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## Element budgets of forest biomass combustion and ash fertilisation – A Danish case-study

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### ABSTRACT

Harvest of forest biomass for energy production may lead to a significant export of nutrients from the forest. Ash spreading and recycling of nutrients from wood chip combustion to the forest has come into focus as a means for counteracting the nutrient export. This study was carried out to examine the retention of various elements in the different ash fractions and utilise the nutrient recovery to evaluate the fertiliser quality of the examined ash. The mass and element flux of wood chips, bottom ash, cyclone fly ash and condensation sludge at Ebeltoft central heating plant was studied over a four day period in spring 2005. On average, 19 ton wood chips (dry weight) were combusted each day. The combustion of the wood chips produced 0.70% ash and sludge (dry weight). The ash and sludge dry matter was distributed as 81% fly ash, 16% bottom and residual grate ash and 3% sludge solid phase. Substantial amounts of nutrients were retained in the fly ash (P, Ca, Mg, Mn and Cu have a recovery higher than 60% and K, S and Fe have a recovery higher than 30%). The recovery of elements in the bottom ash was smaller. The added recovery of the usable fractions of ashes (both fly ash and bottom ash) exceeded 75% for the nutrients P, Ca, Mn and Mg. Both these ash fractions should be considered for fertilisation.

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## 1. Introduction

Sustainable forest management implies a balanced ecosystem in terms of nutrient input and output to insure the fertility of the forest ecosystem. Harvesting of forest biomass, such as utilisation of whole-tree biomass and harvest residues for energy production, intensifies the removal of nutrients from the forest ecosystem [1–3].

Decreased tree growth following intensified biomass harvesting has been observed in field experiments and suggested in several studies [2,4–7]. However, the results are often contradictory or the decrease in tree growth is not significant. Fertilisation has been suggested as a means for counteracting decreased tree growth. Recirculation of nutrients, by spreading

the ashes from combustion of forest biomass in heat and power plants, has come into focus as a method for fertilisation [2,5,8,9].

An important question is to what extent the nutrients from the forest biomass are retained in the ash. A prerequisite for making ash act as a fertiliser, that can counteract the nutrient export from a certain area, is that the nutrients are retained in the ash in an amount and combination sufficiently equal to what was exported from that area. If the nutrient retention is relatively low, the ash dosage may be increased. If the different nutrients are not retained equally in the ash, application of ash, may introduce nutrient imbalances in the forest. In the last case, addition of the nutrients that are less retained in the ash may be necessary to avoid imbalanced plant nutrition. These considerations are made by disregarding the nutrient deposition of

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e.g. nitrogen (N) and sulfur (S) thus, the deposition needs to be taken into account when regarding the nutrient budget.

Nitrogen (N) and to some degree sulfur (S) evaporate during combustion, thus the concentrations of these components are often negligible in the ash. However, the biomass ash often have a notable concentration of other macro nutrients e.g. potassium (K), calcium (Ca), magnesium (Mg), phosphor (P) and micronutrients e.g. iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B) and molybdenum (Mo). The ash also contain ecotoxic components such as heavy metals e.g. arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), polycyclic aromatic hydrocarbons (PAH) and dioxins [2,5,8,10–12].

Deposition of acidifying air pollution compounds has been observed to affect the forest ecosystem and especially the soil conditions, in undesirable ways [13–18]. Hence, liming of the acidified forest soils has been suggested and in some cases carried out [13,19–23]. Biomass ash react alkaline and can neutralise acidity. Application of biomass ash has thus been suggested as a means of counteracting the acidification of forest soils [2,24–29].

Furthermore, forest biomass ashes are often deposited on waste disposal sites with high costs. Recirculation of ash nutrients back to the forest may thus, solve several problems; counteracting the intensified nutrient removal during harvesting of forest biomass fuel, counteracting the acidification of the forest soil, and diminishing the amount of waste for deposit.

This study was carried out to get an overview of the element budget of a wood chip fired Danish heating plant and thus examined the retention of various components in the different ash fractions. The first hypothesis was that relatively large amounts of the various nutrients were retained in the ashes with exception from N. The second hypothesis was that ash spreading can be applied to counteract the nutrient export due to harvesting. Hence, the aim of this study was to utilise the nutrient retention to evaluate the fertiliser quality of the examined ash, with respect to the applicable amount of nutrients.

