

Comparison of standard methods for evaluating the metal concentrations in bio ash

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Abstract

The current growth strategy and environmental legislation of the European Union both aim to increase the amount of renewable energy and to improve the use of waste streams. These policies mean there will be an increasing need to utilise bio ash. Currently Finland and Denmark are the only European countries with specific national legislation concerning bio ash use. Sweden has recommendations concerning the use of bio ash fertilisers. Besides having different limit values for harmful elements and nutrients in ash fertilisers, all these countries have different digestion methods that are allowed for element content determinations. This study compared the results of the five digestion methods (aqua regia, nitric acid, nitric/hydrochloric acids, nitric/hydrochloric/hydrogen fluoride acids, and lithium tetraborate fusion) established by Nordic authorities. Two Finnish peat-wood fly ash samples were studied. Our results indicate that the choice of digestion methods produces a significant difference in the obtained heavy metal or nutrient concentration of bio ash, especially regarding the potassium concentration.

Keywords: bio ash, digestion method, environmental legislation, heavy metals, fertilisers, earth construction, metal concentration

1. Introduction

The European Union (EU) growth strategy for this decade is called Europe 2020. One main priority of this strategy is sustainable growth, which means that the EU should create a more competitive low-carbon economy, protect the environment, and develop new green technologies. The key targets for sustainable growth include a 20% reduction in greenhouse gas (GHG) emissions and 20% increases in the use of renewable-energy sources and in energy efficiency by 2020 (European Commission, 2015).

In addition, the EU's Waste Framework Directive (2008/98/EC) introduced a hierarchy (consisting of five levels) that describes the options for dealing with waste. The first goal of the hierarchy is the prevention of waste streams. If this is not possible, the next step in the hierarchy is reuse, followed by recycling, and other recovery techniques (e.g., energy recovery). Waste disposal is the last option, and applies only if none of the previous steps prove feasible (European Commission, 2008).

Sustainable growth during this decade, according to Europe 2020, will increase the amount of bio ash from biomass combustion all across the EU. The recent changes to the EU waste legislation mean an increased need to use that bio ash. In the forest-rich Nordic countries, such as Finland and Sweden, biomass combustion is already responsible for a considerable amount of the total energy production (European Commission, 2015). In Finland, over 500 000 tons of fly ash from wood and peat combustion and in Sweden over

100 000 tons of fly ash from wood combustion is produced annually (Pohjala, 2015; Statistics Sweden, 2013). Approximately 200 000 tons of the Finnish wood and peat ashes are utilized in earth construction and over 50 000 tons in fertilizers (Pohjala, 2015). In total, approximately 90 million tons of waste is produced in Finland annually and 160 million tons in Sweden (Eurostat, 2016). Current options for using bio ash include fertilisers, earth construction and soil stabilisation (van Ejjik et al., 2012).

Among these options, fertiliser use is the most natural choice. Wood ash, in particular, contains all the nutrients plants need in almost the correct proportions, excluding nitrogen, which is released into the atmosphere during combustion (Karlton et al., 2008; Vesterinen, 2003). The nutrients removed from the forest soil as a result of logging and removal of forest residues can be restored in the form of ash. Earth construction (e.g., in the base of roads or parking areas) is another option that requires large quantities of bio ash, especially in the form of ash granules.

The increasing need to utilise bio ashes means also that there is a need for legislation concerning how it is used. No EU-wide legislation exists that regulates the allowable content of the different harmful elements in the ash. Instead, there are national laws and decrees that differ from country to country. For example, in the Netherlands, it is forbidden to use biomass ash as a forest fertiliser; in Austria, the addition of 2 wt.% of bio ash is allowed in compost materials (van Ejjik et al., 2012). In Slovakia, wood ash use is allowed only for scientific purposes (Otepka and Habán, 2013). In Finland and

Denmark, the use of bio ash as a fertiliser is regulated by national legislation (Finnish Ministry of Agriculture and Forestry, 2011; Danish Ministry of the Environment, 2008a). Finland also has a decree concerning the use of ash in earth construction (Finnish Ministry of the Environment, 2006). The Finnish and Danish decrees set limits on the maximum amount of various harmful elements allowed in the ash and regulate the digestion methods used to determine the element contents. In Sweden, there is no ash-fertiliser legislation, but the Swedish Forest Agency makes recommendations on the minimum and maximum amounts of the various nutrients and harmful elements allowed in ash fertilisers (Swedish Forest Agency, 2008). Besides having different limit values for harmful elements and nutrients in ash fertilisers, all these countries have different digestion methods that are allowed for element content determinations.

