Utilization and recycling of wood ashes from industrial heat and power plants regarding fertilizer use

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A R T I C L E   I N F O

A B S T R A C T

To achieve a sustainable circular economy for wood ash, the reuse of wood ash in agriculture and forestry is important. To evaluate the usability of ash from the combustion of natural as well as waste wood for application as fertilizer, wood fuel and corresponding ash fraction samples (n = 86) of four industrial wood-fired heat and power plants (>20 MW) were investigated. In different ash fractions, the concentrations of heavy metals (As, Cd, Pb, Ni, Tl, Zn) and plant nutrients (N, P, K, Ca) were assessed with regard to relevant legislation from the European Union and from selected European countries (Germany, Austria and Finland). Depending on fuel composition and combustion kinetics within the respective plants, the investigated ash fractions showed a wide range of nutrient and heavy metal contents. Apart from N which is mainly emitted with the flue gas, plant nutrients were present in substantial concentrations with mean values corresponding to 20% P, 55 % K and >95% Ca content compared to nutrient compound fertilizer. A direct application of most ash fractions from both natural and waste wood combustion is however not possible due to high contents of Cd, Pb and Ni. In order to develop the ash for secondary use, investigation for a suitable treatment process is necessary. An estimation of the nutrient recovery potential from industrial wood energy plants in southwest Germany showed that approx. 3.1% (P), 7.5% (K) and 22.8% (Ca) of raw material for fertilizers could be substituted by ash.

1. Introduction

Global goals call for increased efforts to mitigate climate change and increase resource efficiency (European Commission, 2019; European Union, 2016; United Nations General Assembly, 2015). Therefore, recycling and resource recovery in terms of a circular and bio-based economy have become essential. Simultaneously, increasing efforts to reduce greenhouse gas emissions to mitigate climate change have led to a growing interest in sustainable energy. Wooden biomass is a relatively abundant renewable resource that will contribute CO_2-neutral heat and power in future energy systems (Brosowski et al., 2016; Demirbas et al., 2009; Schulze et al., 2020). Chemically stored energy can be provided as it is required, e.g., during the winter months. Especially wood and wood-wastes belong to the most important biomass energy sources. Their use for energy production could increase the share of energy from renewable resources and reduce the greenhouse effect on a global scale. The

expansion of the energetic use of wood, however, leads to an increasing amount of ash that still has to be disposed. This results in high costs and the loss of valuable resources, although wood ashes have already been identified as attractive for resource recovery in terms of urban mining approaches (Girón et al., 2013; Reimann et al., 2008; Silva et al., 2019). The composition and application potentials of biomass ashes are therefore of growing interest to scientists (Symanowicz et al., 2018; Tejada et al., 2019; Umamaheswaran and Batra, 2008; Vassilev et al., 2013a, 2013b; Werkelin et al., 2010; Zevenhoven et al., 2012). Most recently, Bachmaier et al. (2021) mapped the ash quality (n = 50) of bottom, mixed bottom and cyclone, and cyclone ashes from 17 typical heating plants between 0.8 and 31.6 MW (14 plants < 10 MW) in Bavaria, fired with wood chips or pellets from untreated wood, and investigated relevant nutrient and pollutant contents for the use as a fertilizer. Results showed that bottom ashes are basically suitable for use as fertilizers or as raw material for fertilizers, despite the low maximum

values in the German Fertilizer Ordinance.

In the present study, the definition of wood fuel encompasses both untreated lignocellulose material (i.e., forest residues, landscaping material) and processed wood waste assortments according to classes AI and AII according to the German Waste Wood Ordinance (BGBl, 2002).

1.1. Ash fractions and their properties

In industrial heating plants (HP) or heat and power plants (HPP), up to four ash fractions are precipitated and removed from the plant. Typically, these are distinguished into bottom ash, boiler and cyclone fly-ash, filter fly-ash and flue dust. The ash fractions differ in their point of origin and their average share in the total ash quantity (Obernberger et al., 1997). The ash forming constituents and the trace element (TE) concentrations are influenced by, e. g., the wood source, including potential contamination, as well as the combustion and flue gas cleaning technologies applied (Fahlke, 1993; Frandsen et al., 1994; Hilber et al., 2007; Martel, 1998; Meij, 1994; Tejada et al., 2020; Tejada et al., 2019; Thorwarth, 2007). Depending on the phase mineral transformation and volatile character of trace and nutrient elements with specific boiling temperatures resp. dew points, the element composition of the ash fractions varies. Modeling approaches for ash formation and chemistry during biomass combustion have been developed by Boström et al. (2012), Doshi et al. (2009). An extensive review on the state of the art has been compiled by Kleinhans et al. (2018). The following main mechanisms and influences on ash formation have been identified: (I) the fuel composition in terms of relative concentrations of ash forming elements along with the total concentration of ash forming matter (i.e., inorganic wood constituents); (II) the mineral transformation of the inorganic components depending on their kinetic properties, aggregation states and relative mutual stability; and III) the process parameters such as flue gas composition and temperature. It is therefore to be expected that ash fractions differ in their composition and thus further usability.