## 2. Materials and methods

The mass and element flux at Ebeltoft district heating plant (DH) system was studied over a period of four days in spring 2005, from March 14<sup>th</sup>, 09:00 am to March 18<sup>th</sup>, 09:00 am (here referred to as the study period). Ebeltoft DH delivers heat to the city of Ebeltoft, which is situated in the eastern part of mid Jutland.

### 2.1. Forest biomass fuel supply

In the study period Ebeltoft DH was supplied with wood chips from whole fresh tree harvesting (including green needles but excluding roots) of a 52 years old Scots pine (*Pinus sylvestris* L.) stand. The trees were harvested in Valeurs Plantage, located approximately 5 km NNW of Ebeltoft DH (the centre of the harvested area is situated at UTM, zone 32 (West): 601.96 E; 6.234.39 N). The time span between harvesting and combustion was less than two days (in cold periods at the end of the winter, where most of the pre-dried biomass have been used, there will often be a period where freshly harvested biomass is the only available source).

### 2.2. Ebeltoft central heating plant (DH)

Ebeltoft DH has two individual wood chip fired combustion systems and two oil fired back up boilers. Only one of the wood chip fired systems was examined in this study. The production in the examined combustion system was kept relatively constant already three days prior to the start of the study as well as during the study to ensure stable conditions in the boiler from the beginning of the study period. The wood chip source was also the same throughout the start up period and during the study period. At the same time the other wood chip fired system was continually adjusted to ensure that the combined production from the two systems met the fluctuating demand for heat.

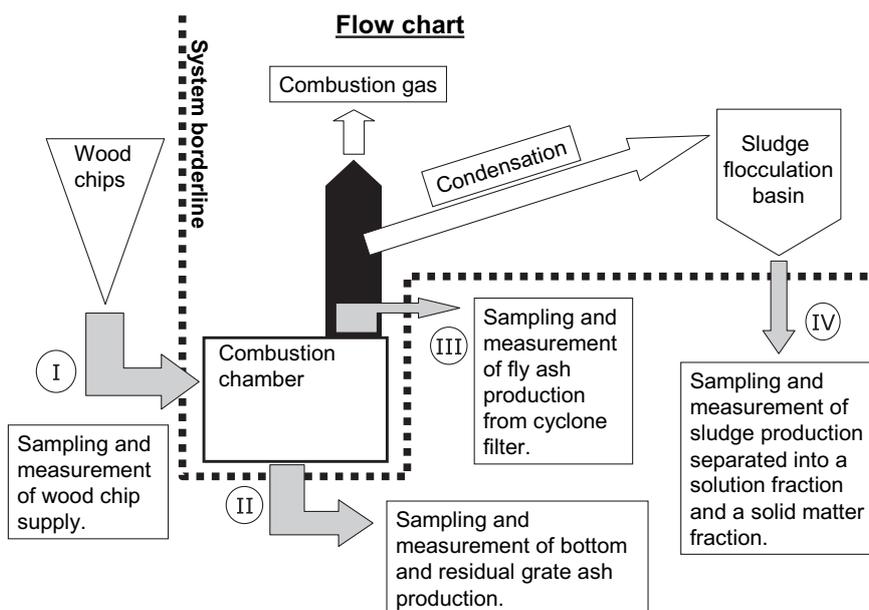
The boiler at Ebeltoft DH was produced by Vølund Varmeteknik and started to produce heat in 1994. It consists of a fixed bed combustion system with a hydraulic fuel feeder and a 5 m long combustion chamber. The grate furnace system consists of three sections with inclined moving grates. Each section is managed individually with respect to air supply rate and air composition regarding the mixture of fresh and recirculated air. The management of the sections reflects the needs in each of the three different stages of combustion; drying, gasification and charcoal combustion. In the drying section, only recycled air with approximately 6% oxygen and a temperature of 300 °C is applied, in the gasification section a mixture of recycled air and primary air is applied and no air is applied in the charcoal combustion section.

The examined system has a maximum nominal production of 5.0 MW from the convection unit, and 1.0 MW from the condensation unit. The heat production from the combustion unit was aimed at being constant and approximately 3.8 MW (75% of maximum). During the study, the average production was 3.7 MW and in 85% of the time, the production was within the target limits of  $\pm 10\%$  of 3.8 MW. However, during the study the heat production from the combustion unit varied from a minimum of 2.9 MW to a maximum of 4.7 MW. The heat production from the condensation unit was kept constant at 0.6 MW. The average combustion temperature was 709 °C and varied only within the limits of  $\pm 10\%$ . The oxygen concentration in the boiler after combustion was on average 6.1%, varying from 4.5% to 8.2% during the study.