The EU must standardise the legislation concerning ash utilisation, as well the chemical digestion methods used for determining the elemental concentrations in the ash in order to increase the utilisation of bio ash. The aim of this study was to compare how much the results obtained using different chemical digestion methods recommended and regulated by the Nordic authorities differ from each other.

2. Materials and Methods

2.1 Fly ash samples

Two fly ash samples (FA1 and FA2) were obtained from two Finnish power plants. Both power plants use a circulating fluidized-bed (CFB) combustion technique. In power plant 1 approximately 50 000 tons of fly ash is produced annually in power plant 1 and 15 000 tons in power plant 2. The fuel ratio at the power plant 1 was approximately 61% peat and 39% wood (FA1). The fuel ratio at power plant 2 was approximately 67% peat, 25% wood, and 8% other fuels (process gas, coal, and oil) (FA2). All samples from both power plants were taken directly from the ash silos situated below the electrostatic precipitators.

2.2 Instrumentation

The water used in the preparation of the reagent solutions was obtained by purifying tap water with a TKA-Pacific reverse osmosis and TKA-GenPure ion-exchange (Thermo Scientific, Niederelbert Germany) water purification system until the resistivity of the water was $18 \text{ M}\Omega \text{ cm}^{-1}$. Acid-washed glass and plastic ware were used throughout this work.

Thermal heating in the normal-pressure *aqua regia* digestion method, based on ISO 11466 (1995) (method 1 in Table 1), was carried out with a Velp Scientifica Eco 6 thermoreactor (Velp Scientifica, Italy). All microwave-assisted acid digestions (methods 2–4) were performed with a CEM Mars microwave oven and CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA). The muffle furnace used in the fusion (method 5) was a Nabertherm B-170 (Nabertherm, Lilienthal/Brehmen, Germany). Element concentrations were determined with a Thermo Fisher Scientific iCAP6500 Duo (Thermo Scientific Corp., Franklin, USA) inductively-coupled plasma optical-emission spectrometer (ICP-OES) equipped with a Cetac ASX-520 HS autosampler (Cetac Technologies, Nebraska, USA).

2.3 Reagents and standards

All analyses were done at a Finnish Accreditation Service (FINAS)-accredited environmental laboratory, following the commonly-used standard methods listed and explained in Table 1. Digestion method 1 is a traditional hotplate acid-digestion method; methods 2–4 are microwave-assisted acid digestions, and method 5 is a fusion method. Digestion methods 1–3 are partial-digestion methods, whereas methods 4 and 5 are total-digestion methods.

Calibration standards for ICP-OES determinations were made by serial dilution of the following Accustandard (AccuStandard Corp., AccuTrace®, New Haven, U.S.A.) multi-element stock solutions: (i) Custom ICP Standard 1 (IS-15239A-R1), containing 1000 mg L⁻¹ of Al, Fe, K, P, and Ca; 500 mg L⁻¹ of S, Mg, Na, and Ti, and (ii) Custom ICP Standard 2 (IS-15239B), containing 400 mg L⁻¹ of Ba, Mn, Zn, Pb; 200 mg L⁻¹ of Cr, Cu, Ni, and V; 100 mg L⁻¹ of As, Cd, Co, and Sb; 50 mg L⁻¹ of B, Be, Se, Mo, and Sn. Second-source quality-control standards were made of similar custom-calibration mixes manufactured by SPEX CertiPrep Corp. (SPEX CertiPrep Corp. Metuchen, NJ, U.S.A.). To obtain careful matrix matching of the calibration standards and samples, all calibration solutions were made with the same reagents used in preparing the samples. For quality-control purposes all analyses from real samples and method blanks were carried out as triplicate determinations. The method quantification limits for methods 1– 5 are shown in Table 2. One-way ANOVA analysis of the results assessed whether the results differed statistically. The critical level was set to $p < 0.05$.

Table 1. Digestion methods used in this study.

