



Total and size fractionated concentrations of metals in combustion ash from forest residues and peat

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Abstract. Environmental characteristics of the total and size fractionated concentrations of metals in bottom ash and fly ash from a large (246 MW) fluidized-bed boiler incinerating forest residues and peat at a pulp and paper mill complex in Finland were studied. Although the enrichment factors for total metal concentrations in the fly ash varied between 1.3 (potassium and sodium) and 34.5 (sulphur), all metal concentrations in both the bottom ash and fly ash were significantly lower than the current Finnish limit values for maximum allowable metal concentrations for forest fertilizers. Therefore, both the studied ashes are residues with a potential to be utilized as forest fertilizers as such. Only the arsenic concentration of 33.0 mg/kg (d.w.) in the fly ash fraction between 1.0–2.0 mm exceeded the Finnish limit value of 30 mg/kg (d.w.) set for arsenic in the forestry fertilizers. This means that the fly ash fraction of 1.0–2.0 mm is not suitable for a forestry fertilizer alone.

Key words: environmental research, ash, forest industry, fluidized bed boiler, heavy metals, particle size distribution, waste.

1. INTRODUCTION

Forest industry residues (i.e. clean wood chips, sawdust, and bark) as well as commercial peat are important heating fuels in Scandinavia. The use of forest industry residues, in particular for energy production, has a number of advantages over the combustion of fuel oil and coal in Finland: residues are a domestically available resource and their recycling creates jobs and promotes silviculture locally. In addition, the extraction of forest residues from the harvesting chain for utilization in energy production is already common practice in Finland, providing an extra source of income for forest owners and having a positive effect on the economic viability of forest operations [1]. Furthermore, and perhaps critically, in the face of the global challenges of energy security and climate change, the generation of energy from local forest residues is a sustainable and environmentally friendly way to produce energy since it can significantly reduce the use of and reliance on fossil

fuels. The use of wood chips, sawdust, and bark as fuel allows the beneficial utilization of renewable, natural raw materials as an energy source without having any marked effects on the carbon balance of ecosystems [2].

However, a disadvantage of incinerating forest residues and peat fuel is that it produces large amounts of ash. Traditionally disposal in landfill sites has been the most widely used method in their waste management. Due to the recent rise in the cost of waste disposal via landfill, regulations designed to protect the environment, and the added problem of acquiring and developing new waste disposal sites, ash management and disposal present an ongoing challenge for the energy generation industry, e.g. municipal district heating plants. The utilization of solid wastes allows industry to reuse and recycle residue streams to generate beneficial products and energy, and there is therefore a growing trend towards the increased utilization of solid wastes for beneficial purposes in Finland [3].

The aim of this study was to determine the most important physical and chemical properties (i.e. pH, electrical conductivity, dry matter content, and particle

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size distribution) of the bottom ash and fly ash originating from a large (246 MW) fluidized-bed boiler at a pulp and paper mill complex located in northern Finland, in which forest residues (i.e. clean wood chips, sawdust, and bark) as well as peat are incinerated. This study is part of a major project in which the physical and chemical properties of bottom ash and fly ash originating from different kinds of Finnish energy generating plants (i.e. fluidized-bed boilers, grate-fired boilers) are investigated in order to utilize and reuse these ashes [4–6].

2. EXPERIMENTAL

2.1. Sampling

The bottom and fly ashes investigated in this study originate from a large (246 MW) bubbling fluidized-bed boiler (BFB) at a pulp and paper mill complex located in northern Finland. The plant produces about 15 430 tonnes of ash (ca. 2580 tonnes of bottom ash and ca. 12 850 tonnes of fly ash) per year. During the last few years, about 40% of the fly ash has been used as a hardener in filling local mine cavities. The rest of the fly ash (60%) and all bottom ash have been used for landscaping the ash basin. At the present time, approximately 45% of the energy produced by the BFB originates from the incineration of clean forest residues (i.e. bark, wood chips, and sawdust) and ca. 55% from the incineration of commercial peat fuel.