### 2.3. Measuring the mass flux and sampling of wood chips, ashes and sludge

Fig. 1 presents a flow chart of the examined mass fluxes. The experiment was started at 09:00 am on March 14<sup>th</sup>, by emptying all ash transporters and ash containers. The study also terminated by emptying all ash systems at 09:00 am on March 18<sup>th</sup>. During this study period, the mass flux of chips, bottom ash, and fly ash was measured by weighing the total mass that either entered or left the combustion chamber. The mass flux of the condensation sludge was not measured directly for all the sludge due to the large amount, but another method, which is described below, was applied. The combustion smoke that left the chimney was the only mass flux leaving the combustion chamber that was not measured in this study.

The mass flux of wood chips into the combustion chamber was measured by weighing each batch in the feeder crane bucket during the four days. The weighing cell in the feeder



**Fig. 1 – Flow chart of Ebeltoft DH. All four mass fluxes that cross the system borderline were examined both with respect to mass flux rate and chemical composition. These mass fluxes are indicated by grey arrows and encircled roman numbers, I: wood chips, II: bottom and residual grate ash, III: fly ash, and IV: condensation sludge.**

crane was calibrated before the experiment started. After the experiment, the calibration was checked, and the difference was less than 2%. A representative chip sample of approximately 2 kg was collected directly from the stock pile twice a day, at 09:00 am and at 02:00 pm during the study (total: 8 wood chip samples).

All the bottom ash and fly ash that were produced since the beginning of the study were measured and sampled for chemical analyses twice a day, at 09:00 am and at 02:00 pm during the period from two 02:00 pm of March 14<sup>th</sup> till 09:00 am on March 18<sup>th</sup> (one sample of each ash type at each sampling occasion, giving a total of eight fly ash samples and eight bottom ash samples). The weight of the bottom ash samples was approximately 2 kg each, and the weight of the fly ash samples was approximately 1 kg each. Some of the ash falls through the grates and ends up in the bottom of the boiler. This ash fraction is referred to as 'residual grate ash'. The residual grate ash that was produced during the four days study period was measured and sampled for chemical analyses once at the end of the period (one representative sample of approximately 2 kg).

The sludge flocculation basin was flushed through the bottom valve on average 55 times each day (55, 52, 53 and 60 times per day respectively during the study period). No flocculation agent was added during the period. The volume of the flushed sludge was estimated by measuring the volume of one flush twice a day, at 09:00 am and at 02:00 pm during the study period. Representative sludge samples of approximately 2 l each were also taken on these occasions. The sludge samples were taken from a sampling container immediately after a sludge flush had entered the empty container. At this point in time the sludge solid and liquid phase was mixed well in the sampling container and it was possible to take a representative sample of the sludge.

## 2.4. Chemical analysis

The water content and dry weight (55 °C) was measured for wood chips, bottom and fly ash samples by weighing before and after drying at 55 °C for minimum two days (until constant weight). The sludge samples were filtered through a 0.45 µm filter, and the dry weight of the filter cake was measured by drying at 55 °C until constant weight.

The wood chip samples were ground before sampling subsamples for chemical analyses and combustion experiments. Fly ash and bottom ash samples were crushed in a mortar before sampling subsamples for chemical analysis.

The concentration of N and carbon (C) was determined for 0.2 g wood chip subsamples or 0.5 g ash subsamples by infrared absorption spectroscopy (IR) after dry combustion in an oven (LECO-CNS 2000). From each sample, 150 mg was digested in nitric acid (HNO<sub>3</sub>) in PTFE bombs in a microwave oven (CEM, DMS-2000). After digestion the concentration of P, K, Ca, Mg, S, Fe, Mn, B, Zn, Cu, aluminium (Al), sodium (Na), Cd, Pb, Cr, Ni and silicon (Si) was measured by inductively coupled plasma atomic emission spectroscopy ICP-AES (Perkin–Elmer, optima 3000 XL). All concentrations of solid material refer to dry weight at 55 °C.

## 2.5. Calculations and statistics

The mass and element flux was calculated for a period of four days, from 09:00 am of March 14<sup>th</sup> till 09:00 am of March 18<sup>th</sup>. The flux of elements was calculated by multiplying the element concentrations with the corresponding mass flux of wood chips, fly ash, bottom ash, residual grate ash, sludge solid phase or sludge liquid phase. When calculating the element and mass flux of the ashes, residual grate ash was

regarded as being a part of the bottom ash. Hence, in the element and mass flux budgets, the residual grate ash production, that was measured by the end of the period, was divided into four study days and added to the measured daily bottom ash production and element flux.

