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Hanne Soininen

**IMPROVING THE ENVIRONMENTAL SAFETY OF  
ASH FROM BIOENERGY PRODUCTION PLANTS**

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## **IMPROVING THE ENVIRONMENTAL SAFETY OF ASH FROM BIOENERGY PRODUCTION PLANTS**

Dissertation for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium in MUC, Mikkeli University Consortium, Mikkeli, Finland on the 14<sup>th</sup> of December, 2018, at noon.

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## **Abstract**

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Each year, energy production plants in Eastern Finland produce just under 100,000 tonnes of different types of ash and slag in the process of energy production. The utilisation of energy production ash flows has made progress in a variety of ways, but it is still difficult to find the right utilisation applications for some of these fractions due to, among other things, the hazardous substances they contain. According to the most recent Finnish government programme, Finland will be a leader in the bio- and circular economy as well as cleantech. The side-streams produced by energy production plants and the trace elements contained in them should indeed be returned to forests as fertiliser, whilst taking environmental safety into consideration.

This thesis investigated ash fractions formed in Eastern Finland energy production and the ash processing technologies designed for the purpose of promoting their utilisation. The methods used in the thesis research include ash fractionation and ageing. Furthermore, assessed the volume, types and properties (e.g. the total and soluble concentrations of various hazardous substances) of various ash and compared them with statutory requirements.

Based on the analysis results of solubility tests, approximately half of the bottom and fly ash produced by energy production plants would be suitable for disposal in non-hazardous waste landfills and a third would require disposal in hazardous waste landfills when comparing the results with the limit values specified in Government Decree 331/2013. A portion of the ash (15%) could not be disposed of in hazardous waste landfills without pre-processing. In comparing the solubility of ash with the limit values set for earth construction, a total of 47.5% of the analysed bottom and fly ash met the standards laid out in the Government Decree on the Recovery of Certain Wastes in Earth Construction (843/2017). The remaining 52.5% of ash failed to meet the current limit values, instead requiring pre-processing by some means prior to being utilised. The analysis of heavy metals revealed that approximately 84% of the bottom and fly ash produced by energy production plants would be suitable for use as fertiliser. 15% of the bottom and fly ash would require processing before being utilised as fertiliser.

The As, Cd, Pb and Zn concentrations found in ash produced in Eastern Finland hampers their utilisation in forests and for other purposes. Fractionation tests conducted with an electrostatic precipitator reduced the As, Cd and Zn concentrations of fly ash.

Fractionation reduced Cd and Zn concentrations to a point where the fly ash could be used as fertiliser (forest use). However, universally applicable values cannot be defined for the electrostatic precipitator parameters used in fractionation. According to the research results obtained, ageing cannot alone be considered a reliable processing method for the reduction of heavy metal concentrations and solubility properties of fly ash. In the case of certain, individual hazardous substances, ageing can, however, be used to achieve an adequate reduction in concentration. In such cases, ageing would still require some sort of enhancement.

During research, a soil improver made up of compost and fractionated, processed fly ash was granulated using a layering method. The granulation of materials improved their process ability and reduced the spread of dust. The ash mixture had a positive impact on compost quality where fertility nutrients were concerned. However, the ash mixture increased the heavy metal concentrations of the granules, despite the second fraction processing. The productising of ash by means of granulation is used as a method in, for example, forest fertilisers.

Amendments to legislation concerning the utilisation of ash and national requirements in the circular economy will increase the need for ash post-processing. The trace elements and other nutrients found in fly ash would be a positive addition to the circular economy. In the future, the processing of various types of ash should be further researched and post-processing should be developed in order to meet the requirements and limit values (earth construction and fertiliser use) for the utilisation of bottom and fly ash produced by all energy production plants run on wood-based fuels.

Keywords: ash, heavy metals, ageing, fractionation, utilisation

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Hanne Soininen (née Orava)  
November 2018  
Juva, Finland



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## List of publications

This thesis is based on the following papers. The rights have been granted by publishers to include the papers in dissertation.

- I. Soininen, H., Mäkelä, L., and Valkeapää, A. (2010). Utilisation of Biofuel Consuming Energy Plants' Ash Material Flows in Eastern Finland. Conference article. In: *Proceedings of a Conference the 18th European Biomass Conference and Exhibition*, pp. 190-194. Lyon, France.
- II. Soininen, H., Kontinen, K., and Luste, S. (2012). Quality and Characteristics of Ash Material from Energy Plants in Eastern Finland. Conference article. In: *Proceedings of a Conference 20th European Biomass Conference and Exhibition*, pp. 1963-1967. Milan, Italy.
- III. Orava, H., Nordman, T., and Kuopanportti, H. (2006). Increase the utilisation of fly ash with electrostatic precipitation. *Journal of Minerals Engineering* 19(15), pp. 1596-1602.
- IV. Soininen, H., Manskinen, K., and Ranta, T. (2018). Closing the material cycle of biomass derived fly ashes: a regional case study of natural ageing in Finland. *Journal of Material Cycles and Waste Management*, 20(3), pp. 1832-1841.
- V. Orava, H., Kuopanportti, H., and Tontti, T. (2006). Pelletizing Waste Compost and Fly Ash Mixture to Produce Fertilizing Material. Conference article. In: *Proceedings of a Conference, The 5<sup>th</sup> international conference for conveying and handling of particulate solids (CHoPs-05, 2006)*, pp. 1-7. Sorrento, Italy.

## Author's contribution

Hanne Soininen (née Orava) is the principal author and investigator in papers I-V. In paper I, Hanne Soininen was responsible for research plan and carried out the literature review. Leena Mäkelä conducted the interviews and interpreted the results and wrote the article together with Hanne Soininen. In paper II, Hanne Soininen was responsible for research plan and sampling procedure. She interpreted the results and was mainly writing the article. In paper III, Hanne Soininen was responsible for the research plan and sampling procedure in power plant A. Timo Nordman conducted the sampling in power plant B-D. Hanne Soininen interpreted the results and wrote the article with Timo Nordman and Hannu Kuopanportti. In paper IV, Hanne Soininen was responsible for the research plan and sampling procedure. Kati Manskinen carried out the literature review. Hanne Soininen interpreted the results and wrote the article together with Kati Manskinen and Tapio Ranta. In paper V, Hanne Soininen was main responsible for research plan, fly ash collection and granulation tests. Tiina Tontti conducted the field plant experiment and material analyses. Hanne Soininen wrote the article together with Tiina Tontti and Hannu Kuopanportti.



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## Nomenclature

### Abbreviations

CBO	cycle block in operation
DOC	dissolved organic carbon
d.w.	dry weight
D10	particle size with respect to which 90 % of the sample's particles are larger and 10 % are smaller
D50	halving particle size class, or the particle size with respect to which sample's particles are larger and smaller in the ratio of 50/50
ESP	electrostatic precipitator
ET	Finnish Energy
EVIRA	Finnish Food Safety Authority
FINAS	Finnish Accreditation Service
ICP-OES	inductively coupled plasma optical emission spectrometer
ISO	International Organization for Standardization
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
SFS	Finnish Standards Association
TEM	Ministry of Economic Affairs and Employment
TOC	total organic carbon
VTT	Technical Research Centre of Finland
wt%	Weight percent



## 1 Introduction

According to the most recent Finnish Government Programme, Finland will be a leader in the bio- and circular economy as well as cleantech. According to Sitra, the circular economy maximises the use of products, components and materials and retains their value in the loop for as long as possible (Sitra 2016). One of the objectives of the Government Programme is to save nutrients by recycling mineral phosphorous reserves and promoting the bio- and circular economy. Indeed, Finland needs ground-breaking solutions on how to discontinue basing economic and welfare growth on the wasteful use of natural resources.

A significant volume of incineration process side-streams (i.e. ash) is produced by energy production plants. Finnish Energy (ET) estimates that 1.34 million tonnes were produced in Finland in 2014, with peat and wood accounting for 0.59 million tonnes (Finnish Energy 2016). Each year, energy production plants in Eastern Finland produce just under 100,000 tonnes of different types of ash and slag in the process of energy production. According to national legislation, ash must be primarily used as a material.

The utilisation of energy production ash flows has made progress in a variety of ways, but it is still difficult to find the right utilisation applications for some of these fractions due to, among other things, the hazardous substances they contain. The side-streams of energy production plants and the trace elements they contain should be recovered for utilisation, such as by returning them to the forest as fertiliser or for use in earth construction.

National waste management legislation promotes the sensible use of natural resources and prevents waste-related hazards (Waste Act 646/2011). In recent years, there have been amendments made to legislation on the utilisation of ash. The utilisation and landfill disposal of ash is regulated by several acts and decrees in Finland. The landfill disposal of ash is regulated by Government Decree 331/2013. Landfills are classified as those for hazardous waste, non-hazardous waste and inert waste. The Decree defines limit values for waste properties by landfill classification. An environmental permit, as specified in section 32 of the Environmental Protection Act (527/2014), is not needed for the professional or institutional processing of waste in cases involving the utilisation and use of harmless ash or slag in accordance with the Fertiliser Product Act (539/2006). In cases where biofuel-based ash is used as a fertiliser, the Decree of the Ministry of Agriculture and Forestry on Fertiliser Products 24/2011 shall apply. The ash being used as a fertiliser product may only contain ash from untreated (pure) wood, peat or agro biomass. The Government Decree on the Recovery of Certain Wastes in Earth Construction (843/2017) specifies limit values for the use of fly and bottom ash from the combustion of coal, peat and wood-based material in earth construction. The purpose of the Decree is to promote the utilisation of waste by setting requirements, which, if met, would mean that the use of waste specified in the Decree for earth construction would not require an environmental permit as stipulated in the Environmental Protection Act (527/2014).

Quantitatively larger and taxable types of waste include municipal waste as well as ash and slag from power plants. Under the Waste Tax Act, beginning in 2017, a waste tax of EUR 70 per tonne must be paid for waste sent to a landfill (Waste Tax Act 1126/2010). Waste tax is not paid on ash fractions which are used as fertilisers or in earth construction. The utilisation of ash can be hindered by the solubility of hazardous substances, heavy metal concentrations and large variations in quality that exceed their limit values. Various processing methods, such as ageing or fractionating, can be used to reduce or eliminate the concentrations of these hazardous substances. The use of ash as, for example, a forest fertiliser, also requires processing. The most commonly used method for productising ash is granulation.

The side-streams of energy production plants in Eastern Finland comprise a significant percentage of the region's waste flows, whose recovery for utilisation is of the utmost importance. The volume of ash generated in a year is affected by, for example, the type of fuel, the length of time an energy production plant has been in operation, and weather fluctuations. This thesis required an examination of the volumes and types of ash produced by energy production plants in Eastern Finland as well as the suitability of ash for landfill disposal, earth construction and fertiliser use (other purposes and forest applications). According to earlier studies, it was assumed that not all ash produced by biofuel-based energy production plants would be suitable for utilisation without any processing. The landfill disposal of ash is cost-ineffective and against the principles of the circular economy. This thesis required an exploration into whether it would be possible to increase the number of possibilities for utilising fly ash produced by energy production plants by reducing their hazardous substance concentrations and enhancing their fertiliser properties using various processing methods.

The type of bottom and fly ash produced by 31 energy production plants in Eastern Finland were analysed during research with regard to utilisation requirements and landfill disposal. During research, ageing, fractionating and granulation tests were conducted on fly ash produced by energy production plants in order that the ash flows produced by municipal and privately-owned energy production plants could be utilised more effectively. Even though a great deal of research has been conducted on ash produced by energy production plants, the results of this thesis will help to further develop ash processing methods. The results of this thesis will also increase knowledge on the environmental impacts of ash in the region as well as the possibilities and potential for utilising ash.

## 2 Aims of the study

Eastern Finland energy production plants produce annually just under 100,000 tonnes of different kinds of ash and slag as a result of energy production processes. The utilisation of energy production ash flows has progressed in a number of ways, but for some of these fractions it is still difficult to find the correct usage owing to factors such as the harmful substances contained within the ash. The Finnish Government Program aims to make Finland a forerunner in bioeconomy, the circular economy and cleantech by 2025. The secondary flows of energy production plants and the trace elements contained within them should indeed be returned to the forests as fertiliser, while at the same time taking environmental safety into consideration.

The main objective of this study was to research the quantity and quality of ash fractions produced by Eastern Finland energy production plants and processing techniques for advancing the utilisation of this ash. The specific research questions were:

1. To estimate the following data for ash produced by energy production plants in Eastern Finland: quantity, quality, and total content and liquid content of harmful substances, taking into account different options for utilisation (Publications I and II).
2. To specify and test different methods for reducing the content of substances that prevent the utilisation of ash. The methods tested included fractionation at the energy production plant using an electrostatic precipitator and the ageing of different types of ash by piling them up (Publications III and IV).
3. To specify and test the suitability of ash as fertiliser by adding organic nutrients and using granulation as the productisation method (Publication V).

Research question 1 was explored for the region of Eastern Finland and its energy production plants. The research included data on ash quantities from 53 South Savo energy production plants, 28 North Savo production plants, and 27 North Karelia production plants. The chemical quality of the ash was analysed for 31 energy production plants. There is analysis data for plants of under 5 MW, between 5 and 10 MW, and over 50 MW. Research question 2 was explored using an electrostatic precipitator at one power plant which is powered by wood and peat. The ageing method was tested on the fly ash from two energy production plants and two industrial energy production plants. The plants were powered by wood and peat. Research question 3 involved studying the fractionated and non-fractionated fly ash from a power plant powered by wood and peat. The fly ash was productised by adding organic compost and using a rotating plate as the granulation method. The structure of this thesis is shown in Table 1.



Table 1: The structure of this thesis.

Research question	Publication numbers
Number 1: The quantity and quality of ash produced by energy production plants in the region of Eastern Finland	Publications I and II
Number 2: The reduction of content of harmful substances in fly ash using fractionation and ageing	Publications III and IV
Number 3: Productisation of fly ash to produce fertiliser using a pelletising granulation method	Publication V

### **3 Ash from biofuel-powered energy production plants as part of the circular economy**

Energy production plants comprise a significant proportion of secondary flows from burning processes, otherwise referred to as ash. Finnish Energy has estimated that in 2014 a total of 1.34 million tonnes of ash were produced, of which the ash from peat and wood comprised a total of 0.59 million tonnes (Finnish Energy 2016). Energy production in South Savo produces around 20,000-22,000 tonnes of ash and slag per year. For Eastern Finland, the total for 2018 was 97,000 tons. According to waste legislation, ash should primarily be utilised in material form. Problems can arise, however, where heavy metal content in the ash exceed the limits for utilisation and where there are large variations in quality. The environmental impacts of ash relate primarily to the heavy metals, organic substances and salts contained within them, and above all to the solubility of these harmful substances (Kaartinen et al. 2007). Ageing and fractionation are two of the techniques that have been used to reduce or remove these harmful substances. The use of ash as forest fertiliser, for example, also requires processing. A commonly used productisation method is ash granulation.