The bottom ash was sampled from the outlet of the boiler and the fly ash from the boiler's electrostatic precipitator. The sampling was carried out over a period of five days, and the individual samples (1 kg per day) were combined to give one composite sample with a weight of 5 kg. The sampling period represented normal operating conditions for the combustion plant as to O₂ content and temperature. After sampling, the samples were stored in polyethylene bottles in a refrigerator (+4°C). A coning and quartering method [7] was applied repeatedly to reduce the ash sample to a size suitable for conducting laboratory analyses.

2.2. Determination of physical and chemical properties of ashes

The pH and electrical conductivity (EC) of the ashes were determined by a combination pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium) and a Phoenix conductivity electrode (Phoenix Electrode Co., Texas, USA) with a cell constant of 1.0. The pH and EC were determined according to European standard SFS-EN 13037 at a solid to liquid (S/L) ratio of 1 : 5.

Determination of the dry matter content of the bottom and fly ashes was carried out according to

European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105°C. A comprehensive review of the standards, analytical methods, and instrumentation is given in our previous studies [4–6].

2.3. Determination of total metal concentrations

For the determination of the total metal concentrations in the bottom ash and fly ash, the dried samples were digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [8]. The cooled solutions were transferred to 100 mL volumetric flasks and diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and an Elgastat Maxima ion exchange water purification system (Elga, Ltd., Bucks, England). All reagents and acids were suprapure or pro analysis quality. The total element concentrations in the ash samples were determined with a Thermo Elemental IRIS Intrepid II XDL Duo (Franklin, USA) inductively coupled plasma optical emission spectrometer (ICP-OES). A comprehensive review of the digestion method and instrumentation is given in our previous studies [4–6].

2.4. Determination of metals distribution in different particle size fractions

For the determination of metals distribution in different particle size fractions, the bottom ash and fly ash were dry sieved on an automatic sieve shaker (Retsch Virbo, Haan, Germany) through stainless steel sieves using a stack of nested sieves (DIN 4188, Retsch 5657, Haan, Germany) with the following aperture sizes: 8–4, 4–2, 2–1, 1–0.5, 0.5–0.25, 0.25–0.125, 0.125–0.074, and <0.074 mm. The weight of each size fraction for both ashes was recorded and the percent distribution of weight in each fraction was calculated. For the determination of total metal concentrations in the different particle size fractions, the preparation of each fraction as well as heavy metal measurements were carried out in the same way as described in Section 2.3.

3. RESULTS AND DISCUSSION

3.1. Physical and chemical properties of the ashes

The pH of both ashes was strongly alkaline (pH 12.6). According to Van Herck and Vandecasteele [9], an alkaline pH indicates that part of the dissolved metals occurs as basic metal salts, oxides, hydroxides, and/or carbonates. Therefore, the proportions of soluble basic metal salts, oxides, hydroxides, and carbonates in the

ashes outweigh the proportion of soluble acid components, and both ashes subsequently generate an alkaline pH. The dry matter content of the ashes was very high (99.9%). This is a disadvantage and may increase the amount of dust during handling. The electrical conductivity of the bottom ash was 9.8 and of the fly ash, 14.7 mS/cm.

An important characteristic of biomass-derived ashes is that they usually have high plant nutrient concentrations (i.e. easily soluble forms of P, Ca, Na, K, Mg, Cu, and Zn). This phenomenon indicates that the utilization of biomass-derived ashes as a forest fertilizer is recommended. The nutrient concentrations of the ashes investigated in this study are given in our previous publications [4–6].

3.2. Total metal concentrations in the ashes and the enrichment factors

Table 1 shows the total metal concentrations in both types of ash, as well as the enrichment factor (EF) for each element. The EF value is determined as the ratio of an element's concentration in the fly ash to its concentration in the bottom ash. An elevated EF value indicates a high degree of element volatilization during the combustion process and subsequent condensation, whereas a low EF value is indicative of non-volatile behaviour under normal operating conditions and formation of a heavier mineral phase. The ratio of various elements in bottom ash and fly ash depends on the type of boiler, operating conditions, fuel mix, and efficiency of flue gas cleaning devices [10]. The EF values for Be, Cd, Mo, Pb, and Se are given in parentheses because the concentrations of these elements in the bottom ash were lower than their detection limit. In addition, there is no EF value for Hg, because it was impossible to calculate as its concentration both in the bottom ash and fly ash was lower than its detection limit.