Concerning element recovery and the potential use as a fertilizer, the availability of plant nutrients, the alkaline effect of ashes and the concentrations of heavy metals as potentially toxic elements have to be taken into account (Ohenoja et al., 2020). As the ashes also contain high levels of essential elements such as phosphorus (P) bound in phosphate (PO_4^{3-}), a finite and non-substitutable raw material, they appear to be particularly valuable. Previous studies by Pinnekamp (2014), Schoumans et al. (2015), Egle et al. (2015) and Egle et al. (2016) attributed an increasing role to P recovery from waste products. This was underlined when the European Commission added raw phosphate and elemental phosphorus to the list of 20 critical raw materials in 2014 and 2017 (EC, 2017). Depending on the composition, wood ash could therefore be an interesting raw material for fertilizer production.

1.2. Legal framework for the utilization of wood ash as fertilizer

Uncoupling biomass production from the petrochemical industry with the increased use of renewable fertilizers has been identified as a key challenge (Sherwood, 2020). In terms of a circular economy, ashes from wood combustion can be returned to natural cycles as a fertilizer or as a soil conditioner. However, the composition of combustion residues from biomass varies greatly, containing both nutrient and potentially harmful substances such as heavy metals (Vance, 1996; Wójcik et al., 2020; Zając et al., 2018). In Scandinavian countries, wood ash properties have been researched, tested and the use as fertilizer especially in forestry has successfully been implemented for decades (Hakkila, 1989; Nieminen et al., 2005; Pesonen et al., 2017; Pitman, 2006). The application of wood ash to forest soil appears to be very promising and may help achieve several forest management objectives. An improvement in tree growth has mainly been observed in combination with N-rich soils (Huotari et al., 2015). Ash application mimics some of the beneficial effects of wildfire on soil properties, such as enhanced concentrations of

Ca, Mg, K and increased soil pH. Further, nutrients that are removed together with harvested biomass, such as Ca, Mg, K and P are replaced. The application of alkaline ashes to soil has a liming effect that counteracts the acidification of ecosystems through atmospheric S and N deposition (Hannam et al., 2018). Moreover, the inherent plant nutrients (except for N) make wood ashes attractive for an application in agriculture (Karps et al., 2017). In terms of circular economy, wood ashes resulting from incineration can be returned to the forest to utilize the nutrients they contain. Recycling on other utilization areas is also conceivable, if pollutant accumulation in the nutrient cycle is excluded (Pasquali et al., 2018).

From a European perspective, the Waste Framework Directive (2008/98/EC) sets the framework for waste management and defines basic principles such as the waste hierarchy (EPC, 2008). Although ashes from biomass combustion are classified as solid waste under the European Waste List (EC, 2000), they can provide significant resources as alternative raw material, contributing to overall goals to minimize waste generation. Reduction targets for landfilling have been further developed within the last two decades (EC, 1999; EPC, 2018) and complemented by the EU action plan for the circular economy, fostering recycling and resource recovery (EPC, 2015). As part of this action plan, the new EU fertilizer regulation (EPC, 2019) intends to facilitate the use of domestic secondary raw materials and harmonize EU-wide fertilizer legislation. However, regulatory requirements for fertilizers and utilization options for ashes still differ substantially among EU member states, as shown in Table 1.

In this paper, three countries have been selected that represent an exemplary spectrum of requirements. Relatively strict regulations can be found in Austria, where utilization of ash in fertilizer products is generally not permitted. By contrast, Finland's fertilizer ordinance defines a separate category for ash fertilizers and stands for a more progressive handling with ash utilization potentials. In Finland and Germany, combustion ashes from natural, untreated wood can be applied to forest to maintain nutrient balance and for soil liming to counteract soil acidification. As long as wood ashes comply with legal fertilizer requirements, they may be used also in agriculture according to their nutrient content. In Germany, only combustion chamber ashes, i.e., grate or boiler ashes from the incineration of natural, i.e., untreated or solely mechanically treated wood, may be used. The use of fly ashes is not permitted, except for fly ashes from a first filter unit that must be followed by further flue gas cleaning. In Finland, however, finer fractions may be used as well.