The recovery (%) of the elements was calculated by (1)

$$\text{Recovery} = m_{\text{element,out}}/m_{\text{element,in}} \times 100, \quad (1)$$

where  $m_{\text{element,out}}$  is the element mass flux out of the combustion chamber in a given ash or sludge fraction ( $\text{kg d}^{-1}$ ), and  $m_{\text{element,in}}$  is the flux of the same element that entered the combustion chamber as a part of the biomass fuel ( $\text{kg d}^{-1}$ ).

The differences in element concentration between the different ash and sludge fractions were tested by use of the General Linear Model Procedure (SAS 9.1.3 Service Pack 4, 2002–2003). In this test, the concentration of a specific element in a given ash or sludge fraction from the various times of sampling was used as replicates, as the effect of the time of sampling was found to be negligible compared to the effect of difference in ash or sludge fraction.

### 3. Results

On average, 39.1 ton wood chips (fresh weight) were combusted each day of the study (minimum:  $35.5 \text{ ton d}^{-1}$ , maximum:  $41.6 \text{ ton d}^{-1}$ ). The sludge was on average flushed from the flocculation basin by 55 flushes per day varying from 52 flushes to 60 flushes per day during the study, and each flush consisted on average of 272l sludge (+/–5l).

For most element concentrations in the wood chips the standard error (SE) is relatively small (Table 1), except for Mn, Fe, Zn and Cr where the SE is more pronounced.

Table 2 presents the element concentration in fly, bottom and residual grate ash, and in sludge solid phase. The concentration of a number of elements; both nutrients and heavy metals, are significantly higher in the sludge solid phase fraction (C, N, P, B, Mn, Fe, Zn, Cu, Cd, Pb, Ni and Al) compared to the fly ash and bottom ash, this effect is especially pronounced for the concentration of B, Zn, Cu, Cd and Pb. The highest concentrations of K, Mg, Cr, Na and Si, and at the same time the lowest concentration of C, N, S, B and Zn are found in the bottom ash. In the bottom ash, the element concentration of P, Ca, Fe, Ni and Al is intermediate compared to the other ash and sludge fractions. The element concentration in the fly ash is most often intermediate (C, N, K, Mg, B, Zn, Cd, Cr, Pb, Na and Si) or low (P, Ca, Mn, Fe, Ni and Al) compared to the other ash and sludge fractions. The concentration of elements in the residual grate ash is often of the same magnitude as in the bottom ash, with the exception of Pb that is notably higher and Fe that is somewhat higher. For most elements, the SE is relative small. However, in the sludge solid phase the SE is for P, Ca, S, B, Fe, Zn and Cd is somewhat higher compared to the SE for the other elements in the other ash fractions.

The mass and element budget is shown in Table 3. The mass budget for dry matter shows that the combustion of wood chips gives 0.70% ash and sludge. The ash and sludge dry matter is distributed as 81% fly ash, 16% bottom and residual grate ash, and 3% sludge solid phase. The fresh wood

**Table 1 – Water contents in fresh wood chips (dried to 55 °C) and element concentration mean and standard error (SE) in eight wood chip samples (dry weight at 55 °C).**

	Mean (n = 8)	SE
Water (55 °C) %	52.0	0.90
C ( $\text{mg g}^{-1}$ )	489	0.78
N ( $\text{mg g}^{-1}$ )	1.73	0.12
P ( $\text{mg g}^{-1}$ )	0.149	0.011
K ( $\text{mg g}^{-1}$ )	0.509	0.020
Ca ( $\text{mg g}^{-1}$ )	1.07	0.099
Mg ( $\text{mg g}^{-1}$ )	0.232	0.014
S ( $\text{mg g}^{-1}$ )	0.212	0.014
B ( $\mu\text{g g}^{-1}$ )	n.d.	n.d.
Mn ( $\mu\text{g g}^{-1}$ )	146	17
Fe ( $\mu\text{g g}^{-1}$ )	36.9	3.9
Zn ( $\mu\text{g g}^{-1}$ )	11.1	1.5
Cu ( $\mu\text{g g}^{-1}$ )	0.997	0.083
Cd ( $\mu\text{g g}^{-1}$ )	0.217	0.018
Cr ( $\mu\text{g g}^{-1}$ )	0.910	0.098
Pb ( $\mu\text{g g}^{-1}$ )	n.d.	n.d.
Ni ( $\mu\text{g g}^{-1}$ )	1.32	0.076
Na ( $\mu\text{g g}^{-1}$ )	66.5	5.5
Si ( $\mu\text{g g}^{-1}$ )	n.d.	n.d.
Al ( $\mu\text{g g}^{-1}$ )	120	11