#### **3.1 Legislation on productive use**

The utilisation and final deposition of ash in Finland is governed by a number of decrees. The final deposition of ash in landfill sites is regulated by Government Decree 331/2013. Landfill sites are categorised for either hazardous, non-hazardous, or inert waste. The decree specifies the limit values for different waste properties for each type of landfill site. The Government Decree on the Recovery of Certain Wastes in Earth Construction (843/2017) specifies the limit values for the use of fly ash and bottom ash from the combustion of coal, peat and wood-based materials in earthwork construction. Where biofuel-based ash is used as a fertiliser, the decree of the Ministry of Agriculture and Forestry on Fertiliser Products (24/2011) is applied. Ash used as a fertiliser product may only contain ash from pure wood, peat or agro biomass. The following chapters examine more closely the legislation that governs the utilisation and final deposition of ash.

##### **3.1.1 Suitability of waste for landfill sites**

The suitability of waste for landfill sites is assessed in the Government Decree on Landfills (331/2013). Limit values are given in the decree for waste that can be accepted to landfill sites for either hazardous, non-hazardous, or inert waste (Table 2). The following suitability limit values are used in the assessment of waste submitted to inert waste landfill sites. They are calculated using liquid-solid ratios (L/S) of 2 l/kg and 10 l/kg and as the measured substance's proportion of the total quantity, with the results given directly in units of mg/l. In quality control, a two-stage batch leaching (shaking) test maybe used in accordance with standard SFS-EN 12457-3 (SFS-EN 2002). The content of harmful substances from solubility tests shall be specified in accordance with standards SFS-EN 12506 and SFS-EN 13370 and SFS-EN 16192 (Government Decree 331/2013).

Table 2: Limit values used in assessment of waste submitted to landfill sites for hazardous, non-hazardous, or inert waste (Government Decree 331/2013).

Substance/variable	Inert waste landfill site	Non-hazardous waste landfill site	Hazardous waste landfill site
	(mg/kg of dry matter) (L/S = 10 l/kg)		
Arsenic (As)	0.5	2	25
Barium (Ba)	20	100	300
Cadmium (Cd)	0.04	1	5
Chromium (Cr)	0.5	10	70
Copper (Cu)	2	50	100
Mercury (Hg)	0.01	0.2	2
Molybdenum (Mo)	0.5	10	30
Nickel (Ni)	0.4	10	40
Lead (Pb)	0.5	10	50
Antimony (Sb)	0.06	0.7	5
Selenium (Se)	0.1	0.5	7
Zinc (Zn)	4	50	200
Chloride (Cl <sup>-</sup> )	800	15,000	25,000
Fluoride F <sup>-</sup>	10	150	500
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	1,000 <sup>1)</sup>	20,000	50,000
Phenol index	1		
Dissolved organic carbon (DOC <sup>2)</sup> )	500	800	1,000
Total dissolved substances (TDS <sup>3)</sup> )	4,000	60,000	100,000

1) The waste is also considered to fulfil the usage requirements if the sulphate content does not exceed the following values: 1,500 mg/l (first leach in flow-through test with extraction ratio of L/S = 0.1 l/kg) and 6,000 mg/kg (extraction ratio L/S = 10 l/kg). For determining the content with a extraction ratio of L/S = 0.1 l/kg, a flow-through test is to be used. Content in a extraction ratio of L/S = 10 l/kg can be determined using either a shaking test or flow-through test.

2) If the limit value for dissolved organic carbon is exceeded in the waste's own pH, the waste can also alternatively be tested using a extraction ratio of L/S = 10 l/kg in a pH of 7.5-8.0. The waste is considered to fulfil the suitability requirement for dissolved organic carbon if the content is below 500 mg/kg for a inert waste landfill site, below 800 mg/kg for a non-hazardous waste to landfill site, and below 1000 mg/kg for a hazardous waste landfill site.

3) The limit value for total dissolved solids may be applied instead of the limit values for sulphate and chloride.

### 3.1.2 Requirements for utilisation applications

Government Decree 843/2017 specifies the limit values for the use of fly ash and bottom ash from the combustion of coal, peat and wood-based materials in earthwork

construction. Where biofuel-based ash is used as a fertiliser, the Decree of the Ministry of Agriculture and Forestry on Fertiliser Products (24/2011) is applied.

The purpose of Government Decree 843/2017 is to promote the utilisation of waste by specifying the conditions which must be fulfilled in order for the types of waste covered by the decree to not require an environmental permit as specified by the environmental protection act (527/2014) when used for earthwork construction. Table 3 presents the limit values set for the use of ash from the combustion of coal, peat and wood-based materials in earth construction sites. An road constructed of crushed stone and ash, as referred to in the decree, is a forest road which is used by vehicles and has a surface layer composed of a combination of ash and stone. The aggregate sample for the ash fractions being studied may be a maximum of 5,000 tonnes and the minimum amount of primary samples for one aggregate sample must be at least 50 (Government Decree 843/2017).

Table 3: Limit values set for the use of fly ash and bottom ash from the combustion of coal, peat and wood-based materials in earth construction sites. Highest permitted solubility (mg/kg L/S ratio 10 l/kg) and content (mg/kg of dry matter) of harmful substances and highest permitted layer thickness for earth construction sites: roadway and road constructed of crushed stone and ash (Government Decree 843/2017).

Harmful substance	Limit value Roadway (thickness of waste layer $\leq 1.5$ m)		Limit value Road constructed of crushed stone and ash <sup>1)</sup> (thickness of waste layer $\leq 0.2$ m)
	Solubility (mg/kg L/S = 10 l/kg) Covered structure	Solubility (mg/kg L/S = 10 l/kg) Paved structure	Solubility (mg/kg L/S = 10 l/kg)
Sb	0.7	0.7	0.7
As	1	2	2
Ba	40	100	80
Cd	0.04	0.06	0.06
Cr	2	10	5
Cu	10	10	10
Hg	0.03	0.03	0.03
Pb	0.5	2	1
Mo	1.5	6	2
Ni	2	2	2
V	2	3	3
Zn	15	15	15
Se	1	1	1
Fluoride <sup>2)</sup>	50	150	100
Sulphate <sup>2)</sup>	5,900	18,000	6,500
Chloride <sup>2)</sup>	3,200	11,000	4,700
DOC	500	500	500
Harmful substance	Content (mg/kg of dry matter) Covered structure	Content (mg/kg of dry matter) Paved structure	Content (mg/kg of dry matter)
PCB <sup>6)</sup>	1	1	1
PAH <sup>4)</sup>	30	30	30
Benzene	0.2	0.2	0.2
TEX <sup>3)</sup>	25	25	25
Naphthalene	5	5	5
Phenol compounds <sup>5)</sup>	10	10	10
Oil hydrocarbons C10-C40	500	500	500

1) The layer thickness of a road constructed of crushed stone and ash has been set as the calculated thickness of the filling layer

2) The limit values given in the table for chloride, sulphate and fluoride are not applied to structures which fulfil all the following conditions: location is no more than 500m from the sea, the discharge direction for

water percolating through the structure is towards the sea, and there are no wells located between the structure and the sea which are used for domestic water supply

3) Toluene, ethylbenzene and xylene (total content)

4) Polyaromatic hydrocarbons: anthracene, acenaphthene, acenaphthylene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, chrysene, naphthalene and pyrene (total content)

5) Phenol, o-cresol, m-kresol, p-kresol, bisphenol-A (total content)

6) Polychlorinated biphenyl congeners 28, 52, 101, 118, 138, 153 and 180 (total content).

The other quality requirements for the utilisation of ash stipulated in the decree are as follows:

- the utilisation of ash from the combustion of peat and wood-based substances must take into account the restrictions on the radioactivity of construction materials and ash as stipulated in the current instructions provided by the Radiation and Nuclear Safety Authority.
- the quantity of ash used for road constructed of crushed stone and ash may not exceed 30% by mass in the mixture of ash and stone aggregate used
- the largest permitted granular size is 50 mm for waste combustion slag, 90 mm for concrete, aerated concrete and asphalt waste and 150 mm for brick waste. (Government Decree 843/2017)

Ministry of Agriculture and Forestry decree on fertiliser products (24/2011), covering fertiliser product types, names of type groups and type-group-specific requirements, fertiliser product requirements regarding quality, marking, packaging, transport, storage, use and other matters, and raw materials for fertiliser products. The decree does not cover fertiliser products to be used in the landscaping of landfill sites and other confined areas. The by-product of an industrial or processing plant used as ash fertiliser or as a fertiliser ingredient is such that it can be shown to have a beneficial effect on plant growth which primarily results from the quantity of usable nutrients in the plants contained in the by-product. The following substances can be used as fertiliser or as ingredients for such fertiliser: peat, agro biomass, wood ash and animal-based ash. (Decree 24/2011) Table 4 presents the maximum content of hazardous metals for fertiliser products.

Table 4: Maximum content of harmful substances in ash used for ash fertiliser or in ash used as their raw material used in forestry (mg/kg of dry matter). Other use refers to use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Chemical element	Forest use (mg/kg of dry matter)	Other use (mg/kg of dry matter)
As	40	25
Hg	1.0	1.0
Cd	25	2.5
Cr	300	300
Cu	700	600
Pb	150	100
Ni	150	100
Zn	4,500	1,500

The use of ash in its normal state as a forest fertiliser or in other ways as a fertiliser product does not require an environmental permit for professional or institutional utilisation provided that the ash's quality and use fulfil the conditions laid out in fertiliser legislation. The storage and granulation (or other preliminary treatment) of ash prior to its use as forest fertiliser is classified as waste utilisation that requires an environmental permit in cases where the activity is professional or institutional in nature. In contrast, small-scale granulation of ash that takes place on a farm using a concrete mill or some other technique, for example, does not require an environmental permit. The use of granulated ash as a fertiliser product does not require an environmental permit. Manufacturing fertiliser products from ash also requires notification to be made to the Finnish Food Safety Authority (EVIRA) in line with the Fertiliser Product Act (539/2006). In addition, heating plants that deliver the ash produced by their operations to another operator to be used in the manufacture of fertiliser products must also give notification to EVIRA. (Ministry of the Environment 2014)

### 3.2 Properties of fly ash

Ash is the non-combustible residue left by an organic fuel, and is composed of those chemical elements within the fuel for which the oxides are non-volatile at combustion temperature. The composition of the ash is derived from the fuel's mineral composition and therefore depends on the fuel used. In general, fuels are a mixture of two or more different fuel types, with oil also being used as a supporting fuel. As a result, ash is rarely composed of pure peat or wood ash, but is instead some form of mixed ash. (Orava 2003)

The main components of fly ash for coal and peat are silicon, aluminium and iron oxides. Wood ash is mostly composed of calcium oxide, which makes the ash alkaline. The pH of wood ash is around 12, while the pH of peat ash is between 7 and 12. (Palola 1998) In addition to their primary components, fly ash also contain magnesium, potassium and

sodium oxides, heavy metals and non-combustible coal. The proportions of different chemical element components in ash are presented in Table 5. Bottom ash is composed mainly of aluminium silicates, which are also major soil components (Walsh 1997).

Table 5: Contents of primary ash components as percentages by mass in dry matter. Wood ash is composed of ash from different tree species and bark (Palola 1998).

Compound component	Coal ash (wt%)	Peat ash (wt%)	Wood ash (wt%)
SiO <sub>2</sub>	20-65	40-75	0.9-22
Fe <sub>2</sub> O <sub>3</sub>	3-40	4-7	0.3-8.5
Al <sub>2</sub> O <sub>3</sub>	11-41	1-16	0.3-2
CaO	0-31	1.5-12	37-60
MgO	0-10	0.5-2.5	4.5-16
K <sub>2</sub> O	0-5	0.1-0.5	3.5-30
Na <sub>2</sub> O	0-5	<1-3	0.7-8.6
P <sub>2</sub> O <sub>5</sub>	0-1	2-4	1-15
SO <sub>3</sub>	0-7	0.4-4	1.6-4.8

The chemical and physical properties and quantities of ash produced by combustion depend on the composition and quality of the fuel used. Other factors affecting the quality of the ash include the combustion technique and parameters – such as temperature, combustion speed and air intake – as well as the condition of the boiler and the ash capture systems in use. Of particular importance for the properties of the fly ash is the separation mechanism for the ash, as the fine fraction carried in the gases are an important variable in the composition of the ash. (Walsh 1997)

Ash also contains small quantities of many other chemical elements, including heavy metals. Coal ash has significantly higher heavy metal content than wood or peat ash. The most critical heavy metal in wood ash is cadmium, which may limit the utilisation of nutrition-rich wood ash, for example as fertiliser. The content of heavy metals in different types of ash are presented in Table 6. Heavy metal content in ash can be reduced by removing from the main fraction the small particulate matter that contains high levels of heavy metals. (Orava et al. 2004)



Table 6: Heavy metal content for different types of fly ash and the Decree 24/2011 limit values for forest use of ash (mg/kg of dry matter) (Palola 1998; Korpijärvi et al. 2009; Decree 24/2011).

Heavy metal (mg/kg)	Coal fly ash	Peat fly ash	Wood fly ash	Wood bark fly ash	Peat and wood fly ash	Decree 24/2011 Limit value (forest use)
As	2.3-200	2-200	0.2-60	7-28	30-120	40
Ba	-		200-1,300		150-2,200	
Cd	0.01-250	0.05-8	0.4-40	4-20	0.5-5	25
Co	40-100		3-200		10-50	
Cr	3.6-7,400	15-250	15-250	40-230	43-130	300
Cu	14-3,000	20-400	15-300	52-144	60-200	700
Hg	0.005-80	0.001-1	0.02-1	0.004-1.1	0.3-2	1.0
Mo	1.2-236	-	15	-	10-50	
Ni	1.8-800	15-200	20-250	36-89	30-700	150
Pb	3.1-2,120	5-150	3-1,100	34-140	99-1,100	150
Se	0.2-134	-	-	-	<10-26	
V	12-1,180	-	20-30	-	20-500	
Zn	14-13,000	10-600	15-10,000	790-5,100	50-2,200	4,500

Fly ash is fine-grained (2-200  $\mu\text{m}$ ), equivalent in particle size to silt and fine sand. In its natural state, fly ash has few reinforcement properties, but when combined with water and free calcium oxide it produces compounds that have strength properties. (Orava et al. 2004) The ash produced by wood combustion normally has a particle size of 0.002-1 mm, with over 80% of ash particles having a diameter of less than 1 mm, and over half having a diameter of less than 0.1 mm (Palola 1998). The specific weight of wood ash is 210-510  $\text{kg}/\text{m}^3$ . The variables affecting density include the tree species and fraction, the tree age and seasonal variations (Kytö 1983). The composition of ash produced in wood and bark combustion depends on many different variables. These include the tree species in question, place of growth, age of tree, tree sections burnt (branches, trunk, bark), type of soil in place of growth, combustion technique, combustion temperature, and ash removal method. The heavy metals contained in wood ash can limit its utilisation. Table 7 presents the typical heavy metal contents for wood ash.