In both countries as well as according to the EU regulation, source materials such as ashes as well as fertilizer products must comply with legal requirements. Those further define maximum contents for trace elements (As, Pb, Cd, Cr, Ni, Hg, Tl, Zn) and minimum contents of macronutrients (N, Ca, Mg, K, P, S) in fertilizers. Distinctions are made between the use as a fertilizer in an agricultural context or for direct application in forestry (liming) where maximum TE contents can be up to 50% higher (Table 1). If ashes are merchandised as fertilizers, they must correspond to an approved fertilizer type such as mineral compound fertilizer or lime fertilizer. As a further utilization option according to the German Biowaste Ordinance, grate or boiler ashes from the combustion of natural fuel wood may be added for the treatment of biowaste or as an additive to already treated biowaste, e.g., compost or digestate products (BGBl, 1998).

According to current practice, ashes from industrial-scale wood combustion are excluded from re-use in forestry or agriculture depending on their content of trace metals. This results in large disposal quantities and excluding valuable elements from the utilization cycle. In the context of the aspired bio-based and circular economy, this needs to be changed and ways must be identified to close material cycles. While the combination of heavy metals and plant nutrients in ash is challenging, both groups of elements are valuable in a closed material circle. Next to a lack of technical solutions to separate these material flows, legal standards are currently inhibiting utilization.

Table 1
Legal requirements for solid mineral compound fertilizers in the EU and selected member states for the use of ash in fertilizers for application in agriculture or forestry (BGBI, 2012; BMLFUW, 2021; EPC, 2019; Ministry of Agriculture and Forestry of Finland, 2011).

	Element	Germany		Austria	Finland		EU
		Application in agriculture	Application in forestry	Application in agriculture	Application in agriculture	Application in forestry	Application in agriculture
Maximum heavy metal concentration [mg kg^{-1}]	As	40	60	40	25	40	40
	Pb	150	225	150	100	150	120
	Cd	1.5	2.0	3	2.5	25	3.0
	Cd (in fertilizers > 5% P_2O_5)	50	75	75	50	n.a.	60
	Cr (total)	n.a.	n.a.	100	300	300	n.a.
	Cr (VI)	2.0	n.a.	2.0	2.0	n.a.	2.0
	Ni	80	120	100	100	150	100
	Hg	1.0	1.5	1.0	1.0	1.0	1.0
	TI	1.0	1.5	n.a	n.a	n.a.	n.a.
	Cu	n.a.	0.09	100	600	700	600
	Zn	n.a.	n.a.	300	1500	4500	1500
	N	3	n.a.	3	1**	P + K > 2%	3
Minimum plant nutrient concentration [%]	P_2O_5	5	n.a.	5	2.29 (1% P)**	Ca > 6%*	3
	CaO	30	n.a.	10			1.5
	K_2O	5	n.a.	5	1.20 (1 % K)**		3

n.a.: not applicable.
* Category "Ash fertilizers".
** N + P + K > 7%.

Therefore, this study evaluates the quality, properties and usability of wood combustion ashes from four industrial wood-fired heat and power plants (>20 MW) for fertilizer applications according to legal requirements. Thus, different ash fractions are assessed with regard to the concentrations of heavy metals (As, Cd, Pb, Ni, Tl, Zn) and plant nutrients (N, P, K, Ca) in relation to the maximum resp. minimum concentrations in solid mineral fertilizers as stated by EU-wide and national legislation in Germany, Austria and Finland. Based on this assessment, this study evaluates the potential of wood ash to be returned to the natural cycle as a fertilizer against the background of differences in European states.

2. Material and methods

Wood ash and corresponding fuel samples were obtained from four industrial scale plants differing in terms of their heat and power production, fuel composition and combustion technology. The selected plants are installed in southwestern Germany. They are representative for existing heating plants as well as heat and power plants > 20 MW. All samples were analyzed at the laboratory of the University of Applied Forest Sciences Rottenburg (Germany).

2.1. Investigated heat and power plants and sampling process

Different ash fractions from two wood-fired heat and power plants named HPP A and HPP B and two heating plants named HP C and HP D were selected for this study. Table 2 shows the utilized wood fuel composition and the number of samples corresponding to the ash fractions and plants investigated.

For general analysis of variability between plants, mean values and standard deviation of ash quality per plant were calculated. The sampling process, characteristics of the applied combustion technology, flue gas cleaning technology and characteristics of the employed wood fueled are described in Tejada et al. (2020). This paper is based on the fuel resp. ash analyses and data published there.

Fuel and ash samples were taken in the four plants over the course of several consecutive days during the heating period from November 2017 to March 2018. The time frame was chosen so that for each plant, corresponding fuel and ash samples could be taken. In HPP A and HPP B, three ash fractions were removed separately from the plant. Fraction I was bottom ash taken at the end of the grate at approx. 950 °C resp. the bottom of the circulating fluidized bed boiler at 880 °C. Fraction II consisted of fly ash removed from an economizer and a cyclone at 165 °C (HPP A) resp. a cyclone only at 173 °C (HPP B). Fraction III consisted of

Table 2
Overview of sampled heating (and power) plants: Fuel wood composition as described by Tejada et al. (2020) and sample size per ash fraction and investigated HP(P).