n.d.: not detected, the detection limits are B:  $14 \mu\text{g g}^{-1}$ , Pb:  $4 \mu\text{g g}^{-1}$  and Si:  $7 \mu\text{g g}^{-1}$ . n: number of observations.

chips contain 52% water and water is also produced in the combustion process; 38% of the wood chip fresh weight ends up in the sludge liquid phase and the rest of the water ends up as steam from the chimney.

The recovery of the elements is presented in Fig. 2. The total recovery in ashes and sludge of important nutrients are relatively high; over 80% for P, K, Ca, Mg, Mn and Cu, and over 50% for S and Fe. On the contrary, the total recovery of N is very low; less than 3%. The total recovery of the Cd is approximately 60% where the recovery of Ni is notably lower. The recovery of Cd in bottom and residual ash is notably lower than what is found for fly ash. The recovery in fly ash is generally higher than in bottom and residual grate ash and sludge. The recovery of essential nutrients in the fly ash are higher than 60% for P, Ca, Mg, Mn and Cu and higher than 30% for K, S and Fe. The recovery in bottom and residual ash of essential nutrients such as P, K, Ca, Mg, Mn, Fe and Cu is within the range of 12–22%. In the sludge solid phase, the recovery of the heavy metals Zn, Cu and Cd is notably higher than for the other examined elements. K, S and Na have a relative high recovery in the sludge liquid phase. The output of Cr is larger than the input.

## 4. Discussion and conclusions

### 4.1. Element budget of forest wood chip combustion

In this study we found the ash proportion to be 0.7% of the dry weight of the wood chip fuel. In a review, Karlton et al. [8] found that the amount of ash produced from woody biomass was around 3% of the dry weight of the fuel, and Egnell et al. [5] stated that this proportion was approximately 1–1.5%. Werkelin et al. [30] found that the wood tissue gives a lower amount

**Table 2 – Element concentration mean and standard error (SE) in eight samples of fly ash, bottom ash, sludge solid phase and one sample of residual grate ash (dry weight at 55 °C).**

	Fly ash (n = 8)		Bottom ash (n = 8)		Sludge solid phase (n = 8)		Residual grate ash (n = 1)
	Mean	SE	Mean	SE	Mean	SE	Mean
C (mg g <sup>-1</sup> )	137 <sup>b</sup>	12	11.1 <sup>c</sup>	0.79	183 <sup>a</sup>	4.1	12.1
N (mg g <sup>-1</sup> )	3.15 <sup>b</sup>	0.11	0.0976 <sup>c</sup>	0.012	3.61 <sup>a</sup>	0.14	0.0924
P (mg g <sup>-1</sup> )	16.8 <sup>c</sup>	0.57	22.3 <sup>b</sup>	0.59	45.8 <sup>a</sup>	0.30	23.0
K (mg g <sup>-1</sup> )	43.5 <sup>b</sup>	1.4	70.0 <sup>a</sup>	2.0	4.65 <sup>c</sup>	0.18	58.7
Ca (mg g <sup>-1</sup> )	129 <sup>b</sup>	5.4	178 <sup>a</sup>	4.9	169 <sup>a</sup>	2.4	191
Mg (mg g <sup>-1</sup> )	25.0 <sup>b</sup>	0.66	31.7 <sup>a</sup>	1.0	11.4 <sup>c</sup>	0.76	31.2
S (mg g <sup>-1</sup> )	13.0 <sup>a</sup>	0.47	5.26 <sup>c</sup>	0.12	6.86 <sup>b</sup>	0.095	5.78
B (μg g <sup>-1</sup> )	240 <sup>b</sup>	8.2	166 <sup>c</sup>	4.8	734 <sup>a</sup>	7.2	143
Mn (mg g <sup>-1</sup> )	15.9 <sup>c</sup>	0.74	21.5 <sup>b</sup>	0.76	42.0 <sup>a</sup>	1.4	20.8
Fe (mg g <sup>-1</sup> )	2.72 <sup>c</sup>	0.092	5.43 <sup>b</sup>	0.11	6.38 <sup>a</sup>	0.089	7.65
Zn (mg g <sup>-1</sup> )	0.530 <sup>b</sup>	0.023	0.0556 <sup>c</sup>	0.0039	10.7 <sup>a</sup>	0.21	0.0815
Cu (μg g <sup>-1</sup> )	110 <sup>b</sup>	4.3	108 <sup>b</sup>	3.8	981 <sup>a</sup>	20	93.2
Cd (μg g <sup>-1</sup> )	14.6 <sup>b</sup>	0.56	n.d.	n.d.	217 <sup>a</sup>	2.7	n.d.
Cr (μg g <sup>-1</sup> )	159 <sup>b</sup>	7.2	505 <sup>a</sup>	26	204 <sup>b</sup>	7.0	601
Pb (μg g <sup>-1</sup> )	19.3 <sup>b</sup>	1.3	3.93 <sup>b</sup>	1.6	479 <sup>a</sup>	15	73.4
Ni (μg g <sup>-1</sup> )	18.8 <sup>c</sup>	1.1	32.3 <sup>b</sup>	1.3	53.2 <sup>a</sup>	2.2	36.8
Na (mg g <sup>-1</sup> )	5.97 <sup>b</sup>	0.22	9.52 <sup>a</sup>	0.44	1.80 <sup>c</sup>	0.062	9.43
Si (mg g <sup>-1</sup> )	1.40 <sup>b</sup>	0.059	2.10 <sup>a</sup>	0.13	0.932 <sup>c</sup>	0.10	2.47
Al (mg g <sup>-1</sup> )	10.4 <sup>c</sup>	0.65	18.0 <sup>b</sup>	1.3	29.3 <sup>a</sup>	2.3	19.9