The FBB's combustion temperature of 800–1200°C is high enough to vaporize some elements. In addition to the element volatilization characteristics, element retention in fly ash through other processes (i.e. primarily the condensation process) determines the final fate of volatilizable elements [11]. Most of these species form compounds that condense on the surface of particles in the flue gas, leading to the enrichment of some elements in the fly ash fractions. Consequently, the bottom ash has an enhanced content of non-volatile components, and frequently contains sintered or melted particles. Cadmium and mercury, especially, will be evaporated at least partially under certain conditions, and thus be carried into flue channels together with the flue gases, and be subsequently precipitated on the surface of particulate matter, or continue partly in a gaseous state into the atmosphere [12,13].

Table 1. Total metal concentrations (mg/kg, d.w.) in the bottom ash and fly ash, the enrichment factor (EF) of metals, and the current maximum allowable heavy metal concentrations (mg/kg, d.w.) of Finnish legislation for ash used as a forest fertilizer

Metal	Bottom ash	Fly ash	EF ^a	Limit value
Al	12 300	23 700	1.9	
As	5	27	5.4	30
B	110	200	1.8	
Ba	570	1 730	3.0	
Be	<0.5	0.7	(>1.4)	
Ca	53 800	231 000	4.3	
Cd	<0.3	4	(>13.3)	17.5
Co	3	13	4.3	
Cr	20	43	2.2	300
Cu	19	120	6.3	700
Fe	12 600	132 000	10.5	
K	8 580	11 200	1.3	
Mg	4 740	18 300	3.9	
Mn	1 420	5 600	3.9	
Mo	<1	7	(>7)	
Na	4 440	5 800	1.3	
Ni	14	53	3.8	150
P	1 750	10 600	6.1	
Pb	<3	36	(>12)	150
S	600	20 700	34.5	
Se	<4	7	(>1.8)	
Ti	210	610	2.9	
V	16	81	5.1	
Zn	440	680	1.5	4 500
Hg	<0.03	<0.03	n.c.	1.0

^a EF = [total element concentration in the fly ash/total element concentration in the bottom ash].
n.c. = not calculated.

The relatively high enrichment of sulphur in the fly ash (with an EF value of 34.5) is also worth noting. During combustion, sulphur sublimates or reacts by forming gaseous compounds such as SO₂ and SO₃. As a result, most of the sulphur passes to the vapour phase and reacts with inorganic components to form sulphates. During combustion, solid organic matter is decomposed and elements that form ash such as alkali metals and alkaline earth metals are released. In the upper part of the boiler, where the flue gas is rapidly cooled, the sulphates condense on the particles of fly ash or on the tube surfaces. In wood ash, alkaline and alkaline earth elements are primarily present as oxides, hydroxides, or carbonates, but also as chlorides [14,15]. According to Obernberger [16], the efficiency of sulphur fixation in the ash depends on the concentrations of alkaline earth elements, especially of calcium in the ash, as well as on the efficiency and technology used for dust precipitation. However, this is beneficial from an environmental point of view because SO₂ is removed from the flue

gases, thus decreasing the plant's SO₂ emissions in flue gases. Obernberger [16] reported that 40% to 90% of the total sulphur in biofuel remains in the ash and the rest is emitted as SO₂ and SO₃ in the flue gases.