Table 7: Content of heavy metals (mg/kg of dry matter) produced by wood combustion for both bottom ash and fly ash (Taipale 1996; Alakangas et al. 2016; Isännäinen and Huotari 1994).

Chemical element	Bottom ash (mg/kg)	Fly ash (mg/kg)
As	0.2-3.0	1-60
Cd	0.4-0.7	6-40
Co	0-7	3-200
Cr	60	40-250
Cu	15-300	200
Hg	0-0.4	0-1
Mn	2,500-5,500	6,000-9,000
Ni	40-250	20-100
Pb	15-60	40-1,000
Se	-	5-15
Zn	15-1,000	40-700
V	10-120	20-30

The fly ash particulate matter produced in peat combustion is composed of the ash contained in the peat, residual unburnt substances such as mineral matter and minerals, and the non-combustible wood contained in the peat. The distribution of particle sizes in the ash and the proportion of non-combustible components vary greatly depending on the combustion method, but typically, there is a broad particle size range (1-50  $\mu\text{m}$  for fly ash and 10-30 mm for bottom ash) and low density (around 500-1,100  $\text{kg/m}^3$ ). The most important source of variations comes from the starting values of the combusted peat, which vary between different production sites. Peat quality varies depending on factors such as bog type, depth of peat and quality of groundwater. Less of the metals contained in peat bind to the bottom ash as compared to the fly ash, although the chemical composition of bottom ash is otherwise similar to fly ash. (Orava 2003; Alakangas 2000; Helenius et al. 1992; Leijting 1999)

The composition of ash produced by mixed combustion of wood and peat varies depending on the fuel mixture. Mixed combustion ash typically has a composition and solubility similar to peat and coal fly ash. In general, chromium and vanadium content are nevertheless lower than those of coal ash. (Laine-Ylijoki et al. 2002) Mixed combustion has not been found to have any effect on contents of chromium and nickel in ash. In contrast, mixed combustion has been found to decrease arsenic, cadmium, mercury, molybdenum and lead content, and increase manganese content. (Harju et al. 2001) Pure wood combustion only has been found to increase calcium, cadmium, manganese, zinc and sulphate content in ash. The use of peat, on the other hand, increases aluminium and nickel content. (Laine-Ylijoki et al. 2002) Table 8 summarises the solubility properties of fly ash from peat, wood and sawdust.

Table 8: Solubility properties of peat, wood and coal fly ash with an L/S ratio of 10 and the limit values used in assessment of waste submitted to landfill sites for inert, non-hazardous and hazardous waste (Government Decree 331/2013). Test method: two-stage CEN test EN 12457-3 or flow-through test (prCEN/TS 14405, NEN7343) (Korpijärvi et al. 2009).

Substance /variable	Inert waste landfill site	Non-hazardous waste landfill site	Hazardous waste landfill site	Coal fly ash	Coal fly ash range of variation	Wood and peat fly ash	Wood and peat fly ash range of variation
	(mg/kg) dry matter, (L/S = 10 l/kg)						
As	0.5	2	25	0.15	0.02-2	0.1	0.001-0.6
Ba	20	100	300	45	1-106	15	0.6-120
Cd	0.04	1	5	0.01	0.001-0.02	0.02	0.003-0.5
Cr <sub>kok</sub>	0.5	10	70	1.5	0.02-10	3.5	0.02-34
Cu	2	50	100	0.1	0.01-1	0.08	0.01-0.4
Hg	0.01	0.2	2	0.003	0.002-0.004	0.01	0.001-0.02
Mo	0.5	10	30	4	0.3-50	2.5	0.05-7.5
Ni	0.4	10	40	0.03	0.01-0.1	0.1	0.002-0.2
Pb	0.5	10	50	0.2	0.02-0.4	3	0.001-90
Sb	0.06	0.7	5	0.1	0.01-0.5	0.1	0.001-0.2
Se	0.1	0.5	7	0.3	0.05-0.5	0.45	0.05-5
Zn	4	50	200	0.2	0.01-9	6	0.02-60
Cl <sup>-</sup>	800	15,000	25,000	75	6-4,200	2,800	2-28,000
F <sup>-</sup>	10	150	500	20	3-90	120	7-600
SO <sub>4</sub> <sup>2-</sup>	1,000 <sup>1)</sup>	20,000	50,000	4,000	65-30,000	9,000	1-130,000
DOC	500	800	1,000	7	7-8	60	8 - 210

Ash often contains surprisingly high amounts of harmful substances even when the fuel should basically be pure. For example, a small quantity of impregnated wood contained within the wood fuel significantly raises the content of chromium, copper and arsenic in the fly ash. (Korpijärvi et al. 2009) According to the calculated potential ecological risk index in Jukić et al. 2017, the mobility of nickel and arsenic has major environmental impacts. According to Pitman 2006 the effects of cadmium on ecosystems are of particular concern (Pitman 2006). However, the results of potential ecological risk calculations show that biomass fly ash causes a low risk (Jukić et al. 2017).

### 3.3 Quantities of ash produced by energy production in Finland

Efforts are being made to increase the use of renewable energy in Finland in line with the energy and climate strategy and the objectives of the government programme. The EU's (European Union) renewable energy directive set the goal for Finland for 2020 of achieving a 38% renewable energy proportion of its final energy consumption. This goal was reached already in 2014. (MOTIVA 2018) Bioenergy has an important long-term role in the EU and especially in Finland. The measures, which Finland must nevertheless implement to reduce greenhouse gas emissions by 80-95% are related to renewable energy, energy efficiency and cleantech solutions. Finland must increase the proportion of renewable energy in both energy production and consumption. Maximum use of domestic bioenergy must be ensured and the use of biofuels as an energy source for transport must be increased. (TEM 2014)

Total energy consumption in Finland on 2017 was 1.36 million terajoules (TJ). In 2017, renewable energy comprised 36% of total energy consumption. Wood fuels remained as Finland's largest energy source, comprising 27% of total energy consumption. (Statistics Finland 2018)

Finnish Energy has estimated that around 1.34 million tonnes of ash were produced by energy production plants in Finland in 2014. Peat and wood ash were together the most significant ash fractions in relation to total ash production (580,000 tonnes/year). Around 130,000 tonnes of ash were produced by co-incineration, while around 630,000 tonnes were produced by coal and waste combustion. (Finnish Energy 2016) In 2006, around 900,000 tonnes of ash were produced in Finland, with wood and peat combustion accounting for 362,000 tonnes (Finnish Energy 2010). Quantities of ash from peat and wood combustion have been increasing due to increases in the use of biofuels. According to Voshell et al. the generation of biomass ash is expected to increase also in the future because wood-based biomass is generally recognized as carbon neutral fuel (Voshell et al. 2018).

The majority of ash and other by-products are recycled through use in earthwork construction. Another main use for coal fly ash is as an alloying component. The utilisation of ash and other by-products produced by combustion processes is an excellent way to substitute for untouched raw materials. (Finnish Energy 2016)

In the region of Eastern Finland (South Savo, North Karelia and North Savo), biofuel-powered energy production plants produced in 2008 a total of 97,000 tonnes of bottom ash and fly ash. The plants' annual ash output depends on many factors, such as the quality of fuel used in each plant, levels of plant maintenance, and the weather-dependent levels of demand for heat energy production. In addition, the operations of power plants in industrial localities are dependent on the country's economic conditions. (Soininen et al. 2010) Presently, ash produced in the region of Eastern Finland is utilised in road construction, landfill site construction and other earthwork construction, as well as in forest fertiliser.

The use of ash as forest fertiliser has increased in recent years. The effects of the growth reaction from the slowly dissolving phosphorus contained in ash can be seen in timber for at least 30 to 40 years, and the more easily leaching potash for between 20 and 25 years. A realistic objective for South Savo, for example, would be to maintain an annual ash fertilisation area of between 2,000 and 3,000 hectares (4.5 tonnes of ash per hectare), which would mean a regional requirement of 10,000 tonnes of ash per year. (Kontinen et al. 2015) Nieminen et al. investigated the rate of release of nutrients and heavy metals from wood and peat ash fertilizers in forest soils (after 3 and 5 years after spreading). According to Nieminen et al. the results showed that potassium (K), sodium (Na), boron and sulphur are easily released from wood ash, whereas heavy metals are highly insoluble in all types of ash fertilizer products. Granulated ash fertilizers were less soluble than powdered fertilizers and the products stabilized by self-hardening. (Nieminen et al. 2005) According to Maljanen et al. there is no major risk of increasing greenhouse gas emissions after granulated wood-ash fertilization in peatland forests (Maljanen et al. 2014).

### 3.4 Ash processing techniques

#### 3.4.1 Ageing

Ash ageing refers to the practice of storing ash in a damp pile. When stored in such conditions, the ash reacts with the carbon dioxide and moisture in the air. This can even lead, for example, to the formation of cement like substances (such as ettringite) from calcium oxide, if there is calcium carbonate or aluminium and sulphate compounds present. During the ageing process, metal salts dissolve out of the material and alkalinity is reduced, which either can positively or negatively affect solubility, depending on the substance in question. The natural ageing of ash can be boosted using carbon dioxide. (Southwest Finland Environment Institute 2009; Korpijärvi et al. 2009) According to Nilsson the most common way to perform chemical hardening of the ash is by using carbon dioxide from the air (Nilsson 2016).

According to research carried out in Sweden, storage of ash causes little change during the summer. Changes were observed in the surface sections of the ash pile (less potassium), while the moisture content remained roughly the same. During the autumn, potassium dissolved, the pH dropped slightly, moisture content increased and fine fraction content remained the same. (Toikka 1999) Storage of ash as an uncovered pile or mound can cause significant dust formation. The presence of water can also lead to the dissolving of harmful substances if there is no isolating material placed under the pile. Covering or dousing the pile reduces dust formation. (Wahlström et al. 1999)

The forestry and energy industry's project on the environmental suitability of waste fractions for earthwork construction involved research on the effects of ash ageing on harmful substance solubility in fly ash from nine Finnish power plants. The research

obtained different results for each kind of ash, and the ash samples from the different power plants showed significant differences in the effects of ageing on harmful substance solubility. The tests indicated that ageing can decrease the solubility of sulphate especially, but also of chromium, molybdenum and selenium. Because the pH of originally alkaline ash is decreased significantly by ageing, changes in the solubility of harmful substances must be identified ash-specifically using an equilibria pH. In the research, the pH during the ageing process was set to 8.5 once the ash had obtained in equilibrium state with the carbon dioxide in the air. Establishing the equilibria for very alkaline ash takes longer than for less alkaline ash. The time needed to obtain the equilibrium state in the tests ranged from one month to many months. (Lindroos et al. 2016)

Lindroos et al. have found that ageing leads to a significant decrease in the ash's calcium solubility. During the ageing process, calcium forms weakly soluble calcium carbonate, which can be indirectly observed through decreased calcium solubility (the calcium carbonate has precipitated) and decreased pH. After the ageing process, the electrical conductivity of a water filtrate also decreases significantly. The results indicate that a short ageing period (2.5 months) does not decisively decrease the solubility of harmful substances to the extent that the fly ash would fulfil the solubility criteria of environmental legislation for ash used in earthwork construction. However, the quality of the ash of particular power plants can be improved through ageing. Depending on the intended use of the ash, the ageing period can be lengthened, which will most likely lead to further solubility reductions. If the reactivity of the ash is an important parameter for the utilisation in question, the length for which the damp ash is stored in a pile should be kept as short as possible so that the ash's technical properties are not significantly weakened. (Lindroos et al. 2016)

### 3.4.2 Fractionation

The chemical and physical properties and quantities of ash produced by combustion depend on the composition and quality of the fuel used. Other factors affecting the quality of the ash include the combustion technique and parameters – such as temperature combustion speed and air intake – as well as the condition of the boiler and the ash capture systems in use. Of particular importance for the properties of the fly ash is the separation mechanism for the ash, as the fine fraction carried in the gases are an important variable in the composition of the ash. Fly ash fine particles are often rich in heavy metals. The utilisation of fly ash is inhibited by the large variations in heavy metal content. The ash may contain quantities of heavy metals that exceed the limit values given in fertiliser legislation. (Orava 2003)

Heavy metal emissions from fly ash can be reduced in many cases using process engineering methods. These process engineering reduction methods include the minimisation of flue gas quantities, gas collection, air recirculation, efficient use of raw materials and energy, and use of raw materials and fuels that contain minimal amounts of heavy metals. Fly ash quality can also be influenced using fractionation. The purpose of

fractionation is to separate out the ash fraction that contains a lot of fine particles and is high in heavy metal content from the fly ash that is suitable for utilisation. (Orava 2003)

Electrostatic precipitators are nowadays the most common solid matter purification method used in power plants. The advantages of electrostatic precipitators include their high separation efficiency (as high as 99.9%) as well as their suitability for varying particle sizes (also for those below 1  $\mu\text{m}$ ) and for even large quantities of flue gas. Other benefits include their long operating life, high reliability and low use and maintenance costs. (Walsh 1997; Immonen 1987; Jalovaara et al. 2003; Kotola 2010)

The quantity and size distribution of particles to be removed are significant factors in the operation of an electrostatic precipitator. Although the separation efficiency of an electrostatic precipitator is relatively constant regardless of the particle mass, the effective migration rate is lower if particle content is smaller. It follows from the varying accumulation properties of different particles that the separation efficiency will vary as a function of particle size. The most difficult particle size category is 0.2-0.5  $\mu\text{m}$ . (Nykänen 1993; Kouvo 2003)

Figure 1 present the results of fractionation experiments carried out using an electrostatic precipitator. Based on the research, it can be stated that heavy metal content is lowest in the electrostatic precipitator's first field and highest in the third field. This is due to the fact that the largest fly ash particles collect in the first field, whereas the third field has more ash that contains fine particles. According to Dahl et al. (2009) the particle size distribution, the mass loadings of heavy metals in the fly ash were more than 90% contributed by the smallest particle size fraction lower than 0.074 mm.