n.d.: not detected, the detection limit of Cd is 1 μg g<sup>-1</sup>. Different index letters indicate significant ( $P \leq 0.05$ ) different concentrations between ash type or sludge. n: number of observations.

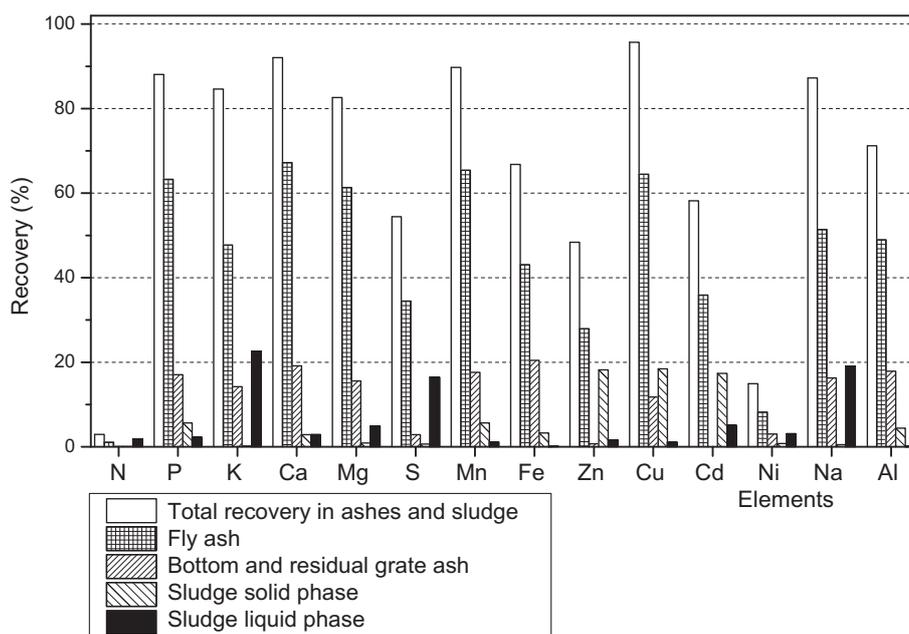
of ash (0.2–0.7% of the dry wood) compared to bark tissue (1.9–6.4% of the dry bark) and foliage (2.4–7.7% of the dry foliage). In this study we found the ash proportion to be low compared to Karlton et al. [8] but somewhat closer to ash proportion reported by Egnell et al. [5]. The reason for the

relatively low ash proportion found in this study is presumably that the wood chips were made only from whole trees and not just from harvest residues and thus contained a relative high proportion of stem wood. Furthermore, the wood chips presumably had a lower content of soil and dirt, as it was