Digestion method no.	Description	Reagents	Sample [g]
1	ISO 11466 (2007) Soil quality – Extraction of trace elements in aqua regia.	21 ml HCl 7 ml HNO ₃	3.0
2	EPA Method 3051A (2007): Microwave assisted acid digestion of sediments, sludges, soils and oils.	10 ml HNO ₃	0.5
3	EPA Method 3051A (2007): Microwave assisted acid digestion of sediments, sludges, soils and oils.	9 ml HNO ₃ 3 ml HCl	0.5
4	SFS-EN 13656 (2003) Characterization of waste. Microwave assisted digestion with hydrofluoric (HF), nitric (HNO ₃) and hydrochloric (HCl) acid mixture for subsequent determination of elements.	6 ml HCl 2 ml HNO ₃ 1 ml HF	0.5
5	Fusion method with lithium tetraborate (Li ₂ B ₄ O ₇): ASTM C 1301 – 95 (2009), Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption. CEN ENV 955-4 (1997), Chemical Analysis of Refractory Products – part 4: Products Containing Silica and/or Alumina (Analysis by Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Atomic Emission Spectrography (ICP)).	1 g + 0.5 g Li ₂ B ₄ O + a few drops of HBr Dissolution of the fused residue with diluted HNO ₃ (12.5 ml concentrated HNO ₃ + 40 ml H ₂ O)	0.25

Table 2. Method quantification limits (10s values are given).

	As	Ba	Ca	Cd	Cr	Cu	K	Mo	Ni	P	Pb	V	Zn
Methods 1 – 4													
Quantification limit [mg kg⁻¹ dry weight]	3	1	50	0,3	2	2	200	1	1	20	3	2	3

3. Results and discussion

3.1 Comparison of the digestion methods set by the Finnish, Danish, and Swedish authorities for fertiliser use

According to the Finnish fertiliser product decree (Finnish Ministry of Agriculture and Forestry, 2011), the allowed pre-treatment methods for determining the concentration of harmful elements are HNO₃ extraction (method 2) for inorganic fertilizers (including fly ash) and HNO₃-HCl extraction for organic fertilizers (method 3). The decree places no limits on the digestion methods used for determining the concentrations of nutrients, other than that the analysis method must suit the type of fertiliser studied. According to the national fertiliser product-type name list (Evira, 2011), the digestion methods used for pre-treatment of samples for the concentration studies include EPA Method 3051A (2007) (methods 2 and 3) and CEN/TS 15290 (2006) or CEN/TS 15410 (2006). Both are total-digestion methods similar to method 4. In Danish legislation (Danish Ministry of the Environment, 2008a; Danish Ministry of the Environment 2008b), standard DS259 (2002) provides for heavy metal determinations using nitric-acid extraction. This method is comparable to a method used in Finland (EPA 3051A, 2007). The recommendations of the Swedish National Board of Forestry (Swedish Forest Agency, 2008) call for using an accredited laboratory to determine the total content of heavy metals and nutrients, but the

digestion method is not defined. In practise, the total content determination is always made either by a mixture of three acids (HNO₃, HCl and HF; method 4) or by a fusion method (method 5).

3.1.1 Harmful elements

The total heavy metal (Cd, Cu, Ni, Pb, Zn) concentrations of FA1 determined by method 4 were quite low—clearly lower than the limits set by the Finnish, Danish, and Swedish authorities (Table 3). Total concentration of arsenic (35 mg kg⁻¹) exceeded the Swedish limit value (30 mg kg⁻¹). Based on the nitric-acid extraction (method 2), the arsenic concentration (34.4 mg kg⁻¹) exceeded the Finnish limit for field fertilisers (25 mg kg⁻¹), but was below the Finnish limit for forest fertilisers (40 mg kg⁻¹). The total content of chrome (148 mg kg⁻¹) exceeded the Swedish limit (100 mg kg⁻¹). Chrome content exceeded also the Danish limit (100 mg kg⁻¹) with nitric acid extraction (116 mg kg⁻¹; method 2).

In Finland, only digestion method 2 is allowed for ash fertilisers; method 3 is intended for organic fertilisers. In the case of FA1, the stronger digestion conditions of method 3 gave 3–4% higher results for copper and nickel than obtained by method 2. For chrome and zinc, method 3 gave 11–17 % higher results than method 2. There was no significant statistical difference between the two methods for lead.

In addition, statistically there were no significant differences among methods 2, 3, and 4 for arsenic and cadmium. Digestion method 2 gave over 85% recovery of the total concentration of nickel (87.9 %) and zinc (85.7 %) for FA1. The recovery for copper (81.3%), lead (80.8%), and chrome (78.4%) were slightly lower.