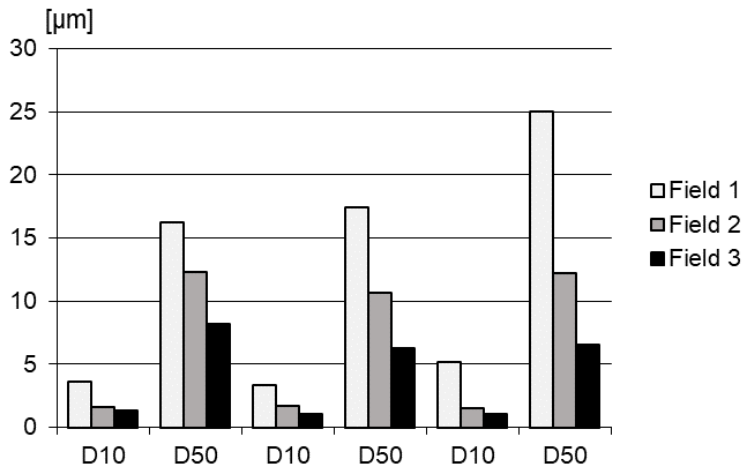


Figure 1: Granule size categories ( $\mu\text{m}$ ) D10 and D50 for electrostatic precipitator fields 1-3 (Paper I).

Heavy metal content in the ash influence the filter voltage, fuel quality and flow rate of flue gas, among other things. The separation efficiency of the electrostatic precipitator can be modified by changing its maximum voltage setting and its CBO ratio. Using these settings, the first field can be made less powerful, thus reducing further the heavy metal content from the ash that accumulate in this field. Heavy metal emissions containing particulate matter can be reduced, on the other hand, by making the electrostatic precipitator's final field more powerful.

The Technical Research Centre of Finland (VTT) has researched the possibilities for reducing heavy metal content in ash by fractionating the ash using a 3-field electrostatic precipitator. The Cd content in the filter's first field was 3.2 mg/kg of ash, while in the third field it was 14 mg/kg of ash. In the electrostatic precipitator being studied, the proportion of ash accumulating in the three fields was, depending on the running conditions, 84-95% for the first field, 4-15% for the second, and around 1% for the third. (Thun and Korhonen 1999) In the VTT study of ash to be used as fertiliser, Cd content was reduced by 15 to 25% by grading the ash with an electrostatic precipitator, and it was possible to improve the separation efficiency by modifying the electrostatic precipitator or using a different discriminator (Thun and Korhonen 1999; Matilainen et al. 2014).

The cadmium content of ash to be used as fertiliser can be reduced by up to 70% using electrostatic precipitator fractionation. Contents of other heavy metals are not reduced so significantly. (Orava 2003; Orava et al. 2004) As much as 75-90% of the heavy metals in fly ash (Cd and Zn) are bound to the fine fly ash fraction separated by the electric field (Dahl et al. 2002).

The percentages by mass (depending on boiler type) for the different types of ash from power plants fuelled by bark and wood chips (grate boilers) are as follows: bottom ash 70-90%, cyclone fly ash 10-30%, electrostatic precipitator fly ash 2-8% and dust emissions 0.1-3% (Agarwal and Agarwal 1999). In pulverised fuel firing and fluidized-bed combustion, fly ash comprises 80-100%. As much as 75-90% of the heavy metals (Cd and Zn) are bound to the fine fly ash fraction separated by the electric field (Dahl et al. 2002).

The simplest method would be to handle fly ash in dry form, because wetting the ash adds extra process stages and costs related to water removal. Using a dry fraction also makes it possible to grade the ash externally to the power plant process. When grading, the ash can be separated according to particle size and specific weight using an air separator and into different fractions using a filter equipped with an ultrasonic vibrator. Proportions of reactive, soluble substances and heavy metals are highest in the fine particles which are separated in the grading process from the larger ash fraction. Owing to the fine-grained nature of ash, effective dust control is important. (Korpijärvi et al. 2009)



### 3.4.3 Processing ash by granulation

Ash can be processed before being utilised using procedures such as stabilisation, granulation and self-hardening. Ash to be used as fertiliser is processed using water-assisted granulation in order to facilitate the spreading of the fertiliser and to reduce dusting. Fertiliser use needs a process to agglomerate the ash, because untreated ash is a dust hazard for workers and is difficult to spread evenly on forest soil (Sarenbo et al. 2009). If the ash contains too many hazardous heavy metals or other harmful substances, its utilisation can be boosted using chemical or binder stabilisation. According to Ulatowska, fly ash has a pozzolanic property and therefore it is a valuable and desirable material (Ulatowska et al. 2014).

The alkaline metals potassium and sodium and the alkaline-earth metal calcium react with the sulphur compounds in the flue gas to produce solid sulphate that remain in the fly ash. Regarding ash hardening, the most important variable is the quantities of free calcium or calcium oxide, which react with aluminium and sulphate to form cement-like substances. When precipitating into the internal water voids in the ash particles, they condense the particles, and when precipitating into the water voids between the ash particles, they bind the ash particles together into compact particles. The reactivity of the ash (pH and salt effect) decreases as the particle size increases and the quantity of fine fraction decreases. This reduces the risks of causing damage to the forest ecosystem. The ash's nutrition content and the essential data for the granulation, such as the quantities of calcium and non-combustible coal, should be established before the stabilising, because lower levels of coal and high levels of calcium will lead to better granulation results. (Matilainen et al. 2014)

Ash can be processed with granulation using both compression and water-assisted layering. The forms of compression granulation are briquetting, tableting and extrusion. When using the layering granulation method, the granules are formed by mixing the dry substances with the right amount of liquid in a barrel or cone or on a plate or shaking table (Capes 1980; Emilsson 2006). Granulation seeks to improve the material's flow and processing properties, dust resistance, strength, external appearance, solubility and separation resistance. Granulation increases the product's market value and reduces the health risks associated with handling. Transport and storage of the material are also improved by the increased packing density. (Kuopanportti 2003) The ash's properties influence the effectiveness of the granulation process. The best granules are obtained with the use of pure, dry and fresh wood ash.

Ash granulation also provides the opportunity to change the ash's nutrition ratios by adding to it fertiliser or waste substances (Huotari 2012). According to Obernberger and Supancic, the recycling of ash to agricultural and forest land is already implemented to some extent in some European countries, for example, Finland, Sweden, Austria and Germany (Obernberger and Supancic 2009).

## 4 Materials and methods

### 4.1 The quantity and quality of ash produced in the region of Eastern Finland

The study investigated the quantities and quality of the grate and fly ash produced annually by biofuel-powered energy production plants in Eastern Finland (South Savo, North Karelia and North Savo). The ash quantities were obtained using a questionnaire survey, the environmental protection VAHTI information system, and relevant literature. The plants' annual ash output depends on many factors, such as the quality of fuel used in each plant, levels of plant maintenance, and the weather-dependent levels of demand for heat energy production. In addition, the operations of power plants in industrial localities are dependent on the country's economic conditions.

Samples of bottom and fly ash were taken from 31 Eastern Finland energy production plants in order to study the ash's properties and quality. The energy production plants were divided into the following size categories: under 5 MW, 5-10 MW, 11-50 MW and over 50 MW. 15 under 5 MW energy production plants were included in the sampling process. The boilers were grate boilers, and the main fuels used in them were wood-based fuels (bark, sawdust, whole tree chips, stem chips, forest processed chips, and industrial by-products). 10 of the study's production plants were in the 5-10 MW category. Four of these plants used a fluidised-bed boiler, nine had a grate boiler and two used pyrolysis. These plants primarily used wood-based fuels (wood residue chips, stump chips, whole tree chips, forest processed chips, sawdust and bark). Two other fuels used were milled peat and sod peat. There were four energy production plants in the 11-50 MW category, and all of these used fluidised-bed boilers. The fuels used were peat (60-100%) and wood-based fuels (sawdust, chips and bark). There were two power plants in the over 50 MW category, both of which used fluidised-bed boilers. These power plants used wood-based fuels and peat.

Bottom and fly ash samples were taken for analysis in line with the energy production plants' current ash processing systems either as combined bottom and fly ash samples or as separate samples. The samples were taken as composite samples. A composite sample is composed of primary samples taken daily over a period of two weeks. The staff of the energy production plants took the samples for the analysis in accordance with the instructions provided for the project.

The analysis of the bottom and fly ash samples from the energy production plants focused on contents of heavy metals and other harmful substances. To determine the total heavy metal concentrations in the ashes, the standard SFS-EN ISO 15587-2 was followed with modifications. The dried sample (about 0.5 g) was digested with a nitric acid (supra pure, 69 %) in a closed system using an autoclave (1.5 h). The total heavy metal concentration in the ashes was determined with a Thermo iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES). For determination of leached concentration of

dissolved heavy metals, the two-stage batch test according to standard SFS-EN 12457-3 was used (SFS-EN 2002). The metal concentrations (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Zn) in the extracts were determined with a Thermo Fisher Sciences iCAP6 Duo ICP-OES.

## **4.2 Processing fly ash using fractionation and ageing**

### **4.2.1 Processing power plant ash using fractionation**

Fly ash fractionation experiments were carried out in four different power plants (A, B, C, and D). The experiments were carried out in process conditions using the plants' electrostatic precipitators. During the experiments, the field voltages of the electrostatic precipitator were adjusted. Ash samples were taken during the experiments from the electrostatic precipitators' different fields. The ash samples were collected from the ash transmitter in the lower section of the electrostatic precipitator fields before the ash was fed into the silo. During the experiments, peat and wood-based fuels we used to fuel the energy production plants.

The analysis of the samples included measuring the ash particle size and the contents of heavy metals that inhibit fertiliser use (Pb, Cu, Zn, Ni, As and Cd). Heavy metal content was measured using the graphite method and particle size was determined using a Malvern device at the University of Oulu.

The fuels used in the fluidised-bed boiler in power plant A during the experiment included peat forest processed chips and the by-products of the mechanical wood processing industry. The power plant's flue gases were purified using the same 3-field electrostatic precipitator as was used for the fractionation experiments. The fuel used during the experiment in the fluidised-bed boiler in power plant B was milled peat mixed with wood fuels, soot and aluminium oxide. The experiments were carried out with a 2-field electrostatic precipitator. In power plant C, the experiments were carried out using a Pyroflow circulating fluidised-bed boiler. The fuels used in the power plant were primarily peat and different kinds of wood fuel. The boiler used a 3-field electrostatic precipitator, and the plant also had a second boiler in use. The fourth power plant (D) had a fluidised-bed boiler fuelled by milled peat and wood waste. The flue gases were processed at the plant using a 3-field electrostatic precipitator.

### **4.2.2 Processing of fly ash from energy production plants using ageing**

The ageing experiments on fly ash from energy production plants were carried out at the Metsäsairila Oy waste centre in a separately demarcated area. The research made use of fly ash from two different energy production plants (power plant and heating plant, fluidised-bed boilers). The fuels used were milled peat and different kinds of wood fuels

(including chips and sawdust). In addition, the research included fly ash from two industrial energy production plants which were fuelled primarily by wood-based industrial by-products.

As part of the ageing experiments, the ash samples were taken four times a year from the ash of two energy production plants and two industrial power plants. The samples were taken from the ash when it was fresh and then at an age of three months, six months, and around one year. The ash had been brought to the spoil tip around one month before the sampling.

For each ash pile, primary samples were taken from four different points and three different depths. The primary sample size was around two litres for each depth. The primary samples were mixed in a vat to produce a composite sample, from which around ten litres was taken for analysis. The ash samples from the energy production plants and the industrial energy production plants were taken in accordance with the sampling diagram shown in Table 9. One composite sample was composed of 24 primary samples.

Table 9: Sampling diagram for samples of landfilled fly ashes used in the ageing experiment.

Sampling chart of landfilled fly ashes																										
1. Depth of sampling point (cm)			2. Depth of sampling point (cm)			3. Depth of sampling point (cm)			4. Depth of sampling point (cm)			1. Depth of sampling point (cm)			2. Depth of sampling point (cm)			3. Depth of sampling point (cm)			4. Depth of sampling point (cm)					
0	3	5	0	3	5	0	3	5	0	3	5	0	3	5	0	3	5	0	3	5	0	3	5	0	3	5
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Combined composite sample: 24 pieces of sub-samples																										

To determine the total heavy metal concentrations in the ashes, the standard SFS-EN ISO 15587-2 was followed with modifications. The dried sample (about 0.5 g) was digested with a nitric acid (supra pure, 69 %) in a closed system using an autoclave (1.5 h). The total heavy metal concentration in the ashes was determined with a Thermo iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES). For determination of leached concentration of dissolved heavy metals, the two-stage batch test according to standard SFS-EN 12457-3 was used (SFS-EN 2002).

### 4.3 Granulation experiments on energy production plant fly ash

The experiments tested the productisation of mixtures of fractionated and unprocessed energy production plant fly ash and organic compost for use as fertiliser. The graded fly ash sample was collected in the first field of the energy production plant's 3-field electrostatic precipitator. The other type of fly ash used was taken from the energy

production plant's ash silos. During the experiments, the plants were primarily fuelled by wood-based fuels and peat.

The organic matter used in the experiments consisted of two sets of full grown compost filtered with a 20 mm filter. One of the composts used household biowaste as its raw material, while the other one used urban waste water.

The productisation was tested first at laboratory scale using a laboratory-scale granulation plate (diameter 0.4 m). The pilot productisation experiments also used a rotating granulation plate with a diameter of 1.0 m. The experiments used a mix ratio of 30% ash content and 70% fertiliser. Water was used as an additive in the granulation process. The functionality of the pilot experiment granules for arable farming were tested on a test field in Mikkeli. The nutrition and heavy metal content of the prepared granules was tested in an external laboratory. The soluble heavy metal contents were analysed by AAAC-EDTA leaching.

## 5 Results and discussions

### 5.1 Ash quantities and ash quality in Eastern Finland (I, II)

#### 5.1.1 Quantities of ash produced in the region of Eastern Finland (I)

According to this study, around 97,000 tonnes of bottom and fly ash were produced in the region of Eastern Finland. Of the energy production plants included in the research, the largest were producing over 10,000 tonnes of ash per year, while the smallest produced only a few tonnes per year. It can be assumed that the total annual quantity of ash would not significantly increase even if the smallest energy production plants in Eastern Finland were added to the calculations. The ash quantities are primarily based on the production plants' data for 2008. It should also be remembered that the plants' annual ash output depends on many factors, such as the type of fuel available at any point, levels of plant maintenance, and the weather-dependent levels of demand for heat energy production. In addition, the operations of power plants are dependent on the country's economic conditions. Annual variations in ash figures for the region can therefore be significant.