Table 1 also shows the total heavy metal concentrations (i.e. As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg) in both ashes with respect to current Finnish limit values for fertilizers used in forestry. These limit values came into force in March 2007. This comparison is made only in order to obtain information about the heavy metal concentrations in ash, not for recommendation purposes. It would be ecologically beneficial if solid residues, e.g. ash, from industrial plants could be returned to the forest as this would save primary resources and could be regarded as an example of sustainable use of industrial residues. However, it is worth noting that the physical and chemical quality of ashes varies significantly depending on e.g. the ratio of fuels burnt, tree species, growing site, climate, and tree components (e.g. bark, wood, leaves). Other factors that have an effect on the physical and chemical quality of the ash are size and age of the tree, logging technique, collection and storage, as well as the combustion technique and operating conditions such as the combustion temperature and type of boiler [10,14–16]. Therefore, according to Aronsson and Ekelund [17], caution must be exercised if application of ash is to occur in the natural environment, and thus the process conditions during sampling must be known exactly.

From the utilization point of view, it is worth noting that the total heavy metal concentrations (see Table 1) in both types of ash were significantly lower than the Finnish maximum allowable heavy metal concentrations in forestry fertilizers. However, we have not determined the toxicity properties of the ashes in this study, because according to Finnish legislation, if ash is beneficially utilized, the knowledge of toxic properties is not necessarily needed; yet, in some cases the competent authority may decide that toxicity properties do have to be determined before a decision can be made on whether the ash can be utilized. Furthermore, it is worth noting that many European countries, e.g. Finland, Sweden, Germany, Spain, and France, have established legislation that enables and controls beneficial use of ashes via recycling in the forest environment, and the existing legislation must always be applied.

3.3. Particle size distribution of heavy metals in the ashes

According to Table 2, the particle size distributions of the bottom and fly ashes differ significantly. Practically no particles in the diameter range between 4.0 and 8.0 mm existed in the fly ash. The particles smaller than 0.125 mm in diameter accounted for 90.1% of the fly ash weight, whereas in the bottom ash, the particles in the range between 0.5 and 2.0 mm accounted for 97.3%

Table 2. Size distribution of ash particles of the bottom ash and fly ash (weight percent)

Particle size, mm	Bottom ash	Fly ash
4.0–8.0	0.5	0
2.0–4.0	0.6	0
1.0–2.0	37.5	0.2
0.5–1.0	46.3	0.1
0.25–0.5	13.5	1.4
0.125–0.25	0.9	8.2
0.074–0.125	0.2	19.2
<0.074	0.5	70.9

of its weight. These results indicate that the fly ash consists of particles with a relatively small diameter, which could be attributed to mechanical grinding of fly ash particles during combustion and in the solid transport system inside the furnace [16–18]. We reported this phenomenon also in our previous publications [4,5]. The very high dry matter content of fly ash coupled with predominance of small particles is a disadvantage as these properties can cause dust problems during handling. The smallest particles are of greatest concern because of their dust generation potential when ash is handled at landfill sites [19,20].

Particle size analysis of the ashes is important and useful in assessing the utilization potentials, as well as for evaluating potential environmental hazards [17–20]. The distribution of heavy metals (Zn, Ba, Cu, As, Cd, Cr, Pb, Ni, and V) in different particle size fractions of the bottom ash and the fly ash are shown in Figs 1 and 2, respectively. These heavy metals were selected because the concentrations of other elements were lower (in certain fractions) than their detection limits. The highest concentration for barium (1700 mg/kg, d.w.) in the fly ash was found in the smallest particle size fraction (<0.074 mm) and of vanadium (81 mg/kg, d.w.) in the smallest (<0.074 mm) and second smallest (0.074–0.125) particle size fractions. The highest concentrations of other metals (Zn, Cu, As, Cd, Cr, Pb, and Ni) in the fly ash were found in the particle size fraction of 1.0–2.0 mm, which was the coarsest fly ash fraction. However, in the bottom ash, all heavy metals were enriched in the finest particle fraction.

The enrichment of metals in small particles could be explained by vaporization and condensation mechanisms. According to Liao et al. [21], some metals are volatilized in high-temperature combustion and then either condense or adsorb on the surface of smaller particles in flue gas as cooling occurs. These particles have a greater surface area to volume ratio than coarse particles. From the toxicological standpoint, the smallest particles are of greatest concern when ash is handled at landfill disposal sites (i.e. in transport and disposal, particularly in dry and windy weather conditions), and some researchers have reported risks to workers with prolonged exposure to ash [22,23].