EPA 3051A (2007) (methods 2 and 3) is intended to digest the samples almost completely, except for the elements that are tightly bound to fractions, such as silicate or alumina, making them non-mobile. According to Lind et al. (1999), copper and lead can react with SiO_2 during combustion in CFB. Pöykiö et al. (2005) studied the bioavailability of heavy metals from CFB combustion fly ash using a sequential-extraction procedure. The bioavailabilities of chrome, lead, nickel, zinc, and copper were low in FA1, suggesting that these metals were associated with silicates. Our results show that overall recoveries with method 2 were quite good. Only a small portion of nickel, zinc, copper, lead, and chrome were more tightly bound to silicate fractions in FA1.

Table 3. Heavy metal concentrations in FA1 based on three digestion methods, and a comparison with Finnish, Danish, and Swedish limits and recommendations (Finnish Ministry of Agriculture and Forestry, 2011; Danish Ministry of the Environment, 2008a; Swedish Forest Agency, 2008).

Metal	Finland ^{a,b}	Denmark ^a	Sweden ^a	Digestion method 2 ^a	Recovery % ^e	Digestion method 3 ^a	Recovery % ^e	Digestion method 4 ^a
As	25/40		30	33.2 (± 1.4)	94.9	34.4 (± 0.6)	98.3	35.0 (± 0.4)
Cd	2.5/25	5/20 ^c	30	2.2 (± 0.03)	100.0	2.2 (± 0.1)	100.0	2.2 (± 0.1)
Cr	300	100	100	116 (± 3)	78.4	136 (± 2)	91.9	148 (± 3)
Cu	600/700		400	104 (± 1)	81.3	108 (± 1)	84.4	128 (± 2)
Ni	100/150	60	70	51.4 (± 0.2)	87.9	53.5 (± 0.4)	91.5	58.5 (± 1.6)
Pb	100/150	120/250 ^d	300	42.9 (± 1.0)	80.8	44.2 (± 1.2)	83.2	53.1 (± 0.7)
Zn	1500/4500		7000	269 (± 6)	85.7	299 (± 4)	95.2	314 (± 7)

^aMean result (± standard deviation) [mg kg⁻¹] dry weight.

^bField fertilisers/Forest fertilisers.

^cStraw ash/Wood ash.

^dStraw ash or straw + wood ash/Wood ash used in forestry.

^eRecovery % = [measured value]/[measured value with digestion method 4] x 100.

3.1.2 Nutrients Ca, K, P

The recovery of calcium ranged from 83.4% (method 2) to 87.3% (method 3), and for phosphorus, from 91.3% (method 2) to 97.4% (method 3) in FA1 (Table 4). Method 3 gave approximately 5–7 % higher results than method 2 for calcium and phosphorus. The

results determined with the total-digestion methods (4 and 5) showed no statistical differences.

The largest differences were with potassium. For FA1, method 3 gave slightly over 20% higher results than method 2. Compared to the total concentration (method 4), only 34.6% (method 2) to 42.1% (method 3) of the potassium was obtained with methods 2 and 3. An even larger difference for potassium was found with FA2 (Table 4). Method 3 (30.3%) gave over 30% higher results than method 2 and the recovery percentage for method 2 was only 22.7%. We studied the concentrations of another alkali metal, sodium, which behaved like potassium in both FA1 and FA2.

According to Valmari (2000), potassium is present in the fly ash originating from CFB combustion of wood as sulphides, chlorides, and silicates. Increasing the amount of silicon in the fuel increases the extent of alkali-silicate formation, which decreases the concentrations of alkali sulphates and chlorides. High potassium-silicate content could explain the low potassium concentrations found with methods 2 and 3, since silicate dissolution requires very strong conditions. Furthermore, in our study, the fuel in both power plants was mainly peat (61–67%), which contains significantly more silicon than wood fuels (Raiko et al., 2002).