Around 21,350 tonnes of ash were produced in South Savo. This figure includes the energy production plants' bottom and fly ash. The region's largest ash producers are Etelä-Savon Energia Oy's Pursiala power plant, Suur-Savon Sähkö Oy's Savonlinna power plant, Versowood Oy, Järvi-Suomen Voima Oy UPM's Pellos plywood factory, Finnforest Oy's Punkaharju plywood factory and Savon Voima Oyj's Pieksämäki power plant. These six plants account for 93% of total ash production in the area. Around 51,800 tonnes of ash were produced in North Savo. This figure includes both bottom and fly ash. The area's largest ash producers are Kuopio Energia Oy's Haapaniemi power plant, Stora Enso's Varkaus power plant, Savon Sellu Oy's power plant, Savon Voima Oyj's Iisalmi power plant, UPM-Kymmene Wood Oy's Kuopio plywood factory, Fortum Power and Heat Oy's Lapinlahti power plant, Savon Voima Oyj's Suonenjoki power plant, Juankosken biolämpö Oy and Lapinlahden Ekolämpö Oy. These nine plants account for 97% of total ash production in the area. In 2008, around 24,000 tonnes of ash were produced in North Karelia. This figure includes both bottom and fly ash. The area's largest ash producers are Fortum Power and Heat Oy's Joensuu power plant, Fortum Power and Heat Oy's Uimaharju power plant, Vapo Oy's Kevätniemi power plant, UPM-Kymmene Wood Oy's Joensuu plywood factory and Nurmeksen lämpö Oy's Ritoniemi heating plant. These five plants account for around 94% of total ash production in the area. (Paper I) Table 10 presents the ash volumes generated in three provinces involved.

Table 10: The ash volumes generated in the region of Eastern Finland (Paper I).

Area	Ash amount (t/a)	Ash proportion (%)
South Savo	21,350	22
North Savo	51,800	53
North Karelia	24,000	25
Total	97,150	100

### 5.1.2 Quality of ash produced in the region of Eastern Finland (II)

Table 11 presents the lowest and highest values from the analysis results of the solubility experiments on the bottom and fly ash samples collected from the under 5 MW plants. There were a total of 17 samples analysed. The table also presents the limit values for waste submitted to inert, non-hazardous or hazardous waste landfill sites, as laid down in the relevant government decree (Government Decree 331/2013). In the original Paper II, the limit values of the previous Decree (Government Decree 202/2006) were presented. Therefore, in addition to the results and conclusions published in the original Paper II, some new conclusions about the fulfilments of the new limits value are also now presented.

Table 11: Range of variation of results for solubility tests of bottom and fly ash (L/S = 10 l/kg) from energy production plants (under 5 MW) and limit values used in assessment of waste submitted to landfill sites for inert, non-hazardous and hazardous waste (Government Decree 331/2013).

Substance/ variable	Inert waste landfill site	Non- hazardous waste landfill site	Hazardous waste landfill site	Bottom ash	Fly ash	Bottom and fly ash
(mg/kg) dry matter, (L/S = 10 l/kg)						
As	0.5	2	25	0.02-0.1	0.04-0.3	<0.02-0.2
Ba	20	100	300	3-11	2	1-300
Cd	0.04	1	5	<0.02	<0.02	<0.02
Cr	0.5	10	70	0.88-2.1	0.11-8.7	0.05-7.7
Cu	2	50	100	0.04-3.8	0.04-0.2	<0.02-6.9
Mo	0.5	10	30	0.32-0.9	0.95-4.3	0.07-3.4
Ni	0.4	10	40	0.03-0.4	<0.02	<0.02-0.9
Pb	0.5	10	50	0.05-0.1	0.04-1.0	<0.02-1.8
Sb	0.06	0.7	5	<0.06	<0.06	<0.06-0.15
Se	0.1	0.5	7	<0.1	<0.1-0.7	<0.1-1.9
Zn	4	50	200	0.06-1.2	12.1-14.3	<0.22-10.1
Cl <sup>-</sup>	800	15,000	25,000	176-853	3,219- 19,264	137-2,114
F <sup>-</sup>	10	150	500	<1-2	12-28	<1-9
SO <sub>4</sub> <sup>2-</sup>	1,000 <sup>1)</sup>	20,000	50,000	537-4,335	20,758	<80-7,310
DOC <sup>2)</sup>	500	800	1,000	<10-214	135-1604	<10-2,708
<p>1) The waste is also considered to fulfil the usage requirements if the sulphate content does not exceed the following values: 1,500 mg/l (first leach in flow-through test with extraction ratio of L/S = 0.1 l/kg) and 6,000 mg/kg (extraction ratio L/S = 10 l/kg). For determining the content with a extraction ratio of L/S = 0.1 l/kg, a flow-through test is to be used. Content in a extraction ratio of L/S = 10 l/kg can be determined using either a shaking test or flow-through test.</p>						
<p>2) If the limit value for dissolved organic carbon is exceeded in the waste's own pH, the waste can also alternatively be tested using a extraction ratio of L/S = 10 l/kg in a pH of 7.5-8.0. The waste is considered to fulfil the suitability requirement for dissolved organic carbon if the content is below 500 mg/kg for a inert waste landfill site, below 800 mg/kg for a non-hazardous waste to landfill site, and below 1000 mg/kg for a hazardous waste landfill site.</p>						

Table 12 below presents the lowest and highest values from the analysis results of the solubility experiments on the bottom and fly ash samples collected from the 5-10 MW plants. There were a total of 14 samples analysed.



Table 12: Range of variation of results for solubility tests of bottom and fly ash (L/S = 10 l/kg) from energy production plants (5-10 MW) and limit values used in assessment of waste submitted to landfill sites for inert, non-hazardous and hazardous waste (Government Decree 331/2013).

Substance/ variable	Inert waste landfill site	Non- hazardous waste landfill site	Hazardous waste landfill site	Bottom ash	Fly ash	Bottom and fly ash
(mg/kg) dry matter, (L/S = 10 l/kg)						
As	0.5	2	25	<0.02-0.1	0.02-0.2	<0.02-0.1
Ba	20	100	300	0.66-111	0.64-2	1.25-121
Cd	0.04	1	5	<0.02	<0.02	<0.02
Cr	0.5	10	70	0.03-0.1	0.06-2.2	0.09-1.2
Cu	2	50	100	<0.02	<0.02-2.7	<0.02-1.5
Mo	0.5	10	30	0.19-7.9	1.31-7.4	0.14-4.7
Ni	0.4	10	40	0.02-0.3	<0.02	<0.02-0.2
Pb	0.5	10	50	<0.02-1,1	<0.02-1.0	<0.02-0.2
Sb	0.06	0.7	5	<0.06	<0.06	<0.06
Se	0.1	0.5	7	<0.1-10.6	<0.1-9.9	<0.1-1.6
Zn	4	50	200	0.02-0.3	<0.02-24.7	0.06-6.7
Cl <sup>-</sup>	800	15,000	25,000	<100-136	784- 18,851	<100- 3,292
F <sup>-</sup>	10	150	500	<1	3-10	<1-6
SO <sub>4</sub> <sup>2-</sup>	1,000 <sup>1)</sup>	20,000	50,000	3,559- 4,264	6,924- 151,180	<80- 18,939
DOC <sup>2)</sup>	500	800	1,000	11-15	20-1,457	72-877
<p>1) The waste is also considered to fulfil the usage requirements if the sulphate content does not exceed the following values: 1,500 mg/l (first leach in flow-through test with extraction ratio of L/S = 0.1 l/kg) and 6,000 mg/kg (extraction ratio L/S = 10 l/kg). For determining the content with an extraction ratio of L/S = 0.1 l/kg, a flow-through test is to be used. Content in an extraction ratio of L/S = 10 l/kg can be determined using either a shaking test or flow-through test.</p> <p>2) If the limit value for dissolved organic carbon is exceeded in the waste's own pH, the waste can also alternatively be tested using an extraction ratio of L/S = 10 l/kg in a pH of 7.5-8.0. The waste is considered to fulfil the suitability requirement for dissolved organic carbon if the content is below 500 mg/kg for an inert waste landfill site, below 800 mg/kg for a non-hazardous waste to landfill site, and below 1000 mg/kg for a hazardous waste landfill site.</p>						

Table 13 presents the lowest and highest values from the analysis results of the solubility experiments on the bottom and fly ash samples collected from the 11-50 MW plants. There were a total of 11 samples analysed.

Table 13: Result averages for solubility tests of bottom and fly ash (L/S = 10 l/kg) of energy production plants (11-50 MW and over 50 MW) and limit values used in assessment of waste submitted to landfill sites for inert, non-hazardous and hazardous waste (Government Decree 331/2013).

Substance/variable	Inert waste landfill site	Non-hazardous waste landfill site	Hazardous waste landfill site	Bottom ash	Fly ash	Bottom and fly ash
(mg/kg) dry matter, (L/S = 10 l/kg)						
As	0.5	2	25	0.02-0.1	0.02-0.1	0.02-0.2
Ba	20	100	300	1-20	2	1-5
Cd	0.04	1	5	<0.02	<0.02	<0.02
Cr <sub>kok</sub>	0.5	10	70	0.19-0.4	1.37-2.1	<0.02-0.2
Cu	2	50	100	<0.02	<0.02	<0.02-0.1
Mo	0.5	10	30	0.87-3.9	2.08-5.3	0.15-0.5
Ni	0.4	10	40	<0.02-0.4	<0.02	0.03-0.3
Pb	0.5	10	50	0.02-0.4	0.15-0.4	0.05-0.1
Sb	0.06	0.7	5	<0.06	<0.06	<0.06
Se	0.1	0.5	7	<0.1-7.2	0.9-6.8	<0.1-14.7
Zn	4	50	200	<0.02-3.9	0.08-3.4	0.06-0.3
Cl <sup>-</sup>	800	15,000	25,000	293-2,239	2,787-2,915	17-213
F <sup>-</sup>	10	150	500	<1-15	11-12	<1-5
SO <sub>4</sub> <sup>2-</sup>	1,000 <sup>1)</sup>	20,000	50,000	4,074-6,162	11,855-42638	<80
DOC <sup>2)</sup>	500	800	1,000	10-37	11-115	25-52
<p>1) The waste is also considered to fulfil the usage requirements if the sulphate content does not exceed the following values: 1,500 mg/l (first leach in flow-through test with extraction ratio of L/S = 0.1 l/kg) and 6,000 mg/kg (extraction ratio L/S = 10 l/kg). For determining the content with a extraction ratio of L/S = 0.1 l/kg, a flow-through test is to be used. Content in a extraction ratio of L/S = 10 l/kg can be determined using either a shaking test or flow-through test.</p> <p>2) If the limit value for dissolved organic carbon is exceeded in the waste's own pH, the waste can also alternatively be tested using a extraction ratio of L/S = 10 l/kg in a pH of 7.5-8.0. The waste is considered to fulfil the suitability requirement for dissolved organic carbon if the content is below 500 mg/kg for a inert waste landfill site, below 800 mg/kg for a non-hazardous waste to landfill site, and below 1000 mg/kg for a hazardous waste landfill site.</p>						

Table 14 presents the lowest and highest values from the heavy metals analysis results for the bottom and fly ash samples collected from the under 5 MW plants. There were a total of 17 samples analysed. Table also present the limit values of forest fertiliser given in current Finnish Decree (Decree 24/2011). In the original Paper II, the limit values of the previous Decrees (EVIRA 2008; Government Decree 591/2006) were presented. Therefore, in additional to the results and conclusions published in the original Paper II,

some new conclusions about the fulfilments of the new limits value are also now presented.

Table 14: Range of variation of results from heavy metal analysis of fly ash samples from energy production plants (under 5 MW) and limit values for utilisation of ash fertiliser (mg/kg of dry matter). Other ash use refers to ash use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Harmful substance	Forest use (mg/kg)	Other use (mg/kg)	Bottom ash (mg/kg)	Fly ash (mg/kg)	Bottom and fly ash (mg/kg)
As	40	25	3-4	8-76	1-33
Ba			2,093-2,870	678-1,774	<1,000-3,910
Cd	25	2.5	0.5-2.1	13-37	<0.04-22.5
Cr	300	300	23-67	26-99	12-177
Cu	700	600	99-141	153-258	49-426
Pb	150	100	11-16	29-257	7-84
Mo			<0.04-1	0.92-5	<0.04-3
Ni	150	100	28-32	27-33	13-30
V			18-44	14-35	6-55
Zn	4,500	1,500	256-546	1,889-15,530	62-1,998

Table 15 below presents the lowest and highest values from the heavy metal analysis results on the bottom and fly ash samples collected from the 5-10 MW plants. There were a total of 14 samples analysed.

Table 15: Range of variation of results from heavy metal analysis of fly ash samples from energy production plants (5-10 MW) and limit values for utilisation of ash fertiliser (mg/kg of dry matter). Other ash use refers to ash use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Harmful substance	Forest use (mg/kg)	Other use (mg/kg)	Bottom ash (mg/kg)	Fly ash (mg/kg)	Bottom and fly ash (mg/kg)
As	40	25	1-16	4-64	<0.04-29
Ba			<1,000-3,158	<1,000-1,915	<1,000-3,426
Cd	25	2.5	<0.04-0.4	4.0-19.4	<0.04-6.2
Cr	300	300	9-122	11-159	10-84
Cu	700	600	14-202	61-366	24-197
Pb	150	100	6-23	35-208	6-56
Mo			0.5-5	2-14	<0.04-12
Ni	150	100	9-64	10-81	8-73
V			<400	<400	<400
Zn	4,500	1,500	34-166	199-3,352	65-5,020

Table 16 presents the lowest and highest values from the heavy metal analysis results on the bottom and fly ash samples collected from the 11-50 MW and over 50 MW plants. There were a total of 11 samples analysed.

Table 16: Results' range of variation from heavy metal analysis of fly ash samples from energy production plants (11-50 MW and over 50 MW) and limit values for utilisation of ash fertiliser (mg/kg of dry matter). Other ash use refers to ash use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Harmful substance	Forest use (mg/kg)	Other use (mg/kg)	Bottom ash (mg/kg)	Fly ash (mg/kg)	Bottom and fly ash (mg/kg)
As	40	25	13-65	4-30	1-17
Ba			<1,000-1,422	1,173-1,629	<1,000-1,131
Cd	25	2.5	2.5-5.1	3.1-4.8	<0.04-0.27
Cr	300	300	24-75	26-53	16-29
Cu	700	600	40-99	68-114	47-48
Pb	150	100	28-116	41-70	11-16
Mo			3-8	2-9	<0.04-1
Ni	150	100	24-44	33-39	12-40
V			38-137	62-63	17-38
Zn	4,500	1,500	88 -1,077	649-1,386	1,000-1,510

### 5.1.3 Analysis of results (II)

The following section examines the results of the solubility tests and heavy metal analyses carried out on the bottom and fly ash samples from the Energy production plants (under 5 MW, 5-10 MW, 11-50 MW and over 50 MW). The results have been compared in article II to the Government Decree 202/2006 limit values for solubility properties and, with regards to heavy metal content, to the Government Decree 591/2006 limit values and maximum contents for hazardous field and forest ash substances. In this analysis, the results for solubility properties are compared with the Government Decree 331/2013 and Government Decree 843/2017 limit values and the results for heavy metal content are compared with the maximum contents for harmful substances in ash fertiliser (Decree 24/2011).