Parameter	HPP A	HPP B	HP C	HP D	Total
Technology	Circulating fluidized bed boiler	Grate fired furnace	Grate fired furnace	Grate fired furnace	
Thermal capacity	49 MW	60 MW	50 MW	20 MW	
Fuel wood composition	60% forest residues; 40% waste wood[1]	60% forest residues; 40% waste wood[1]	50% road side wood, forest residues and landscape management material; 50% waste wood[1]	67% landscape management material; 33% forest residues	
Number of samples (n)					
Bottom ash (fraction I)	2	4	28	12	46
Fly ash (fraction II)	2	4	–	–	6
Fine fly ash (fraction III)	2	4	26	2	34
Total	6	12	54	14	86

[1] Waste wood according to the German Waste Wood Ordinance (BGBI, 2002). Mixture of material according to class A I (Natural or only mechanically processed waste wood that has not been more than insignificantly contaminated with non-wood substances during its use) and class A II (Glued, painted, coated, varnished or otherwise treated waste wood without halogen-organic compounds in the coating and without wood preservatives).

fine fly ash removed from a fabric filter at 158 °C (HPP A) resp. 171 °C (HPP B). In HP C and HP D, two ash fractions were removed separately from the plant. Fraction I, the bottom ash was removed correspondingly to A and B at the end of the grate at 840 °C (HP C) resp. 880 °C (HP D). The remaining fly ashes, which were separated by cyclones and fabric filters at 150–200 °C (HP C) and 120–160 °C (HP D), were collected jointly. Those are categorized as fraction III for investigation purposes. Thus, HP C and HP D did not produce fraction II.

2.2. Sample preparation and analytics

After drying at 105 °C in a drying oven (UNP 700, Memmert, Schwabach, Germany), those ash fractions holding coarse material (boiler and bottom ash) were first crushed to the particle size of 1.00 mm by a jawbreaker (Pulverisette 1, Fritsch, Idar-Oberstein, Germany) and then milled to 0.25 mm by a planetary mono mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany). The milling units of both devices consisted of zirconium oxide, preventing sample contamination with trace elements.

The quantification of carbon, hydrogen and nitrogen of the ash fractions was done by an elemental analysis device (vario MACRO cube, elementar, Langenselbold, Germany) with water free ash samples (0.25 mm particle size), weighed to 20 ± 1.0 mg, pressed in a zinc foil tablet together with tungsten(VI)-oxide (weight ratio 1:1), and analyzed in six replications (DIN EN ISO 16948:2015).

TE were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The ashes with a particle size of 0.25 mm were microwave digested in aqua regia (Multi-wave GO 3000, Anton Paar, Graz, Austria). The digested residues were aliquoted to 50 ml with aqua bi-dest and measured in the ICP-OES system (Spectro Blue, ASX-260 auto sampler, SPECTRO Analytical Instruments, Kleve, Germany) in six replicates each (DIN EN 13650:2002-01; DIN EN ISO 16967:2015; DIN EN ISO 16968:2015; DIN EN ISO 11885:2009-09).

2.3. Method for assessment of element concentrations

Minimum or maximum element concentrations as shown in Table 1 served as evaluation criteria for the ash characterization and classification concerning their usability as a fertilizer or additive to fertilizer products. Therefore, representative ash samples were analyzed for their contents of trace elements and major plant nutrients. To compare the element concentrations measured in the ash fractions, the results were set in relation to the respective specified minimum or maximum concentrations. To evaluate the quality of wood ash as fertilizer, heavy metal (As, Cd, Pb, Ni, Tl, Zn) and nutrient (N, P, K, Ca) concentrations in the ash fractions of the investigated plants were compared to the maximum or minimum contents in solid mineral compound fertilizers and lime fertilizer. As reference value (equaling 100%), values specified in the German Fertilizer Ordinance were used with the exemption of Zn where the EU regulation was used. The other legislative requirements (Austria, Finland and EU) are set in relation to the 100% value.

3. Results and discussion

3.1. Element concentrations in fuel and corresponding ash fractions

The TE-concentrations in the ash fractions that are removed from HPPs and HPs are critical concerning potential toxicity and related requirements for adequate utilization, treatment, or disposal. The determined heavy metal (As, Cd, Pb, Ni, Tl, Zn) and plant nutrient (N, P, K, Ca) concentrations in the employed wood fuel as well as corresponding ash fractions are depicted in Fig. 1 and Fig. 2. In addition, Table 3 shows the mean values $\pm$ standard deviation for each plant.