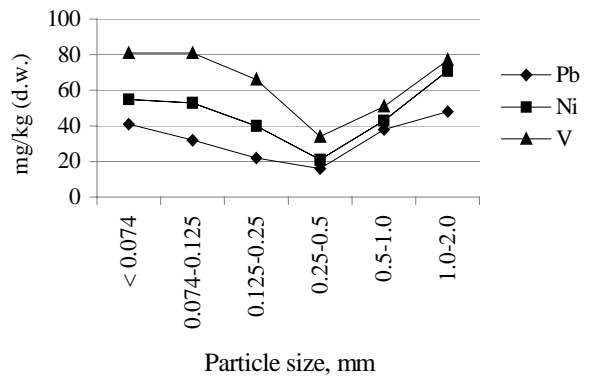
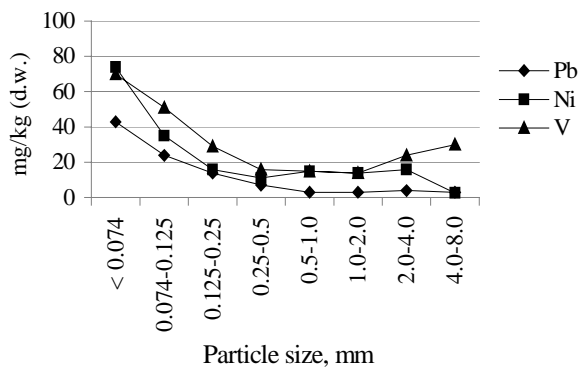
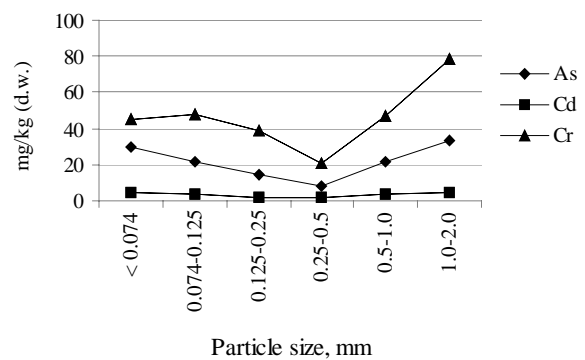
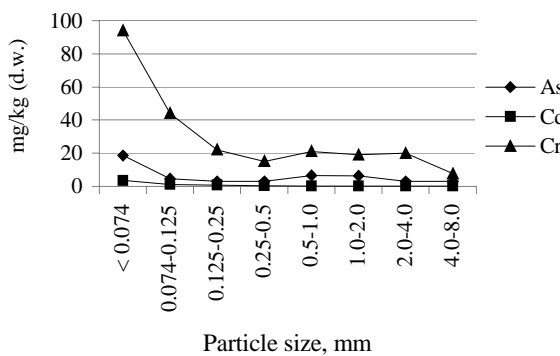
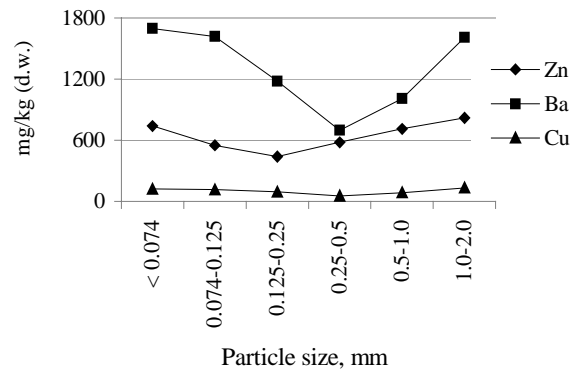
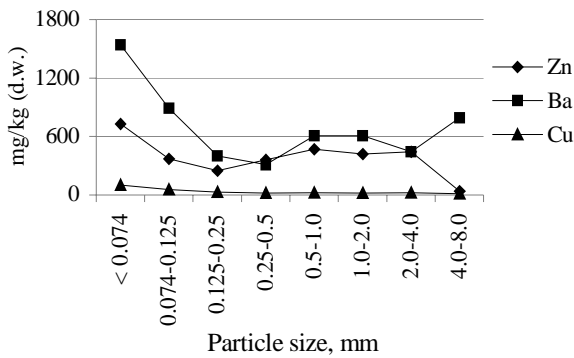