#### *Landfill eligibility*

The study specified the solubility properties of bottom and fly ash samples for fifteen under 5 MW energy production plants, in order to establish the suitability of the material for landfill sites. For thirteen of the energy production plants in the under 5 MW size category, the ash sample was taken from the bottom boiler such that it was composed of both bottom and fly ash. Based on the analysis results, the ash from seven of these plants would be suitable for a non-hazardous waste landfill site, and five would be suitable for a hazardous waste landfill site. One of the ash samples would be suitable for a non-hazardous waste landfill site, but its DOC content exceeds the limit values for landfill sites (the limit value for hazardous waste landfill sites is 1000 mg/kg). Different ash samples exceeded the limit values of inert waste landfill sites for various substances,

including Ba, Cr, Cu, Mo, Ni, Sb, Pb, Se, Cl, sulphate and DOC. For non-hazardous waste landfill sites, the limit values for Ba and Se content were exceeded.

For two under 5 MW plants, the bottom and fly ash samples were analysed separately. The bottom ash from these bottom boiler plants was suitable for non-hazardous waste landfill sites (limit values for inert waste landfill sites were exceeded for Cr, Cu, Mo, Si and sulphate). The plants' wood-based fly ash (logging residue chips and whole tree chips) exceeded the limit values for inert waste landfill sites for Cr, Mo, Pb, Zn, Cl and F. For non-hazardous waste landfill sites, the limit values for Se, Cl and sulphate were exceeded. In addition, the DOC content of one of the fly ash samples exceeded the limit value for hazardous waste landfill sites.

10 of the study's energy production plants were in the 5-10 MW category. The ash sample from seven plants was taken such that it was composed of a mix of the plant's bottom and fly ash. The analysed mixed samples (bottom and fly ash) were suitable for either non-hazardous waste (five plants) or hazardous waste (two plants) landfill sites. For non-hazardous waste landfill sites, the limit values for Se, DOC and Ba were exceeded. Various inert waste landfill site limit values were exceeded by different samples, including Ba, Cr, Mo, Se, Zn, Cl, sulphate and DOC.

For some of the energy production plants (size category 5-10 MW), the bottom and fly ash samples were analysed separately. Of the bottom ash samples, only one was suitable for non-hazardous waste landfill sites (sulphur content exceeded limit value for inert waste landfill sites of 1000 mg/kg). Other samples exceeded the Se content limit values for non-hazardous or hazardous waste landfill sites. Of the fly ash analysed from four different energy production plants, the results indicated that only one was suitable for non-hazardous waste landfill sites. Three of the samples exceeded the non-hazardous waste limit value for Se (0.5 mg/kg), and thus this fly ash produced by peat and wood combustion, if unprocessed, could only be dumped in a hazardous waste landfill site.

For the size category 11-50 MW, an analysis was made of the solubility properties of fly ash samples from four energy production plants. Based on the results, the fly ash from three of the energy production plants would be suitable for non-hazardous waste landfill sites. The solubility properties of all the analysed fly ash exceeded the Mo and sulphate content limit values for inert waste landfill sites. In addition, some samples exceed the inert waste landfill site limit values for Ni, Ba, Cl and fluoride content. The Se content of one fly ash sample exceeded the limit value for hazardous waste landfill sites, although the ash would otherwise be suitable for a non-hazardous waste landfill site.

The ash solubility properties were determined for the bottom and fly ash from two power plants from the over 50 MW size category. Of the bottom ash analysed, one was suitable for a non-hazardous waste landfill site, having exceeded the Mo content limit value for inert waste landfill sites (0.5 mg/kg). The fly ash of the other power plant, on the other hand, exceeded the Se content limit value for hazardous waste landfill sites (7 mg/kg). In other respects, the ash would be suitable for a inert waste landfill site. For the fly ash,

inert waste landfill site limit values were exceeded for Cr, Mo, fluoride and sulphate. For non-hazardous waste landfill sites, the limit values for Se content were exceeded. Based on the results, the power plants' peat and wood-based fly ash would be only be suitable for hazardous waste landfill sites.

#### *Utilisation in earth construction or as an ash fertiliser*

During research, the heavy metal concentrations found in mixed ash samples (bottom and fly ash) taken from thirteen energy production plants under 5 MW were analysed. The analysis revealed that mixed bottom and fly ash from nine grate boiler plants would be suitable for other purposes and the mixed ash from four plants would be suitable for use as a forest fertiliser. The limit values for other purposes were exceeded where As, Cd and Zn concentrations were concerned. The heavy metal concentrations of bottom and fly ash samples were analysed separately at two energy production plants. Bottom ash samples would be suitable for other purposes. Of the fly ash samples taken, only one would be suitable for use as forest fertiliser (As, Cd and Zn concentrations exceeded the limit values for other purposes). The As, Cd, Pb and Zn concentrations in the other sample prevented its use as a fertiliser.

The solubility concentrations of hazardous substances in six mixed ash samples (from plants under 5 MW) exceeded the limit values set for using bottom and fly ash in earth construction (paved structures). The excessive concentrations found in the samples were Ba, Se and DOC. The mixed ash from three grate boiler plants would be suitable for use as an road constructed of crushed stone and ash and the mixed ash from 4 plants would be suitable for paved roadway construction. Wood-based fuels (at one plant, 40% of the fuel used was sod peat) were primarily in use at the time of the sampling.

The heavy metal concentrations of bottom and fly ash samples were analysed separately at two energy production plants. These types of bottom ash would be suitable for use as an road constructed of crushed stone and ash. The fly ash samples would not be suitable for use in road construction without processing, including cases involving paved roadways. National limit values for selenium, sulphate and DOC concentrations were exceeded.

In 5-10 MW plants, mixed ash samples (bottom and fly ash) from seven energy production plants were analysed. Of these plants, four were using grate boilers, two were using pyrolysis systems and one was using a fluidised bed boiler. The heavy metal concentrations in mixed ash from five of the plants made the ash suitable for other purposes and forest applications. Furthermore, the mixed ash from one plant would be suitable for use as a forest fertiliser (Cd concentration exceeds the field ash limit value of 2.5 mg/kg). The Zn concentration at one plant exceeds the limit values required for fertiliser use (4,500 mg/kg). The mixed ash from four plants would not be suitable for use in earth construction. The solubility concentrations for hazardous substances were exceeded with regard to selenium, sulphate and DOC. Two of the ash types would be

suitable for use as a road constructed of crushed stone and ash and one for paved roadway construction.

Fly ash samples from four 5-10 MW energy production plants (two fluidised-bed boilers and one grate boiler) were analysed. The fly ash from three of these plants would be suitable for use as forest fertiliser (the Cd concentration exceeds the limit value for other purposes, i.e. 2.5 mg/kg). The fly ash from one of the plants, which was using wood-based fuels at the time of the sampling, exceeds the statutory requirements for As and Pb concentrations.

Of the analysed ash samples (5-10 MW plants), only the fly ash from one of the plants would be suitable for use in paved roadway construction. The concentrations from four of the plants exceeded the solubility of hazardous substances with regard to, for example, barium, selenium, sulphate and DOC. The heavy metal concentrations in bottom ash samples from three 5-10 MW plants were also analysed. Two of the bottom ash samples would be suitable for use as a road constructed of crushed stone and ash. The bottom ash from one of the plants would not be suitable for use in earth construction without processing due to its excessive solubility concentrations of selenium, molybdenum and barium.

Fly ash samples from four 11-50 MW energy production plants were included in the research. All of the plants used fluidised-bed boilers, whose fuel was 60-100% peat and 0-40% wood at the time samples were taken. According to the heavy metal analysis results, the fly ash from only one of the plants would be suitable for use as a forest fertiliser. The concentrations of fly ash from other plants exceeded statutory fertiliser requirements for As concentration (40 mg/kg).

In terms of solubility concentrations, the fly ash from three of the plants (11-50 MW) would be suitable for use in earth construction (paved roadway construction), while the ash from one of the plants exceeds the limit value requirements for Se (1 mg/kg L/S ratio of 10 l/kg). The fly ash from only one of the plants met the solubility concentration requirements for use as a road constructed of crushed stone and ash.

Two over 50 MW power plants were included in the research. At the time samples were taken, these plants were run on peat and wood-based fuels. Fly ash would be suitable for use as forest fertiliser (Cd concentrations and the As concentration of one plant exceeded the limit values for other purposes). The relatively high Cd concentration of the fly ash samples taken from the power plants is likely due to the use of wood-based fuels. A high As concentration in one of the fly ash samples might have been due to the type of peat used by the power plant.

The bottom ash from only one of the power plants would be suitable for use as a road constructed of crushed stone and ash. The fly ash samples and one of the bottom ash samples exceed the concentrations for hazardous substances (mg/kg L/S-ratio of 10 l/kg)



permitted in earth construction (paved roadway construction) with regard to, for example, selenium and sulphate concentrations.

## 5.2 Processing fly ash using fractionation and ageing (III, IV)

### 5.2.1 Power plant ash processing by fractionation - results and discussions (III)

During the tests, the fuel used by power plant A was 49% peat and 51% wood. The ash funnels of fields' 1-3 of the electrostatic precipitator were sampled and analysed. During trial runs 1-6, the CBO ratio of the fields was changed and, during trial run 7, the maximum voltage setting of electrostatic precipitator field 1 was changed. The Table 17 shows the Cd concentrations during the trial runs. In the original Paper III, the limit values of the previous Decree (46/1994) were presented. Therefore, in addition to the results and conclusions published in the original Paper III, some new conclusions about the fulfilments of the new limits value are also now presented.

Table 17: Cd concentrations (mg/kg of dry matter) of electrostatic precipitator fields at power plant A during trial runs.

Test number	Field 1 (mg/kg)	Field 2 (mg/kg)	Field 3 (mg/kg)
1	3.6	6.6	8.2
2	2.6	6.0	12.4
3	2.9	5.3	9.8
4	2.8	5.1	7.2
5	2.9	5.4	7.4
6	2.4	5.4	7.7
7	2.2	5.1	7.4

According to the results obtained, the Cd concentration is at its minimum level in field 1 and maximum level in field 3. This is due to the fact that fly ash particles with a larger grain size are collected in field 1 and ash mostly containing fine particles is found in field 3. The Cd concentration in field 1 ranged between 2.2-3.6 mg/kg, depending on the trial run. The Cd concentration of the last field ranged between 7.2-12.4 mg/kg. The concentrations were affected by, for example, the field filter voltage, fuel type and flue gas flow rate. The limit value for fertiliser use at the maximum permitted cadmium concentration is, for other purposes, 2.5 mg/kg and, for forest applications, 25 mg/kg (Decree 24/2011; EVIRA 2016). The Cd concentration falls below the limit value for forest use in almost every electrostatic precipitator field, but it fails to reach the permitted ash limit value (2.5 mg/kg) for other purposes in field 1 (as in trial run 7).

During trial runs, the electrostatic precipitator fields' CBO ratio (cycle block in operation) was controlled within the range 0-12. The value 0 means that all the half-cycles of the

field in question are currently active. The most important thing is to be able to influence and change the properties of field 1 in the electrostatic precipitator. The first field enables the production of fly ash with heavy metal concentration levels that make it suitable as a fertiliser, for example.

The results show that an increase in the CBO ratio will reduce the separation efficiency for fine particles. A reduction in the maximum voltage setting will also compromise the filter's separation efficiency of fine particles even more so than a change in the CBO ratio. Changes in the CBO ratio also affect the filter voltage (kV) and filter current (mA).

The particle size distributions of the samples were also defined. The Table 18 shows the particle size classes ( $\mu\text{m}$ ), D10 and D50, for fields 1-3 in trial runs 5, 6 and 7 at power plant A. D10 is the particle size, in which 10% of the sample particles are smaller than D10 and 90% are larger than D10. D50 is the 'mass median diameter', in which 50% of a sample's mass is comprised of smaller particles for a ratio of 50/50.

Table 18: The particle size classes ( $\mu\text{m}$ ) D10 and D50 of the fly ash in the electrostatic precipitator fields and ash Cd concentrations (mg/kg of dry matter).

Test number and particle size classes and Cd concentration	Field 1 ( $\mu\text{m}$ )	Field 2 ( $\mu\text{m}$ )	Field 3 ( $\mu\text{m}$ )	Field 1 (mg/kg)	Field 2 (mg/kg)	Field 3 (mg/kg)
Test 5 D10	3.6	1.6	1.3	2.9	5.4	7.4
Test 5 D50	16.3	12.3	8.2			
Test 6 D10	3.4	1.7	1.1	2.4	5.4	7.7
Test 6 D50	17.4	10.7	6.3			
Test 7 D10	5.2	1.5	1.1	2.2	5.1	7.4
Test 7 D50	25.0	12.2	6.5			

The table shows that the smaller particles are found in the last field of the electrostatic precipitator. These fine particles also contain the most heavy metals. Larger particles are found in the first field of the electrostatic precipitator. In order to meet the permit limit for other purposes (2.5 mg/kg) with regard to Cd concentration, the particle size must be  $<16 \mu\text{m}$ . When interpreting the results, attention should be given to the fact that the fly ash from different power plants have very different particle size distributions.

The cadmium concentrations were highest in power plant D (Table 19). This is due to the higher percentage of wood used in the fuel as compared to other power plants. In fractionation, the ash cadmium concentration in field 3 of the electrostatic precipitator was, at most, five times higher than in field 1. Despite this, ash could not be fractionated effectively enough in power plant D. In power plant B, the Cd concentration falls below the ash limit value for other purposes of 2.5 mg/kg in each field. An acceptable concentration level was also achieved in power plant C. The ash produced by power plant D was only suitable for use in forest applications.

Table 19: Ash Cd concentrations in different electrostatic precipitator fields (mg/kg of dry matter) at power plant B, C and D.