While heavy metal concentrations in natural wood are relatively low, the total mineral matter is also low. Consequently, when metals are concentrated in the remaining ash after combustion, they are present in relatively high concentrations. This effect can be observed for all trace metals as well as P, K and Ca in Table 3 and also in Figs. 1 and 2. The only exemption is N where lower concentrations can be found in the ash compared to the fuel since N is mainly volatilized and leaves the plant with the exhaust gas in high amounts.

However, for some elements concentrations in both fuel and ash fractions are strikingly elevated. Those results can be explained through possible contamination with heavy metals during fuel handling. Pb and Zn concentrations are elevated for HPP B in the fuel and all three ash fractions with a maximum of > 6000 mg kg^{-1} Pb resp. > 22000 mg kg^{-1} Zn in fraction III. This indicates that the feedstock, a mixture of forest residues and waste wood as described in the material and methods section included painted demolition wood.

In pure woody materials, the concentration of Ni is usually low, < 20 mg kg^{-1} depending on the amount of bark within the fuel (DIN EN ISO 17225-1:2021). The fuel of HP D shows an unusual high Ni content which is 35 times higher compared to the fuel mixtures in plants A, B and C. This can probably be explained by a contamination of the fuel during processing, e.g., through cutting instruments. Since Ni concentrations measured in the ash fractions of HP D do not further reflect elevated values, the examined fuel sample might not show a representative result. Elevated Ni concentrations in the formed ash fractions as observed for HPP B often indicate wearing or corrosion of stainless steel inside the combustion plant.

Plant nutrient concentrations of P and K are lower in the fuel as well as in ash fraction I and III of HPP B compared to HPP A, HP C and HP D. This can be explained by a rather low content of P-, K- and Ca-rich fractions of bark or needles within the fuel sample. In the ash fractions, the concentrations of P and K appear to follow a site-specific trend. Following the path of the flue gas with fraction I to III, the situation is reversed in HPP A (high – low – high) compared to HPP B (low – high – low). This may be due to the influence of different combustion technologies (circulating fluidized bed boiler vs. grate-fired furnace). Fraction III contains the highest K and P concentrations. Although the major partition of N leaves the plant in gaseous state, N is detected at concentrations around 1000 mg kg^{-1} through all ash fractions. This corresponds to approx. 10% of the amount brought into the combustion process with the fuel.

### 3.2. Elemental composition of ash compared to legal requirements across Europe

The recyclability of wood ashes is based on the legal requirements listed in Table 1. The maximum permissible concentrations of heavy metals differ depending on the intended use of ashes, which has to be disposed by exceeding the legal requirements. As the results show, the ash fractions investigated (fractions I – III) contain both essential nutrients and critical heavy metals in concentrations that differ significantly between the ash fractions and thus represent a resource for the recovery of valuable components.

According to Fig. 3, the concentrations of the relevant elements, depending on the HP(P)s, in fraction I are generally below or partially slightly above the specified limits. Particularly critical are the concentrations of Cd, Pb and Ni in HPP A and HPP B. It should be noted that the results for fraction I ashes in this study are comparable to the findings on bottom ashes by Bachmaier et al. (2021), where only residues from the combustion of untreated, natural wood fuel were investigated. Bachmaier et al. (2021), Kovacs et al. (2018) suggest to minimize the concentrations of volatile metals such as Cd in bottom ashes by higher temperatures in the combustion chamber. In HPP B fraction II as well as in fraction III ashes from all plants, heavy metal contents do not allow a direct application as fertilizer.