**Table 3 – Mass and element budget for an average day of the four day study period. The elements enter Ebeltoft DH in the wood chips and leave the chamber in fly, bottom or residual grate ash or in sludge solid or liquid phase. The combustion smoke was not included in this study.**

	In		Out			
	Wood chips	Fly ash	Bottom and residual grate ash	Sludge solid phase	Sludge liquid phase	Sum of ash and sludge
Mass (dry) (kg)	18742	107	21	3.4	14892	
C (kg)	9170	14	0.25	0.62	0.011	15
N (kg)	33	0.34	0.0018	0.012	0.59	0.95
P (kg)	2.8	1.8	0.48	0.16	0.061	2.5
K (kg)	9.6	4.6	1.4	0.016	2.2	8.1
Ca (kg)	20	14	3.9	0.58	0.58	19
Mg (kg)	4.3	2.6	0.67	0.037	0.21	3.6
S (kg)	4.0	1.4	0.12	0.024	0.66	2.2
B (g)	n.d.	25	3.2	2.5	17	48
Mn (g)	2578	1687	454	144	28	2313
Fe (g)	666	287	136	22	0.47	445
Zn (g)	200	56	1.4	36	3.1	97
Cu (g)	18	12	2.1	3.3	0.19	17
Cd (g)	4.3	1.5	n.d.	0.74	0.21	2.5
Cr (g)	17	17	12	0.68	0.56	30
Pb (g)	n.d.	2.0	0.71	1.6	0.056	4.4
Ni (g)	25	2.0	0.73	0.18	0.74	3.7
Na (g)	1223	629	199	6.1	234	1067
Si (g)	n.d.	148	51	3.3	29	231
Al (g)	2229	1090	398	97	1.6	1587

For wood chips, fly ash, bottom and residual grate ash, and sludge solid phase the mass refer to dry weight at 55 °C, n.d.: not detected, the detection limit of Cd is 1 μg g<sup>-1</sup>, B: 14 μg g<sup>-1</sup>, Pb: 4 μg g<sup>-1</sup> and Si: 7 μg g<sup>-1</sup>.



**Fig. 2 – Recovery in the various ash and sludge fractions for chosen elements. The recovery was calculated for the four day study period by dividing the element mass flux out of the combustion chamber in a given ash or sludge fraction with the flux of the same element that entered the combustion chamber.**

transported directly to the indoor storage facility, avoiding outdoor storage directly on the ground.

In this study the major part of the ashes was generated as fly ash and only a minor part as bottom ash, residual grate ash and sludge solid phase. However this combination may vary strongly between the different DH's and between the different seasons. When utilising the findings from this study, it is thus important to keep in mind that the presented results only provide a snapshot of the element budget under the given conditions at this particular DH.

The concentrations of elements in the presented ashes are within the range of what is generally found in wood biomass ashes [5,8,10,31]. One exception is the concentration of Cr that is higher in the bottom ash (approximately two times higher) and especially in the fly ash (approximately six and seven times higher) in this study compared to the reported levels. The element budget for Cr also shows that the output is larger than the input. This is most likely an effect of corrosion of the grate system which is enriched in Cr. The element concentration may vary notably between e.g. ashes, power plants, relative production capacity [5,8,10,31] and often depends on the volatilisation conditions e.g. the local temperature, the chemical composition of the fuel, and the surrounding gas atmosphere [32–34]. Hence, the distribution of a given element between the different ash fractions is linked to the volatilisation conditions for that given element. When we compare fly ash and bottom ash, the general rule is that the concentration of elements that have a high volatility is higher in the fly ash compared to the bottom ash and the concentration of elements that have a low volatility is higher in the bottom ash compared to the fly ash [32–34]. This is in agreement with the differences in nutrient concentrations between fly ash and bottom ash, found in this study (the concentrations of B, Zn, Cd are higher in the fly ash compared to the bottom ash and vice versa for K, Ca, Mg, Mn,

Fe, Cr, Ni, Na, Si and S). The high element concentrations in the sludge solid phase of many elements and especially B and the heavy metals Zn, Cu, Cd and Pb that is found in this and other studies, are an effect of the different temperatures in smoke exhaust system and especially the specific aerosol particle size that is caught in the condenser [32,35]. The formation of small particles leads to a high concentration of these elements. Carbon and N reacts with oxygen and form oxides that end up in the smoke that leaves the chimney.