Fig. 1. Concentrations of metals in different particle size fractions in the bottom ash.

Fig. 2. Concentrations of metals in different particle size fractions in the fly ash.

According to Sutherland [24], the most important index of contamination is the mass loadings of metals in different size fractions (see Tables 3 and 4), which combines metal concentrations on a grain size basis with data on percentage of total mass. If the metal concentration for a given fraction is very high but it forms only a small portion of the overall sample mass, the contribution of this fraction to the total sample metal load will be minimal. The results in Table 3 indicate that in the bottom ash between 88.9% and 97.9% of the concentrations (i.e. the metal mass loadings) for all heavy metals are contributed by the particle size fraction

of between 0.25 and 2.0 mm, while these fractions together accounted for 97.3 weight percent (wt%) of the total mass of bottom ash particles (see Table 2). According to the results in Table 4, over 71% of the mass loadings for all heavy metals, except cadmium, in the fly ash was contributed by the particle size fraction smaller than 0.074 mm, which in turn accounted for 70.9 wt% of the total mass of fly ash particles (see Table 1). According to Wang et al. [25], particles finer than 0.125 mm can be especially problematic because they are easily transferred into the atmosphere.

Table 3. Metal mass loadings (%) in different size fractions of the bottom ash

Metal	Size fraction							
	<0.074 mm	0.074–0.125 mm	0.125–0.25 mm	0.25–0.5 mm	0.5–1.0 mm	1.0–2.0 mm	2.0–4.0 mm	4.0–8.0 mm
As	1.4	0.2	0.4	6.7	50.8	40.0	0.3	0.2
Ba	1.3	0.3	0.6	7.3	49.3	40.0	0.5	0.7
Cd	5.6	0.7	2.0	14.3	42.3	34.1	0.5	0.5
Cu	2.6	0.6	1.3	12.0	48.8	33.7	0.7	0.3
Pb	5.6	1.2	3.3	24.3	35.7	28.9	0.6	0.4
Cr	2.4	0.4	1.0	10.2	49.1	36.1	0.6	0.2
Ni	2.6	0.5	1.0	10.3	48.3	36.5	0.7	0.1
V	2.3	0.7	1.7	14.1	45.2	34.1	0.9	1.0
Zn	0.8	0.2	0.5	11.0	50.4	36.5	0.6	(0.05)

Table 4. Metal mass loadings (%) in different size fractions of the fly ash

Metal	Size fraction					
	<0.074 mm	0.074–0.125 mm	0.125–0.25 mm	0.25–0.5 mm	0.5–1.0 mm	1.0–2.0 mm
As	79.2	15.7	4.3	0.4	0.1	0.3
Ba	74.1	19.1	5.9	0.6	0.1	0.2
Cd	54.3	42.0	3.0	0.4	0.1	0.2
Cu	73.7	19.1	6.3	0.6	0.1	0.2
Pb	77.8	16.4	4.8	0.6	0.1	0.3
Cr	71.1	21.0	7.0	0.6	0.1	0.2
Ni	73.6	19.2	6.2	0.6	0.1	0.3
V	72.6	19.7	6.8	0.6	0.1	0.2
Zn	77.5	15.6	5.4	1.2	0.1	0.2

From the utilization point of view, according to Chimenos et al. [18], ash particles of size fractions over 3 mm are suitable for landfilling or being reused as secondary building materials. Although a major proportion of the particle sizes of ashes investigated in this study do not meet the requirements for the particle size reported by Chimenos et al. [18], about 40% (5500 tonnes per year) of the fly ash produced at the energy generation of the pulp and paper mill complex investigated in this study has successfully been used as a hardener for filling local mine cavities (see Section 2.1.). However, according to Sarkar et al. [26], small particles, especially those below 0.045 mm in diameter, are important in the construction industry.

