investigated for different particle size classes present in the ashes (Chapter 6).

Composite waste leachate from the case study site displays almost as much variation as observed in the total Irish composite ash leachate summary (Chapter 4). Thus, although the leaching procedure is standardized, little compositional consistency can be expected for extracts of the composite waste. Any assumption of a general hazard potential from these data is thus very unreliable. The composite waste ashes are being disposed of on a landfill for non-hazardous wastes. However, applying WAC strictly, some of these ashes did not comply with the leaching standards for non-hazardous waste. Non-complying ashes need to be subjected to a MICROTOX screening tests. Whenever this was done, the sceening consistently returned values <2.2 TU. It has been shown (chapter 5) that standard aquatic testing protocols with the luminescent bacterium underestimate the actual inherent toxicity of waste the most (factor between EC_{50} of native and pH neutralized leachates) among the different test species used.

Ash solids from the case study site are also variable over time (Chapter 4), although not to the extent described for the composite waste (Chapter 2). In comparison, case study site ashes are actually better (less contaminated) than half of the ashes samples investigated for the Irish ash summary (Chapter 4). Leachates from bottom and fly ash from the case study site also vary over time and this variation thus limits the predictability of their hazard potentials and toxicity. The bottom ash leachates applied in biological effect assessments (Chapter 5) display lower or similar contaminations of WAC elements than the average values described for those samples collected over-time. In contrast, the concentrations of WAC hazardous elements in fly ash leachates used for testing with aquatic species were higher or similar than the average of fly ash leachates from the case study site over time. The results from ecotoxicological testing of these leachates thus are of limited predictive value for the ashes from the case study site in general. However, the toxicity and hazard assessment of bottom ash leachates may be assumed too conservative while relatively higher toxicity of fly ash bears a risk of still being overestimated.

Both bottom and fly ash from the case study site have been proven to act as a nutrient source for vascular plants (Chapter 3). The presence of ash solids in suspension modifies (improves) the growth response of *Lemna minor* compared to particulate matter free leachate. Only leachate from bottom ash provided the

basis for sustained growth over the test period (Chapter 3). Promotion of *L. minor* growth was observed in ash concentrations of up to 5 g/L (for solid suspensions) and 10 g aeq/L (for bottom ash leachates). Toxicity of bottom and fly ash to the vascular plant model (Chapter 3) and virtually all other aquatic species tested (non-target organisms of a potential application as fertilizer, Chapter 5) can be decreased by neutralization of the pH of the test solution. This emphasized the need for careful management of the pH if ash is applied in the natural environment but also raises doubt about the stand-alone suitability of standard hazard assessment (in pH neutral test solutions) for the estimation of ash hazards outside of controlled environments such as landfills. Only microalgae display similar sensitivity to native as well as pH neutralized fly ash leachates (Chapter 5). Based on toxicity assessments that conform to guidelines, the effects of ash on aquatic species may thus be underestimated.

The ecotoxicological assessment of bottom and fly ash leachates shows single cell organisms to be least tolerant to ash exposure among the species in the aquatic test battery. The trophic levels at the base of the food and energy chain could thus be affected more severely than higher trophic tiers that appear more resilient towards the exposure to ash extracts. Increasing plant nutrient concentrations in soils by ash addition could, in case of appropriate management, have a beneficial effect on higher plants. In contrast, ash addition can detrimentally affect non-target organisms, resulting (at least temporarily) in interruption of mineral and nutrient flow through the trophic stages.

The size fractionation of bottom and fly ashes from the case study site indicated that both hazardous trace elements as well as desirable nutrient elements are most concentrated in the fine particle size fractions of both materials. Mitigation of ash toxicity could thus be achieved by the exclusion of particles <0.125 mm, but desired nutrient element and base cation content would be reduced at the same time.

Recommendations

The weight of evidence against the application of fly ash in the environment for nutrient promotion is clear from this investigation. Alternative after-use options, such as practiced for fly ashes from fossil fuels (i.e. construction materials such as concrete) should be preferred for the material, even when derived from untreated wood fuels. Bottom ashes, in contrast, are less contaminated and less hazardous than fly ashes. The waste status of the bottom ash from untreated wood fuel should be revised, albeit not for wood bottom ash in general but on a case-by-case basis. By-product and end-of-waste (EoW) regulations within European and national law, are in place and allow such a change in classification for materials from a single source.

The availability of an ash waste compliance analysis record and facilities for the separate collection and holding of the ash types should be prerequisites for partaking in a recycling programme. Subsidies for chemical analyses further to waste compliance requirements are conceivable to overcome remaining gaps of knowledge regarding organic contamination and chemical consistency over time. A further option is the admixture of solely bottom or solely fly ashes from several known and monitored sources to generate a more homogenous material for application in the field or non-fertilization purposes respectively.

Domestic wood furnaces and their ashes were not subject to this investigation. However, the stark differences between wood bottom and fly ashes observed for medium to large scale industrial boilers could be present in ashes from small household heating installations. Thus, some general recommendations may be transposed. Soot and residues from the cleaning of chimneys resemble fly ashes and are thus of relatively higher concern than ashes taken out of the firing chamber. Traditional application on private vegetable crops should thus rigorously exclude such fly ash like materials. Generally, ash application on soil should be handled as a discrete fertilization event (e.g. once a year during the vegetation period) and not as opportunity to dispose of ashes whenever and in whatever quantities they occur.

Flue gas cleaning further to passive cooling and deposition in chimneys is not practiced with most domestic wood burning appliances. The extent of particulate atmospheric matter pollution contributed by the immense number of domestic heating appliances, irrespective of the fuel type, is highly debated. Air pollution was not a subject of this study, but is connected to the issue of ash. It is known that the burning of solid fuels, such as wood, coal or peat produces more particulate matter than liquid or gaseous energy carriers. These particulate residues occur in a large range of particle sizes, supposedly from nano-scale (fine dusts) to macroscopic ashes. The use of wood, or solid fuels in general, for domestic heating should thus be discouraged in densely populated, urban or other areas that are already prone to respirable dust pollution. Instead, centralized installations such as district heating plants may offer the potential to harness energy from wood for cities while allowing for improved air particulate matter pollution control and monitoring of the solid ash resource that remains a waste material to date.

In regard of further research enabling ash use as a fertilizer, it is suggested to conduct studies to the end of hazard identification with terrestrial species. Large soil biomass proportion posing species groups such as invertebrates and bacteria should have priority. The investigation of ash layered on soil is recommended to more accurately determine the hazards for the aquatic environment following leaching in a real life situation.