Test boiler	Field 1 (mg/kg)	Field 2 (mg/kg)	Field 3 (mg/kg)
B	1.3	1.8	
B	1.1	1.8	
B	1.0	1.6	
C	1.3	2.1	2.2
C	1.3	2.6	2.6
C	1.6	2.3	2.6
D	4.2		21.0
D	13.4		20.2
D	4.8		16.5

Many hazardous metals, such as arsenic, cadmium, manganese, molybdenum, lead and zinc, are strongly bound to inorganic materials. According to the given evaporative properties, a certain percentage of different metals evaporate during incineration, condensing to form fine particles in the flue gas stack. Lead, cadmium, zinc, selenium, arsenic, antimony and molybdenum, among others, have been found to strongly enrich fine particles. (Aunela and Larjala 1990; Pöykiö et al. 2009) According to Laine-Ylijoki et al., the evaporation temperature of cadmium is 214 degrees, and its state is vapourised/condensed with the fluidised-bed boiler incineration temperature at 800-850 degrees (Laine-Ylijoki et al. 2002). When the temperature is 850 degrees, cadmium is broken down into size classes as follows: size  $<0.6\mu\text{m}$   $<26\%$ ,  $0.6-5\mu\text{m}$   $<24\%$  and  $>5\mu\text{m}$   $66-97\%$  (Hupa 1998). The number of particles being removed and the particle size distribution play key roles in the function of an electrostatic precipitator. Due to the different electric charging properties of particles, their separation efficiency varies as a function of particle size. The most difficult particle size class is  $0.2-0.5\mu\text{m}$ . (Nykänen 1993; Kouvo 2003)

According to fractionating tests conducted with an electrostatic precipitator, it can be stated that heavy metal concentrations are at their lowest level when the electrostatic precipitator is in field 1 and at their highest level when it is in field 3. Fine particles are enriched by heavy metals. The largest fly ash particles are collected in the first field of the electrostatic precipitator, whilst ash containing more fine particles are found in the last field. It is for this reason that the dust in field 1 of the electrostatic precipitator contains fewer heavy metals. The heavy metal concentrations of ash are affected by, for example, the field filter voltage, fuel type and flue gas flow rate. These findings are backed up by studies conducted by Manskinen et al. at a 120 MW power plant and tests conducted by Thun and Korhonen with a three-field electrostatic precipitator, in which the heavy metal concentrations in the last field of the electrostatic precipitator were significantly higher than in the other fields (Manskinen et al. 2011; Thun and Korhonen 1999).

A problem with incinerating wood is that the Cd and Zn concentrations can be increased, whereas As concentration levels are increased when incinerating peat. However, the concentrations of these metals depend a great deal on the fuel being used. Particularly when using wood as a fuel, Cd and Zn concentrations can vary extremely widely. Cadmium was the most problematic metal, and it was not always possible to achieve the statutory fertiliser limit values despite adjustments to the electrostatic precipitator. The cadmium concentration of ash being used for fertiliser can be reduced as much as 70% by fractionating with an electrostatic precipitator. Other heavy metal concentrations cannot be reduced quite as much (Ni, Pb and Cu). Statutory limits can be achieved for arsenic concentrations, but there may be a need to adjust the electrostatic precipitator if the arsenic concentration in the peat being used is very high. Universally applicable values cannot be defined for the electrostatic precipitator parameters used in fractionation. The heavy metal concentrations of the fuels being used can vary a great deal, and there is no way to know what the need for fractionating is if the fuel used has not been analysed.

### **5.2.2 Results and discussion of processing of energy production plant ash using ageing (III)**

Table 20 below presents the results of the solubility experiments carried out on the fly ash from the energy production plants. The table also presents the limit values for the use in earth construction sites of fly and bottom ash produced by combustion of coal, peat and wood-based material, as laid down in the relevant Government Decree (843/2017). In the original Paper IV, the limit values of the previous Government Decree (403/2009) were presented. Therefore, in addition to the results and conclusions published in the original Paper IV, some new conclusions about the fulfilments of the new limits value are also now presented.

Table 20: Results of the solubility tests from the ageing experiment on energy production plant fly ash (L/S = 10 l/kg) and earth construction sites limit values. Highest permitted solubility (mg/kg L/S ratio 10 l/kg) and content (mg/kg of dry matter) of harmful substances and highest permitted layer thickness for earth construction sites: roadway and road constructed of crushed stone and ash (Government Decree 843/2017).

Harmful substance	Limit value Roadway (thickness of waste layer ≤1.5m)		Limit value Road constructed of crushed stone and ash <sup>1)</sup> (thickness of waste layer ≤0.2 m)	Fresh sample	Sample 3 months	Sample 6 months	Sample 11 months
	Solubility (mg/kg L/S = 10 l/kg) Covered structure	Solubility (mg/kg L/S = 10 l/kg) Paved structure					
As	1	2	2	0.04	0.03	0.04	0.03
Ba	40	100	80	1.74	1.54	1.23	1.19
Cd	0.04	0.06	0.06	<0.02	<0.02	<0.02	<0.02
Cr	2	10	5	1.42	0.58	0.48	0.52
Cu	10	10	10	0.21	<0.02	0.02	0.03
Hg	0.03	0.03	0.03	not analysed			
Mo	1.5	6	2	3.27	2.69	2.58	2.96
Ni	2	2	2	0.06	0.07	0.07	<0.02
Pb	0.5	2	1	0.03	0.07	0.05	<0.02
Sb	0.7	0.7	0.7	<0.6	<0.6	<0.6	0.13
Se	1	1	1	<0.1	0.2	0.1	0.2
Zn	15	15	15	1.21	0.09	0.05	0.11
Chloride <sup>2)</sup>	3,200	11,000	4,700	1,588	1,518	798	1,516
Fluoride <sup>2)</sup>	50	150	100	<1	<1	<1	<1
Sulphate <sup>2)</sup>	5,900	18,000	6,500	7,277	9,773	16,247	17,253
DOC	500	500	500	63	34	13	10

1) The layer thickness of a road constructed of crushed stone and ash has been set as the calculated thickness of the filling layer

2) The limit values given in the table for chloride, sulphate and fluoride are not applied to structures which fulfil all the following conditions: location is no more than 500m from the sea, the discharge direction for water percolating through the structure is towards the sea, and there are no wells located between the structure and the sea which are used for domestic water supply

Table 21 below presents the results of the solubility experiments carried out on the fly ash samples from industrial energy production plants. The table also presents the limit values for the use in earth construction sites of fly and bottom ash produced by combustion of coal, peat and wood-based material, as laid down in the relevant Government Decree (843/2017).

Table 21: Results of the solubility tests from the ageing experiment on industrial energy production plant fly ash (L/S = 10 l/kg) and earth construction sites limit values. Highest permitted solubility (mg/kg L/S ratio 10 l/kg) and content (mg/kg of dry matter) of harmful substances and highest permitted layer thickness for earth construction sites: roadway and road constructed of crushed stone and ash (Government Decree 843/2017).

Harmful substance	Limit value Roadway (thickness of waste layer ≤1.5m)		Limit value Road constructed of crushed stone and ash <sup>1)</sup> (thickness of waste layer ≤0.2 m)	Fresh sample	Sample 3 months	Sample 6 months	Sample 11 months
	Solubility (mg/kg L/S = 10 l/kg) Covered structure	Solubility (mg/kg L/S = 10 l/kg) Paved structure					
As	1	2	2	0.21	0.21	0.06	0.06
Ba	40	100	80	27.05	1.21	0.9	<0.02
Cd	0.04	0.06	0.06	<0.02	<0.02	<0.02	<0.02
Cr	2	10	5	1.99	1.71	0.56	0.45
Cu	10	10	10	0.83	2.04	0.41	0.37
Hg	0.03	0.03	0.03	not analysed			
Mo	1.5	6	2	2.15	0.85	0.24	0.15
Ni	2	2	2	0.04	0.18	0.26	<0.02
Pb	0.5	2	1	0.05	0.16	0.18	0.16
Sb	0.7	0.7	0.7	<0.06	<0.06	<0.06	<0.06
Se	1	1	1	<0.1	<0.1	<0.1	<0.1
Zn	15	15	15	1.31	2.15	0.41	0.18
Chloride <sup>2)</sup>	3,200	11,000	4,700	1,267	1,320	677	267
Fluoride <sup>2)</sup>	50	150	100	3.8	<1	<1	2.3
Sulphate <sup>2)</sup>	5,900	18,000	6,500	7,535	10,793	2,430	2,643
DOC	500	500	500	413	421	122	71

1) The layer thickness of a road constructed of crushed stone and ash has been set as the calculated thickness of the filling layer

2) The limit values given in the table for chloride, sulphate and fluoride are not applied to structures which fulfil all the following conditions: location is no more than 500m from the sea, the discharge direction for water percolating through the structure is towards the sea, and there are no wells located between the structure and the sea which are used for domestic water supply

In addition to the solubility test, heavy metal evaluations were also made for the ash samples in the ageing experiment. Table 22 below presents the changes in heavy metal content observed during the ageing experiment in the energy production plant fly ash.

Table 22: Results from heavy metal analysis of fly ash samples from energy production plants and limit values for utilisation of ash fertiliser (mg/kg of dry matter). Other ash use refers to ash use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Harmful substance	Forest use (mg/kg)	Other use (mg/kg)	Fresh sample (mg/kg)	Sample 3 months (mg/kg)	Sample 6 months (mg/kg)	Sample 11 months (mg/kg)
As	40	25	27	23	23	30
Ba			874	727	839	793
Cd	25	2.5	3.6	3.8	2.8	3.5
Cr	300	300	39	43	40	26
Cu	700	600	76	83	77	94
Hg	1	1	not analysed			
Pb	150	100	46	53	42	55
Mo			10	10	7	9
Ni	150	100	31	35	34	34
V			42	40	52	52
Zn	4,500	1,500	492	269	390	509

Table 23 below presents the changes in heavy metal content observed during the ageing experiment in the fly ash samples from industrial energy production plants. The table also presents the limit values for utilisation of ash fertiliser (mg/kg of dry matter).

Table 23: Results from heavy metal analysis of fly ash samples from industrial energy production plants and limit values for utilisation of ash fertiliser (mg/kg of dry matter). Other ash use refers to ash use in agriculture, gardening and landscaping. (Decree 24/2011; EVIRA 2016)

Harmful substance	Forest use (mg/kg)	Other use (mg/kg)	Fresh sample (mg/kg)	Sample 3 months (mg/kg)	Sample 6 months (mg/kg)	Sample 11 months (mg/kg)
As	40	25	5	5	7	6
Ba			2,273	2,389	2,517	2,096
Cd	25	2.5	3.2	3.2	3.5	4.4
Cr	300	300	21	21	25	22
Cu	700	600	105	108	114	129
Hg	1	1	not analysed			
Pb	150	100	28	27	27	34
Mo			2	1	0	0
Ni	150	100	28	28	29	29
V			59	48	56	67
Zn	4,500	1,500	1,584	1,670	1,862	1,855

The fly ash ageing experiment involved observing the changes to the solubility properties and heavy metal contents in the fly ash from two energy production plants and two industrial production plants over a period of just under a year. The samples were taken from the ash when it was fresh and then at an age of three months, six months, and just under a year. The ash piles were not protected or stacked during the experiment. Some of the piles saw hardening of the surface level due to weather effects (such as reactions in the ash caused by moisture). During the storage period, no dust emission from the ash piles was observed, despite the fact that the piles were uncovered.

For the substances analysed, the quality upon arrival of the energy production plants' mixed combustion (peat and wood-based fuels) fly ash met the solubility limit values for paved roadway structures in earth construction sites. The limit values for road constructed of crushed stone and ash and covered roadways were exceeded for molybdenum and sulphate (Government Decree 843/2017). The ageing of the ash piles did not change the contents of the above substances to the extent that the ash would have met the road constructed of crushed stone and ash quality requirements. The ageing process decreased the ash's contents of barium, cadmium, chromium, copper, molybdenum, nickel, lead, zinc, fluorine and dissolved organic carbon (DOC). There was no decrease in arsenic, antimony, selenium, chloride or sulphate content. During the experiment, the samples' pH value dropped from 10.9 to 9.7.

In their initial state, the energy production plant fly ash met the heavy metal content requirements for forest use, while for other use it exceeded the content requirements for arsenic and cadmium. Ageing decreased the contents of barium, cadmium, chromium and molybdenum, but other levels of other metals saw no change during the experiment. Cadmium content did not decrease sufficiently to meet the quality requirements of fertiliser legislation for other use (Decree 24/2011; EVIRA 2016).

The industrial energy production plants had mostly been fuelled by wood-based industrial by-products. The quality upon arrival of the industrial energy production plants' mixed combustion (peat and wood-based fuels) fly ash also met the solubility limit values for paved roadway structures in earth construction sites. The limit values for road constructed of crushed stone and ash and covered roadways were exceeded for molybdenum and sulphate (Government Decree 843/2017). The ageing process reduced the ash's molybdenum and sulphate contents to such a large extent that they fell within the limit values for road constructed of crushed stone and ash and covered roadways. The ageing experiment saw a lowering of the contents of arsenic, barium, cadmium, chromium, copper, molybdenum, nickel, zinc, chloride, fluorine, sulphate and dissolved organic carbon (DOC). There was no decrease in lead content, and no antimony or selenium was found in the samples. During the experiment, the samples' pH content dropped from 13.1 to 12.5.

In their initial state, the industrial energy production plant fly ash met the heavy metal content requirements for forest use, while for other use they exceeded the content requirements for cadmium and zinc. The ageing process decreased only barium content.



The ageing did not decrease cadmium or zinc content sufficiently to meet the quality requirements of the Fertiliser Act for other use (Decree 24/2011; EVIRA 2016).

From the results of the ageing experiment it could be observed that the ash's natural ageing and solubility behaviour were different for the different fly ash being studied. The fly ash samples studied had different pH values and different quantities of DOC compounds, which in turn influenced their solubility properties during the experiment. For the fly ash from industrial energy production plants fuelled by wood-based fuels, a reduction of sulphate content of over 60% was achieved during the experiment. After the experiment, contents of sulphate and all other elements met the current requirements for earthwork construction, including construction of ash aggregate roads (Government Decree 843/2017). A significant difference was observed during the experiment in the sulphate solubility of the fly ash of plants fuelled by both peat and wood compared to those fuelled solely by wood. Natural ageing strongly increased the leaching of sulphate in peat- and wood-powered plants. Sulphate solubility content increased over 130% during the natural ageing test period.

The ageing experiments supported the research carried out in Sweden and Finland which also observed small changes and decreases in pH values of ash piles during storage periods. It seems that ageing alone cannot be considered to be a reliable processing method for reducing the heavy metal contents and solubility properties of fly ash. For some individual harmful substances, however, ageing can achieve a sufficient content reduction. Ageing can possibly be made more effective using carbon dioxide treatment or some other treatment method which would help towards the fly ash's reuse as, for example, an earth construction sites material. Ageing is also not able to produce ash that meets the heavy metal requirements for other use, although the ash tested was at least suitable for use as forest fertilizer.

### **5.3 Granulation tests on fly ash from an energy production plant (V)**

The heavy metal concentration of the processed fly ash used in tests was 4.5 mg/kg and the fractionated concentration was 2.2 mg/kg. According to the analysis results (Figure 2), the cadmium concentration of the granules used in the tests meets the national statutory fertiliser requirements for other ash fertiliser use, i.e. 2.5 mg/kg (Decree 24/2011; EVIRA 2016). Processed fly ash 2 and 5 do not, however, meet the Decree of the Ministry of Agriculture and Forestry on Fertiliser Products 24/2011 requirement for organic mineral fertiliser, which is 1.5 mg/kg. In the original Paper V, the limit values of the previous Decree (46/1994) were presented. Therefore, in addition to the results and conclusions published in the original Paper V, some new conclusions about the fulfilments of the new limits value are also now presented.