The sum of phosphorus and potassium concentrations was 1.49% (method 2) and 1.69% (method 3) for FA1. Both are below the minimum requirements (2%) of the Finnish fertiliser product decree. Method 4 showed the sample met the requirements, with

a sum of phosphorus and potassium of 2.77%. The calcium concentration determined by method 2 (5.78%) was slightly below the minimum requirement (6%) set by the decree, whereas measurement with method 3 (6.06%), it just met the minimum requirements. All of these methods (2–4) are, in principle, allowed by Finnish legislation and environmental administration. This means that choosing the wrong digestion method could, in some cases, prevent the use of ash as a fertiliser, or add significant extra costs, for instance, requiring the addition of potassium to meet the minimum requirements of the fertiliser product decree. In practice, these results demonstrate that total digestion, as in method 4, is the preferred method when the nutrient contents of bio ash fertilizers are analysed in order to maximize the utilisation potential of ash.

Comparing the results to the Swedish recommendations, the phosphorus content (0.86–0.95%) exceeds the limit (0.7 %) when using all methods. The calcium (5.80–7.10 %) and potassium (FA1: 0.63–1.83%; FA2: 0.29–1.28%) content are, however, clearly below the limits, even for the total-digestion methods (4 and 5). This is because the Swedish recommendations are intended for ash originating from forest fuels, whereas Finland also allows peat fuels (Finnish Ministry of Agriculture and Forestry, 2011; Swedish Forest Agency, 2008). The Swedish limits for nutrients are much higher than the Finnish limits.

Table 4. Concentrations of nutrients in FA1 and FA2 resulting from four digestion methods, and a comparison with the Finnish and Swedish limits and recommendations (Finnish Ministry of Agriculture and Forestry, 2011; Swedish Forest Agency, 2008).

Sample	Element	Finland	Sweden	Digestion method 2 ^b	Recovery % ^c	Digestion method 3 ^b	Recovery % ^c	Digestion method 4 ^b	Digestion method 5 ^b	Recovery % ^c
FA1										
	Ca	10/6 ^a %	12.5 %	57810 (± 541)	83.4	60593 (± 629)	87.4	69290 (± 705)	70903 (± 441)	102.3
	K	K + P 2 %	3.0	6305 (± 191)	34.6	7677 (± 180)	42.1	18227 (± 363)	18363 (± 218)	100.7
	P			0.7	8607 (± 130)	91.3	9188 (± 51)	97.4	9429 (± 160)	9456 (± 73)
FA2										
	K			2893 (± 133)	22.7	3874 (± 37)	30.3	12767 (± 445)	12500 (± 95)	97.9

^aField fertilisers/Forest fertilisers.

^b[Mean result ± standard deviation [mg kg⁻¹] dry weight.

^cRecovery % = [measured value]/[measured value with digestion method 4] x 100.

3.2 Comparison of the digestion methods set by the Finnish authorities for earth construction use

To the best of our knowledge, Finland is the only European country with legislation concerning the use of coal, peat, and wood-fly ash in earth construction (Finnish Ministry of the Environment, 2006). This decree also addresses crushed concrete waste. These wastes can be used without an environmental permit if they fulfil the criteria set by the decree, which include the concentration and solubility determinations of harmful elements and compounds. The digestion methods allowed in the decree are acid digestion,

according standard SFS-EN 13656 (2003) (method 4), and *aqua regia* digestion, according standard SFS-EN 13657 (2003) (comparable to method 1). Here, we compare the differences in the results for FA1 obtained using methods 1 and 4 (Table 5).

All results for FA1 obtained with methods 1 and 4 were clearly below the limits of the Finnish Earth Construction Decree (Finnish Ministry of the Environment, 2006). Digestion method 1 gave over 90% recoveries of the total concentrations of arsenic (96.0%), zinc (93.3%), and vanadium (91.9%), and almost 90 % recovery of the total copper (89.1%) and chrome (88.5 %) concentrations. The recovery of cadmium (86.4%) and molybdenum (81.5%) were also quite good, but the total concentrations of both elements were low (Cd 1.9 mg kg⁻¹; Mo 6.6 mg kg⁻¹). For lead (60.8%) and barium (45.6%), method 1 gave significantly smaller recoveries than method 4. The recovery of lead with method 1 was also clearly lower than that obtained with methods 2 and 3, which could indicate some matrix interference with this specific sample and the digestion method. Method 1 was the only conventional hotplate digestion method used in this study; the other methods (2–4) were microwave-assisted digestion. Our results indicate that the results determined with these two methods can differ significantly. This result means that choosing the wrong digestion method can affect the possibility of using the ash in earth construction. Since the Finnish authorities accept both these methods, method 1 should be used for the digestion in order to minimize the heavy metal content analysis results and therefore maximize the utilisation potential in earthworks. However, it should be

noted that the final decision is made based on leaching tests instead of these content analyses. If the heavy metal contents exceed the limit values of the decree, but the results of the leaching tests are below their corresponding limits, then utilisation in earthworks is still possible (without an environmental permit), although in the opposite situation such a use is not possible.