However, wood ashes also consist to a large extent of valuable plant nutrients that can be used to fertilize the soil. Published concentrations of nutrients such as CaO, P_2O_5 and K_2O in ashes vary greatly (Bachmaier et al., 2021; Hannam et al., 2018; Nurmesniemi et al., 2012; Okmanis et al., 2015). Average nutrient contents in fraction I ashes (Table 3) are
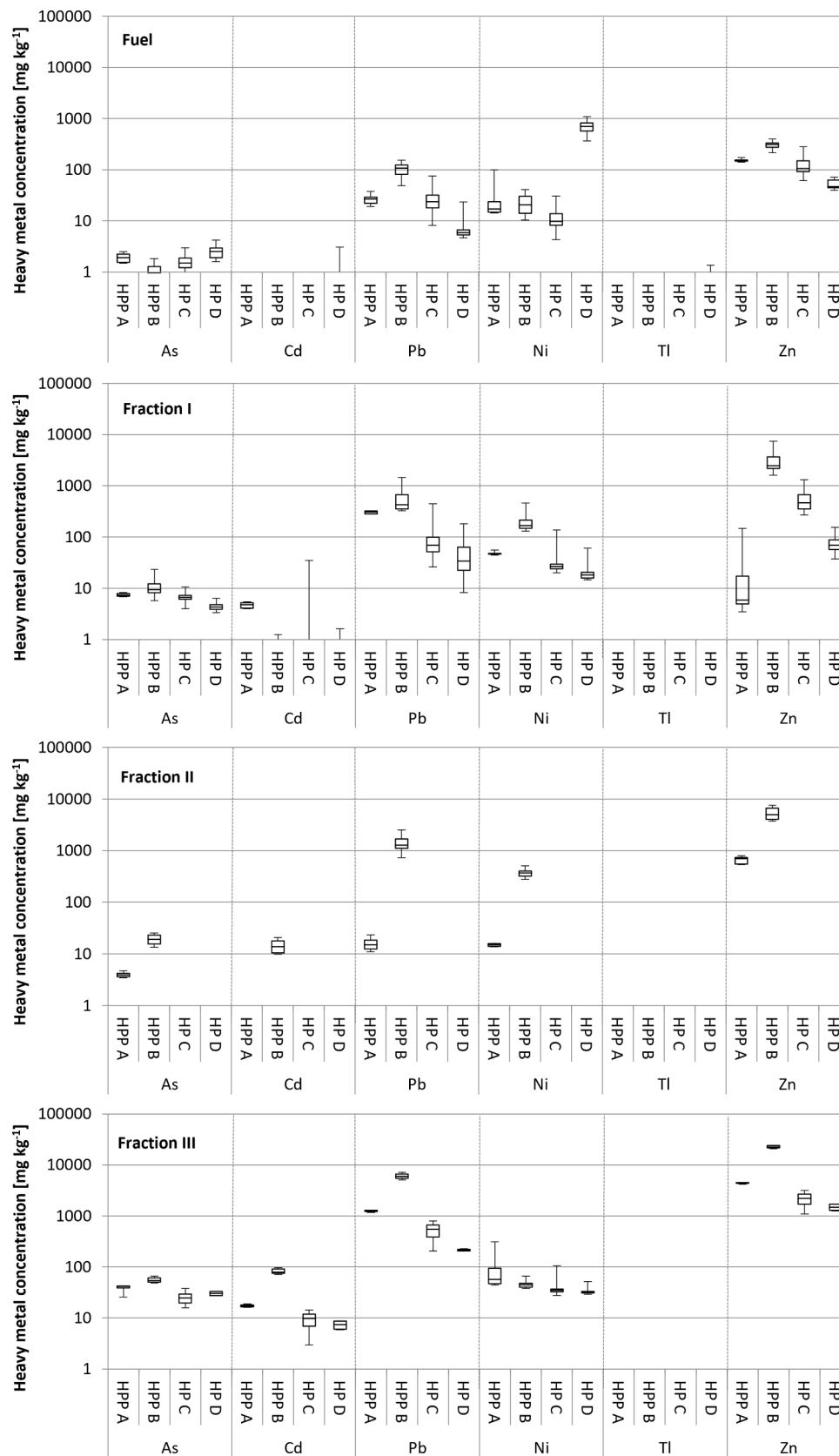