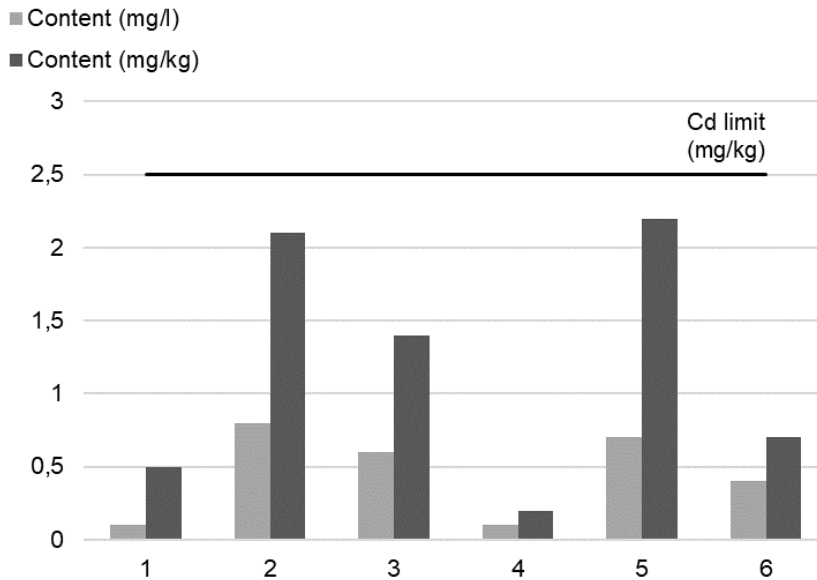


Figure 2: Average cadmium content (soluble AAAC-EDTA mg/l, total aqua regia leaching mg/kg of dry matter) of compost and granule samples: 1 biowaste sewage sludge compost, 4 biowaste compost, and of granule samples: 2 biowaste sewage sludge compost and ash, 3 biowaste sewage sludge compost and cleaned ash, 5 biowaste compost and ash, 6 biowaste and cleaned ash.

The use of clean and uncleaned fly ash did not affect the granulation and mechanical granule characteristics. Meanwhile, the diverse quality of the compost clearly affected the granulation. As a result of the heterogeneous structure of the compost, the size and form of the granules varied significantly. If equal sized granules are aimed at, the compost should be refined before granulation.

Granule durability was tested by conducting compression strength tests with a Penetrometer. According to one recommendation, the smallest granules (approx. 1-2 mm) can withstand processing when their compression strength is approximately 5 N. The compression strength of larger granules (5 mm) must be approximately 10 N. Even though the granule strength ranged between 2-3 N, all the values were below 6 N. The granules were not particularly strong, but they did withstand processing to a certain extent. The granulation of materials improved their processability and reduced the spread of dust.

The mixed ash had a positive impact on compost quality where fertility nutrients were concerned. However, the ash mixture reduced the total nitrogen and carbon concentration. The mixture also increased the granule pH and conductivity compared to composts. According to research, mixed ash also increased the quantity of heavy metals in products made using cleaned ash. Consequently, increases in heavy metal loading should be thoroughly examined. The total and soluble concentrations of heavy metals in soil

remained at the same levels in all processes (with the exception of zinc). All processes containing ash increased the zinc concentration of soil during the tests. The use of ash had no real impact on the heavy metal concentrations in crop yields. According to Joensuu, heavy metals introduced to forest ecosystems through ash fertilising would most likely not accumulate in fungi or berries in large quantities (Joensuu 2017). In order for the use of compost ash granules in crop farming to be effective, the amount of soluble nitrogen in the products must be increased. According to Pesonen et al. nitrogen could also be added to ash fertilizers by co-granulating, for example, with sewage sludge (Pesonen et al. 2016).

## 6 Conclusions

Each year, energy production plants in Eastern Finland produce just under 100,000 tonnes of different types of ash and slag in the process of energy production. The utilisation of energy production ash flows progressed in a variety of ways, but it is still difficult to find the right utilisation applications for some of these fractions due to, among other things, the hazardous substances they contain. According to a Finnish Government Programme, Finland will be a leader in the bio- and circular economy as well as cleantech. The side-streams produced by energy production plants and the trace elements contained in them should indeed be returned to forests as fertiliser, whilst taking environmental safety into consideration.

During this study, the quality and properties of bottom and fly ash produced by energy production plants in Eastern Finland were examined in an effort to determine suitable utilisation alternatives. Bottom and fly ash samples were taken from a total of 31 energy production plants powered by wood and peat fuels. Solubility tests were conducted on ash samples in accordance with standard SFS-EN 12457-3 and heavy metal analyses modified in accordance with standard SFS-EN ISO 15587-2 (SFS-EN 2002; SFS-EN 2002b). The results obtained were used to determine the suitability of ash for landfill disposal as well as the suitability of ash for use in earth construction and as fertiliser.

Based on the analysis results of solubility tests, approximately half of the bottom and fly ash produced by energy production plants would be suitable for disposal in non-hazardous waste landfills and a third would require disposal in hazardous waste landfills when comparing the results with the limit values specified in Government Decree 331/2013. A portion of the ash (15%) could not be disposed of in hazardous waste landfills without pre-processing. Not one of the analysed ash samples would be suitable for inert waste landfill.

Among the analysed bottom ash samples, the limit value for non-hazardous waste landfills is exceeded with regard to the selenium concentration (limit value = 0.5 mg/kg). The selenium concentration limit value (7 mg/kg) for disposal in a hazardous waste landfill was also exceeded in some of the samples. In combined bottom and fly ash samples (mixed ash), the limit values for non-hazardous waste landfill disposal were exceeded with regard to the sulphate, selenium, chloride, barium and DOC concentrations. The DOC concentration limit value for hazardous waste was exceeded in one of the mixed ash samples.

In fly ash samples, the limit values for non-hazardous waste landfill disposal were exceeded with regard to the selenium, barium, sulphate, chloride and DOC concentrations. The limit values for disposal in a hazardous waste landfill were exceeded with regard to the sulphate, DOC and selenium concentrations. In boilers larger than 11 MW, only the selenium concentration in mixed ash samples exceeded limit values when comparing their results for non-hazardous waste and hazardous waste landfill disposal.

The other above-mentioned cases of exceeding the limit values specified in Government Decree 331/2013 occurred in boilers smaller than 10 MW.

When comparing the results of solubility tests with national limit values set for earth construction (Government Decree 843/2017), 27.5% of the analysed bottom and fly ash met the solubility requirements for use in roads constructed of crushed stone and ash (mg/kg L/S = 10 l/kg). In accordance with the Decree, the surface structure and load-bearing layer of roads constructed of crushed stone and ash is formed by a combination of ash and stone aggregate. An exception to the Decree (843/2017) where the utilisation of ash for other purposes is concerned, roads constructed of crushed stone and ash do not require any additional coverage or paving as the ash aggregate mixture forms a dense surface structure that is very similar to a paved roadway. According to the national guidelines, roads constructed of crushed stone and ash may be made using fly ash, bottom ash or fluidised-bed sand from incinerated coal, peat or wood-based materials. (MARA 2018)

A total of 47.5% of the analysed bottom and fly ash met the standards laid out in the Government Decree on the Recovery of Certain Wastes in Earth Construction (843/2017). The remaining 52.5% of ash failed to meet the current limit values, instead requiring pre-processing by some means prior to being utilised.

The analysis of heavy metals revealed that approximately 84% of the bottom and fly ash produced by energy production plants would be suitable for use as fertiliser (in forests or for other purposes). 15% of the bottom and fly ash would require processing before being utilised as fertiliser. In the bottom ash analysed, the limit values for other purposes were exceeded with regard to the Zn concentration. Bottom ash would be suitable for all fertiliser applications where the analysed concentrations are concerned. In combined bottom and fly ash samples (mixed ash), 95% of the samples would be suitable for fertiliser use. The limit values for fertiliser use were exceeded with regard to Zn concentration and the limit values for other purposes were exceeded with regard to, among others, the arsenic, cadmium and zinc concentrations. Of the fly ash samples analysed, 58% would be suitable for use as forest fertiliser. The remainder would require processing before they could be utilised as fertiliser. Forest use limit values were exceeded with regard to, among others As (40 mg/kg), Cd (25 mg/kg), Pb (150 mg/kg) and Zn (4,500 mg/kg) concentrations. In boilers larger than 50 MW, only the As, Cd and Zn concentrations in fly ash samples exceeded limit values for other purposes when utilising fly ash for forest fertilising.

The test results were largely the same as the findings made in other national studies. In his research, Kirjalainen found that ash from wood and peat differed particularly with regard to the high concentrations of the elements molybdenum, selenium, barium and chromium. The total zinc concentration was also high in some of the wood-based ash samples. With regard to ash solubility, the solubility levels of molybdenum, selenium and sulphates were particularly high. (Kirjalainen 2015)

During research, various processing methods were tested to reduce the hazardous properties of fly ash produced by energy production plants. Fractionating and ageing were chosen as the processing methods.

The objective of fractionating tests was to lower hazardous substance concentrations so that they would be suitable for use as fertiliser (other purposes and forest use). According to fractionating tests conducted at a power plant with an electrostatic precipitator, it can be stated that heavy metal concentrations are at their lowest level when the electrostatic precipitator is in field 1 and at their highest level when it is in field 3. Heavy metals are bound to fine particles. The largest fly ash particles are collected in the first field of the electrostatic precipitator, whilst ash containing more fine particles are found in the last field. It is for this reason that the dust in field 1 of the electrostatic precipitator contains fewer heavy metals. The heavy metal concentration is affected by, for example, the fuel type, flue gas flow rate and field filter voltage.

The As, Cd, Pb and Zn concentrations found in ash produced in Eastern Finland hampers their utilisation in forests and for other purposes. In particular, the incineration of wood increases the Cd and Zn concentrations of fly ash, whilst the incineration of peat increases the As concentration. Fractionation tests conducted with an electrostatic precipitator reduced the As, Cd and Zn concentrations of fly ash. Fractionation reduced Cd and Zn concentrations to a point where the fly ash could be used as fertiliser (forest use). Reducing the As concentration by means of fractionating also requires the adjustment of the electrostatic precipitator settings. If the fuel being used contains a large amount of peat, it may be difficult to bring the arsenic concentration down below the limit value. The research findings are also backed up by other fly ash fractionating tests conducted at power plants. For example, fractionating tests conducted by Soininen et al. managed to reduce fly ash As concentration 30-89%, Cd concentration 19-48%, Pb concentration 22-55% and Zn concentration 30-65% at two power plants using peat and wood as fuel (Soininen et al. 2010). In her thesis, Manskinen found that the analysed fly ash from forest industry energy production plants failed to fall below the limit value for forest applications (40 mg/kg) with regard to the As concentration (Manskinen 2013).

Universally applicable values cannot be defined for the electrostatic precipitator parameters used in fractionation. The heavy metal concentrations of the fuels being used can vary a great deal, and there is no way to know what the need for fractionating is if the fuel used has not been analysed. The separation efficiency of the electrostatic precipitator is also affected by, for example, the aerodynamic diameter of the particles, resulting from their size and morphology, and electrical resistivity, which results from chemical composition (Jaworek et al. 2013). According to Jaworek et al., additional research on the effect that particle properties have on collection efficiency would be needed. This, in turn, supports the need for additional processing methods.

The results from ageing tests conducted on the fly ash from energy production plants and industrial power plants revealed that the natural ageing and solubility behaviour of ash

differed with regard to the fly ash analysed. The analysed fly ash had different pH values and varying quantities of DOCs, which affected their solubility properties during the test. Fly ash produced by industrial power plants using wood-based fuels saw an over 60% reduction in sulphates during the test, whilst the sulphate concentration increased in fly ash produced by energy production plants using peat and wood-based fuels.

The ageing test results are supported by research conducted in Sweden and Finland, in which slight changes in concentrations and a reduction in pH value were also found to occur in ash heaps during storage. A reduction in the alkalinity of the material affects its solubility in different ways, depending on the properties of the material. According to the research results obtained, ageing cannot alone be considered a reliable processing method for the reduction of heavy metal concentrations and solubility properties of fly ash. In the case of certain individual hazardous substances, ageing can, however, be used to achieve an adequate reduction in concentration. In such cases, ageing would still require some sort of enhancement. Van Gerven et al. studied, among other things, the effect that carbon dioxide processing has on metal concentrations. The method has had a positive impact on the Cu concentration, but Ba, Cr, Mo and Sb concentrations, among others, remained the same or increased slightly (Van Gerven et al. 2005).

Additional research is still needed in order to prove beyond a shadow of a doubt that statutory requirements would be met by means of fractionating or ageing. Furthermore, additional research should be done on the impact that fractionating and ageing has on other ash fraction fertiliser values, such as trace element concentrations.

During this study, a soil improver made up of compost and fractionated, processed fly ash was granulated using a layering method. No differences were found in the use of unprocessed or processed ash in the granulation method employed. The quality of compost had a significant impact on granulation (e.g. inhomogeneity and changes in moisture content). The particle size and shape of manufactured particles varied, but the particles could be spread and withstood processing well. The granulation of materials improved their processability and reduced the spread of dust. The ash mixture had a positive impact on compost quality where fertility nutrients were concerned. However, the ash mixture increased the heavy metal concentrations of the granules, despite the second fraction processing. The organic nutrient tested was not adequate enough to increase the percentage of soluble nitrogen in the tested product as a crop soil improver. However, the material could be made suitable for use with some garden plants. Fly ash from energy production plants is primarily used as a granulated forest fertiliser. According to a study done by Marttinen et al., ash fertiliser already accounts for over half of the fertilisers used in Finnish forestry as seen in terms of the phosphorous content (Marttinen et al. 2017). Furthermore, where forest applications are concerned, fly ash needs to be productised and, in many cases, it also requires some type of nutrient or trace element additive (nitrogen, boron, etc.).

Amendments to legislation concerning the utilisation of ash and national requirements in the circular economy will increase the need for ash post-processing. The trace elements and other nutrients found in fly ash would be a positive addition to the circular economy. According to this study not all unprocessed fly ash produced by energy production plants is necessarily suitable for utilisation as a fertiliser (other purposes and forest applications) or for road construction. The treatment methods tried during this study, ageing and fractionation, reduced the levels of harmful substances contained in ashes, but not enough for the recovery of all the harmful substances. Research work needs to be further pursued in order to achieve reliable methods of processing on the scale of fractionation and ageing.

In order to ensure that the ash produced by energy production plants is more cost-effectively and ecologically utilised, we would need more intermediate ash storage areas as well as companies that process and use ash. Indeed, intermediate ash storage areas are becoming a material reserve that promotes the utilisation of industrial side-streams. In the future, the processing of various types of ash should be further researched and post-processing should be developed in order to meet the requirements and limit values (earth construction and fertiliser use) for the utilisation of bottom and fly ash produced by all energy production plants run on wood-based fuels.





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