In this context it is worth noting that, especially in large-scale power plants, the utilization of fly ash may be sometimes even increased if electrostatic precipitators are used in the deliberate fractionating of fly ash. In power plants in which multi-chamber electrostatic precipitators are installed, the fly ash particles of the largest particle size accumulate in the first field, while the last field has more small particles. According to Orava et al. [27], electrostatic precipitation is an adequate method for the fractionation of fly ash to be used as a fertilizer or for soil amendment purposes, and therefore the quality of fly ash may be manipulated through suitable fractionation. Designed electrostatic fractionation is geared towards separating the fractions with high fine particle densities and high heavy metal concentration from the portion that is most suitable for practical applications such as reuse in residue derived products.

As Fig. 2 shows, the arsenic concentration of 33.0 mg/kg (d.w.) in the fly ash fraction between 1.0 and 2.0 mm exceeded the Finnish limit value of 30 mg/kg (d.w.) for the maximum allowable arsenic concentration in forestry fertilizers. This means that this fraction is not suitable for a forest fertilizer alone. However, according to Table 2, the particle size fraction of 1.0–2.0 mm accounted for only 0.2 wt% of the total mass of fly ash particles. Furthermore, according to Table 4, only 0.3% of the mass loading of arsenic was contributed by this fraction. Due to these properties, the total concentration of arsenic (27 mg/kg, d.w.) in the fly ash was lower than its maximum allowable concentration in forestry fertilizers (i.e. 30 mg/kg, d.w., see Table 1) and therefore the fly ash as such, not the fraction between 1.0 and 2.0 mm alone, is suitable for a forest fertilizer.

4. CONCLUSIONS

In Finland, the new maximum allowable concentrations for arsenic, cadmium, chromium, copper, nickel, lead, and zinc in forest fertilizers came into force in March 2007. During the combustion of biomass-derived fuels, e.g. forest industry residues such as wood chips, sawdust, and bark, as well as peat fuel, most of the metals in the fuel are retained and enriched in the ash. Although the enrichment factors for total metal concentrations in the fly ash varied between 1.3 (potassium and sodium) and 34.5 (sulphur), all metal concentrations in both the bottom ash and the fly ash were significantly lower than the current Finnish limit values for metal concentrations for forest fertilizer. Therefore, both of the studied ashes are residues with a potential to be utilized as forest fertilizers as such. However, according to the fractionation study, the arsenic concentration of 33.0 mg/kg (d.w.) in the fly ash fraction between 1.0 and 2.0 mm exceeded the Finnish limit value of

30 mg/kg (d.w.) set for arsenic in the forestry fertilizers. This means that this fly ash fraction is not suitable for a forestry fertilizer alone.

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Metallide summaarne ja fraktsioneeritud sisaldus puidujäätmete ning turba põletustuhas

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On uuritud eri metallide sisaldust puidujäätmete ja turba 246 MW keevkihttehnoloogial baseeruva katla kahes põlemisjärgis, st katla- ning lendtuhas. Proovid võeti nii summaarsest tuhast kui ka samast tuhast eraldatud erineva osakeste suurusega fraktsioonidest. Määrati ka tuhavesiekstraktide pH-väärtused ja elektrijuhtivuse näitajad. Töö eesmärgiks oli kontrollida toksiliste metallide sisalduse vastavust kehtivatele keskkonnanormidele. Järeldati, et antud tingimustel puidujäätmete ja turba põletamisel tekkivad tuhad ei sisalda ohtlikul määral toksilisi metalle, välja arvatud lendtuha 1,0–2,0 mm fraktsioon, kus arseeni kontsentratsioon (33,0 mg/kg) oli Soomes lubatud piirnormist (30 mg/kg) kõrgem.