Fig. 1. Concentrations [mg kg^{-1}] of As, Cd, Pb, Ni, Tl and Zn in fuel, bottom ash (fraction I), fly ash (fraction II) and fine fly ash (fraction III). Boxplots with 25% and 75% quantiles (box) and minimum to maximum values (whisker).
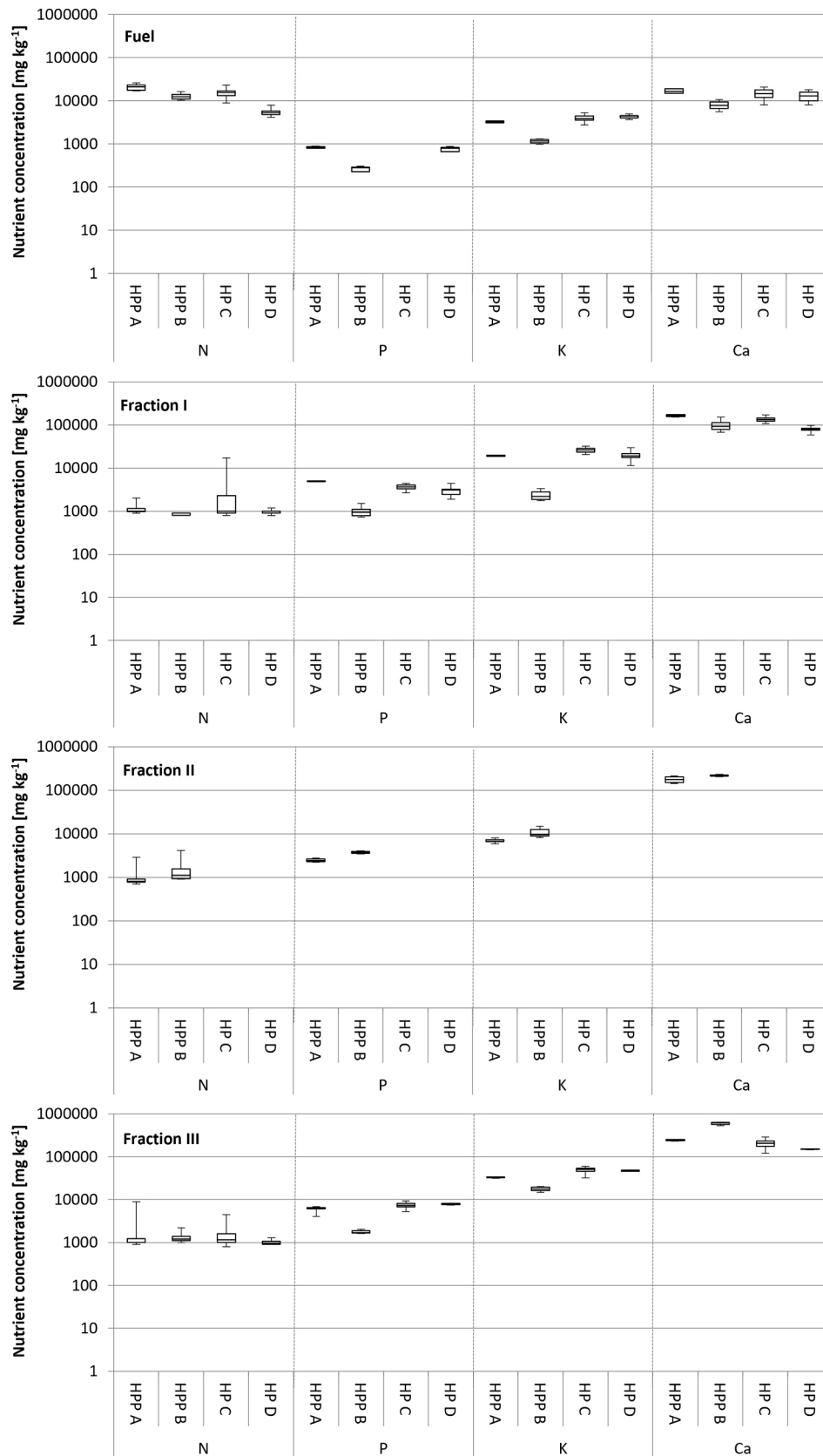
Fig. 2. Concentrations [mg kg^{-1}] of N, P, K and Ca in fuel, bottom ash (fraction I), fly ash (fraction II) and fine fly ash (fraction III). Boxplots with 25% and 75% quantiles (box) and minimum to maximum values (whisker).