For most of the elements the recovery are relatively large. However, more than 80% of the Ni, more than 50% of the Zn, and more than 40% of the S and Cd leave the plant in the combustion smoke. For the rest of the examined elements it is less than 35% of the elements that ends up in the wisp of smoke. During combustion S forms mainly gaseous SO<sub>2</sub> and alkali sulfates [32]. A part of the SO<sub>2</sub> will not be fixated in the ash, but may leave the plant in the smoke, which can explain the recovery of approximately 55%. The low recovery of Zn and Cd has also been observed in other studies and is explained by the volatility and relatively low evaporation temperature of these metals [10,32,36]. However, the low recovery of Ni is difficult to explain. The evaporation temperature for Ni is high and the literature concerning recovery of Ni in bio fuel ashes is sparse.

Substantial amounts of nutrients are retained in the fly ash (P, Ca, Mg, Mn and Cu have a recovery higher than 60% and K, S and Fe have a recovery higher than 30%). The recovery of elements in the bottom ash is smaller, but the concentration of nutrients is notable. The added recovery of the usable fractions of ashes (both fly ash and bottom ash) exceeds 75% for the nutrients P, Ca, Mn and Mg. Both these ash fractions should be considered for fertilisation. Obernberger et al. [32] reported recovery of bottom ash and fly ash from biomass combustion that was a little higher but of the same magnitude, between 85% and 95% for Ca, Mg, K and P.

#### 4.2. Ash fertilisation and nutrient cycling

The recovery of the different nutrients are not equal and additional application of S, K, Zn and Fe could be suggested if a more balanced nutrient composition is desirable. Sulfur and Zn is only poorly retained in the bottom and residual grate ash, thus additional application of these nutrients may be suggested especially for application of this ash fraction. Nitrogen leaves the DH in the combustion smoke and is thus not available in the ashes for fertilisation purposes. Hence, if the trees need N fertilisation, additional N must be applied. However, in Denmark the N deposition is often notable and the N deposition can be of the same magnitude as what is taken up by a mature spruce stand [9,37]. Hence, ash fertilisation could often be made without additional N application in Denmark.

The nutrient retention is lower than 100% for fly ash and notably lower than 100% for bottom and residual grate ash. Hence the ash dosage to the forest area need to be higher than the amount of ash that was produced from combustion of biomass from that area, to insure that the nutrient export is counteracted. As an example, we can estimate the total removal of biomass in the case where we make intensive harvest for bioenergy production of whole trees in all thinnings and final felling. In this case we can estimate the total removal of biomass to e.g. 200 ton ha<sup>-1</sup> (dry matter) over a rotation of 75 years [38]. The dosage of ash application needed to counteract this nutrient export depends on which nutrient we consider. In the case where we want to compensate the removal of P, Ca, Mg and Mn, that has a recovery of approximately 65%, by applying the given fly ash, we should apply 2.2 ton ha<sup>-1</sup> of the fly ash per rotation. If we instead want to compensate for the removal of K, that has a lower recovery (48%), we should apply 2.9 ton ha<sup>-1</sup> of the fly ash per rotation.

According to the legislation it is often the Cd concentration that limits or prohibits fertilisation with ash [39]. In Denmark the maximum threshold value for the Cd concentration is 20 µg Cd g<sup>-1</sup> [39] and in Sweden the maximum threshold value for the Cd concentration is 30 µg Cd g<sup>-1</sup> [40]. The concentration of Cd in the presented fly ash and bottom ash is below these threshold values.

The sludge phases are not suitable for fertilisation; the sludge liquid phase has only a low concentration of nutrients. The relative high heavy metal concentration and especially the high Cd concentration in the sludge solid phase (217 µg Cd g<sup>-1</sup>, Table 2) makes this fraction useless for fertilisation [39]. Furthermore, Danish legislation prohibits mixing of the sludge solid phase and other ash fraction for production fertilisers. However, the positive effect of the heavy metal accumulation in the sludge phase is that it removes a part of the heavy metals from the fly ash. In Denmark, the local municipality decides the fate of the sludge solid phase and it is often treated as chemical waste.

The Cr budget is an example of how corrosion of the DH parts can increase the concentration of elements depending on the chemical composition and the corrosion resistance of the DH parts. In both Denmark and Sweden the maximum threshold value for the Cr concentration is 100 µg Cr g<sup>-1</sup> [39,40]. Hence, neither the presented fly ash nor the bottom ash may be spread in Danish forests.

With regard to the nutrient budget, both fly ash and bottom ash can be applied to counteract the nutrient export due to harvesting.

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