Table 5. The Finnish earth construction decree limits and heavy metal concentrations in FA1 yielded by the two digestion methods (Finnish Ministry of the Environment, 2006).

Metal	Limit value^a	Digestion method 1^a	Recovery %^b	Digestion method 4^a
As	50	33.6 (± 0.4)	96.0	35.0 (± 0.4)
Ba	3000	627 (± 10)	45.6	1375 (± 28)
Cd	15	1.9 (± 0.02)	86.4	2.2 (± 0.1)
Cr	400	131(± 3)	88.5	148 (± 3)
Cu	400	114 (± 3)	89.1	128 (± 2)
Mo	50	6.6 (± 0.06)	81.5	8.1 (± 0.3)
Pb	300	32.3 (± 0.2)	60.8	53.1 (± 0.7)
V	400	272 (± 5)	91.9	296 (± 3)
Zn	2000	293 (± 5)	93.3	314 (± 7)

^aMean result ± standard deviation [mg kg⁻¹] dry weight.

^bRecovery % = [measured value]/[measured value with digestion method 4] x 100.

4. Conclusions

Recent changes in EU environmental legislation and environmental policies have increased the need to utilise bio ashes, however, to date, there is no EU-wide legislation

concerning their use, only national laws and decrees that differ significantly from country to country. The EU must standardise the legislation concerning ash utilisation, as well the chemical digestion methods used for determining the elemental concentrations in the ash in order to increase the utilisation of bio ash.

Our results indicate that different digestion methods can result in significant differences in the obtained heavy metal or nutrient concentrations. Choosing the wrong digestion method could, in some cases, complicate, or even prevent the use of bio ash. The results for potassium content showed a particularly large variation and choosing the wrong digestion method could cause significant extra costs if potassium has to be added to the ash to meet the legislative requirements for the minimum nutrient content in fertilisers.

Planning legislation concerning ash utilisation requires attention to both concentration limits and the preferred digestion methods. Additional research is needed over a broader sampling of bio ash types to determine the optimum digestion methods. Long-term field studies using bio ash as fertiliser should be conducted to assess how the concentration of potassium decreases with time in nature and its true bioavailability in different environments.

References

- American Society for Testing and Materials (2009) ASTM C 1301 – 95: *Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption*. Pennsylvania, ASTM.
- Danish Ministry of the Environment. (2008a) *Lovtidende A. Nr. 818. Bekendtgørelse om anvendelse af bioaske til jordbrugsformål (Bioaskebekendtgørelsen) (Order on the use of bio ash for agricultural purposes (Bio ash order))*. Miljøministeriet, Copenhagen.
- Danish Ministry of the Environment. (2008b) *Miljøstyrelsens metodeblad nr. 1 Bekendtgørelse om anvendelse af aske fra forgasning og forbrænding af biomasse og biomasseaffald til jordbrugsformål (Environmental Protection Agency method no. 1. Order on the use of ash from gasification and combustion of biomass and biomass waste for agricultural purposes)*. Miljøministeriet, Copenhagen.
- European Commission. (2008) ‘Directive 2008/98/EC of the European parliament and of the council of 19 November 2008 on waste and repealing certain directives’, *Official Journal of the European Union*, Vol. 51, No. 1, pp.3-30.
- European Commission. (2015) Europe 2020 [online]. [http://ec.europa.eu/europe2020/index_en .htm](http://ec.europa.eu/europe2020/index_en.htm). (Accessed 1 November 2015).
- European Committee for Standardization (1997) CEN ENV 955-4: *Chemical Analysis of Refractory Products – part 4: Products Containing Silica and/or Alumina (Analysis*

- by Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Atomic Emission Spectrography (ICP)*). Brussels, CEN.
- European Committee for Standardization (2006) CEN/TS 15290: *Solid biofuels. Determination of major elements. Al, Ca, Fe, Mg, P, K, Si, Na and Ti*. Brussels, CEN.
- European Committee for Standardization (2002) DS 259: *Determination of metals in water, sludge and sediments—General guidelines for determination by atomic absorption spectrophotometry in flame*. Brussels, CEN.
- Eurostat (2016) *Generation of waste by waste category, hazardousness and NACE Rev. 2 activity* [online]. http://ec.europa.eu/eurostat/web/products-datasets/-/env_wasgen. (Accessed 11 October 2016).
- Evira. (2011) Kansallinen lannoitevalmisteluettelo (National fertilizer product type name list). Finnish Food Service Authority Evira, Helsinki.
- Finnish Ministry of Agriculture and Forestry. (2011) *Ministry of Agriculture and Forestry Decree on fertilizer products 24/2011*. Maa- ja metsätalousministeriö, Helsinki.
- Finnish Ministry of the Environment. (2006) *Government decree on utilization of certain waste materials in earth construction 202/2006*. Ympäristöministeriö, Helsinki.
- Finnish Standards Institute (2003) SFS-EN 13656: *Characterization of waste. Microwave assisted digestion with hydrofluoric (HF), nitric (HNO₃) and hydrochloric (HCl) acid mixture for subsequent determination of elements*. Helsinki, SFS.

- Finnish Standards Institute (2003) SFS-EN 13657: *Characterization of waste. Digestion for subsequent determination of aqua regia soluble portion of elements*. Helsinki, SFS.
- Finnish Standards Institute (2006) SFS-EN 15410: *Solid recovered fuels. Methods for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)*. Helsinki, SFS.
- International Organization for Standardization (2007) ISO 11466: *Soil quality—Extraction of trace elements in aqua regia*. Geneva, ISO.
- Karlton, E., Saarsalmi, A., Ingerslev, M., Mandre, M., Andersson, S., Gaitnieks, T., Ozolinčius, R. and Varnagiryte-Kabasinskiene, I. (2008) ‘Wood ash recycling – possibilities and risks’, In Röser et al. (Eds.), *Sustainable use of forest biomass for energy - a synthesis with focus on the baltic and nordic region, Managing Forest Ecosystems*, Vol. 12, pp.79-108.
- Lind, T., Valmari, T., Kauppinen, E., Sfiris, G., Nilsson, K. and Maenhaut, W. (1999) ‘Volatilization of the heavy metals during circulating fluidized bed combustion of forest residue’, *Environmental Science and Technology*, Vol. 33, No. 3, pp.496-502.
- Otepka, P. and Habán, M. (2013) ‘Wood ash fertilization of energy plant basket willow (*Salix viminalis* L.)’, *Acta Regionalia et Environmentalica*, Vol. 10, No. 2, pp.46-50.
- Pohjala, M. (2015) *Tuhkien tilastokysely 2014*, Helsinki, Energiateollisuus.

- Pöykiö, R., Nurmesniemi, H., Perämäki, P. and Kuokkanen, T. (2005) 'Leachability of metals in fly ash from a pulp and paper mill complex and environmental risk characterisation for eco-efficient utilization of the fly ash as a fertilizer', *Chemical Speciation and Bioavailability*, Vol. 17, No. 1, pp.1-9.
- Raiko, R., Saastamoinen, J., Hupa, M. and Kurki-Suonio, I. (2002) *Poltto ja palaminen (Incineration and combustion)*, Gummerrus Kirjapaino Oy, Jyväskylä.
- Statistics Sweden (2013) *Askor I Sverige 2012. Statistik utförd av SCB på uppdrag av EnergiAskor*, Stockholm, Svenska EnergiAskor.
- Swedish Forest Agency (2008) *Rekommendationer vid uttag av avverkningsrester och askåterföring (Recommendations for harvesting residues and wood ash recycling)*. Skogsstyrelsens förlag, Jonköping.
- United States Environmental Protection Agency (2007) EPA Method 3051A: *Microwave assisted acid digestion of sediments, sludges, soils and oils*. Washington, USEPA.
- Valmari, T. (2000) *Potassium behaviour during combustion of wood in circulating fluidised bed power plants*, Technical Research Center of Finland, VTT Publications 414.
- van Eijk, R., Obernberger, I. and Supancic, K. (2012) *IEA Bioenergy Task 32. Options for increased utilization of ash from biomass combustion and co-firing*, Kema Nederland, 30102040-PGR/R&E 11-2142.

Vesterinen, P. (2003) *Wood ash recycling—State of the art in Finland and Sweden*,
Technical Research Center of Finland, PRO2/6107/03.