Table 3

Mean values ± standard deviation for the concentration of heavy metals (As, Cd, Pb, Ni, Tl and Zn) and plant nutrients (N, P, K, Ca) in the investigated ash fractions as well as corresponding fuel samples.

Element [mg kg^{-1}]		Plant	Fuel		Ash					
					Fraction I		Fraction II		Fraction III	
Heavy metals	As	HPP A	1.93	± 0.37	7.50	± 0.55	3.97	± 0.43	38.85	± 5.31
		HPP B	1.11	± 0.41	10.65	± 3.87	19.26	± 4.21	56.05	± 6.11
		HP C	1.71	± 1.04	6.80	± 1.35			24.82	± 5.56
		HP D	2.49	± 0.63	4.43	± 0.77			30.45	± 2.94
	Cd	HPP A	0.33	± 0.03	4.72	± 0.57	0.04	± 0.01	17.37	± 0.92
		HPP B	0.47	± 0.15	0.74	± 0.25	14.36	± 4.20	82.84	± 9.08
		HP C	0.41	± 0.61	1.23	± 5.41			9.30	± 3.05
		HP D	0.38	± 0.57	0.17	± 0.27			7.40	± 1.36
	Pb	HPP A	27	± 6	304	± 19	16	± 4	1246	± 37
		HPP B	103	± 29	574	± 292	1439	± 594	6052	± 691
		HP C	27	± 13	99	± 82			517	± 166
		HP D	9	± 7	49	± 43			215	± 7
	Ni	HPP A	28	± 24	48	± 3	15	± 1	96	± 85
		HPP B	22	± 9	196	± 74	371	± 65	46	± 7
		HP C	12	± 5	29	± 13			36	± 10
		HP D	703	± 228	20	± 9			35	± 8
	Tl	HPP A	0.02	± 0.00	0.03	± 0.00	0.03	± 0.00	0.03	± 0.00
		HPP B	0.08	± 0.08	0.03	± 0.00	0.03	± 0.00	0.18	± 0.15
		HP C	0.17	± 0.14	0.03	± 0.00			0.03	± 0.00
		HP D	0.55	± 0.21	0.03	± 0.00			0.03	± 0.00
	Zn	HPP A	154	± 9	2138	± 198	669	± 98	4415	± 94
		HPP B	305	± 53	3051	± 1363	5327	± 1410	22,699	± 1303
		HP C	138	± 72	529	± 205			2180	± 545
		HP D	53	± 11	78	± 32			1483	± 206
Plant nutrients	N	HPP A	20,763	± 3282	1175	± 377	1063	± 698	1057	± 129
		HPP B	12,600	± 1768	493	± 428	1550	± 983	1279	± 307
		HP C	15,356	± 2756	3453	± 4872			1495	± 760
		HP D	5385	± 820	957	± 105			1017	± 146
	P	HPP A	834	± 40	4963	± 111	2461	± 187	6103	± 861
		HPP B	261	± 31	970	± 205	3734	± 198	1763	± 129
		HP C	n.a.		3629	± 482			7368	± 977
		HP D	764	± 77	2985	± 672			7901	± 245
	K	HPP A	3255	± 152	19,308	± 517	6880	± 592	32,749	± 756
		HPP B	1154	± 112	2373	± 550	10,612	± 2209	17,627	± 1902
		HP C	4072	± 779	26,139	± 3139			49,358	± 6163
		HP D	4276	± 361	19,249	± 4282			47,272	± 1700
	Ca	HPP A	16,807	± 1903	164,353	± 8196	176,988	± 27,885	243,298	± 7792
		HPP B	8033	± 1702	99,826	± 27,862	218,586	± 7953	599,594	± 37,796
		HP C	89,662	± 790,742	134,593	± 13,978			203,279	± 38,227
		HP D	12,716	± 3268	79,971	± 9000			149,643	± 2375

n.a.: not applicable.

therefore at the lower end of the range described in literature, but comparable to the composition of bottom ashes from plants of similar size as published by Bachmaier et al. (2021)

Although they are mostly below the minimum requirements for commercially available fertilizers, Fig. 3 shows that significant amounts of nutrients are present in the ash fractions studied. This theoretically qualifies the individual ash fraction (fraction II – III) for use as fertilizers. However, comparing the nutrient concentrations with the defined minimum contents for solid mineral compound fertilizers, the specified values are not reached in fraction I in all HP(P)s and in faction II in HPP A and HPP B (except CaO in HPP B in fraction II). In fraction III, the minimum levels are met for the concentration of K_2O in HP C and HP D, and even exceeded by CaO in HPP A and HPP B. Even though in fraction II and fraction III nutrients are present in sufficient concentrations, with regard to the maximum contents for heavy metals the direct application of the investigated wood ash as fertilizer seems to be critical for common practice.

According to the standards used for evaluation, none of the investigated ash fractions II and III can be labeled as an approved solid compound fertilizer. Application as additive for fertilizer-treated biowaste is also not possible due to the corresponding limit values of the German Biowaste Ordinance (Table 1). Only fraction I of HP D and HP C can be recycled with regard to pollutants and used in agriculture and forestry, but also as an additive in composting. High nutrient contents of CaO, K_2O and P_2O_5 (Fig. 4) combined with a variety of micronutrients important for plant growth (Tejada et al., 2020) make this fraction an interesting nutrient resource.

Currently, both filter and fly ashes from the combustion of untreated wood (except Finland) as well as ashes from thermal valorization of waste wood are exempt from the use as fertilizer. In most cases those ash quantities need to be landfilled, removing valuable elements from the natural cycle. For the application of wood ashes from industrial-scale HP (P)s as fertilizer in agriculture and forestry, suitable treatment methods for a targeted separation of nutrients and heavy metals must be developed and evaluated. In this way, potentially toxic elements (e.g., Cd) can be specifically removed from the cycle, while the nutrients can be put to further use. One possibility is leaching with different solvents (water, acids), as has been researched before by Pettersson et al. (2008) and Sano et al. (2013). Moreover, microbial biotechnology strategies can be used. However, there are several obstacles for their application to element recovery such as finding suitable microorganisms for different types of wastes, yield and/or purity of extracted metals (Abramov et al., 2018; Arvelakis et al., 2001; He and Kappler, 2017; Holmberg et al., 2000; Pettersson et al., 2008; Sano et al., 2013).
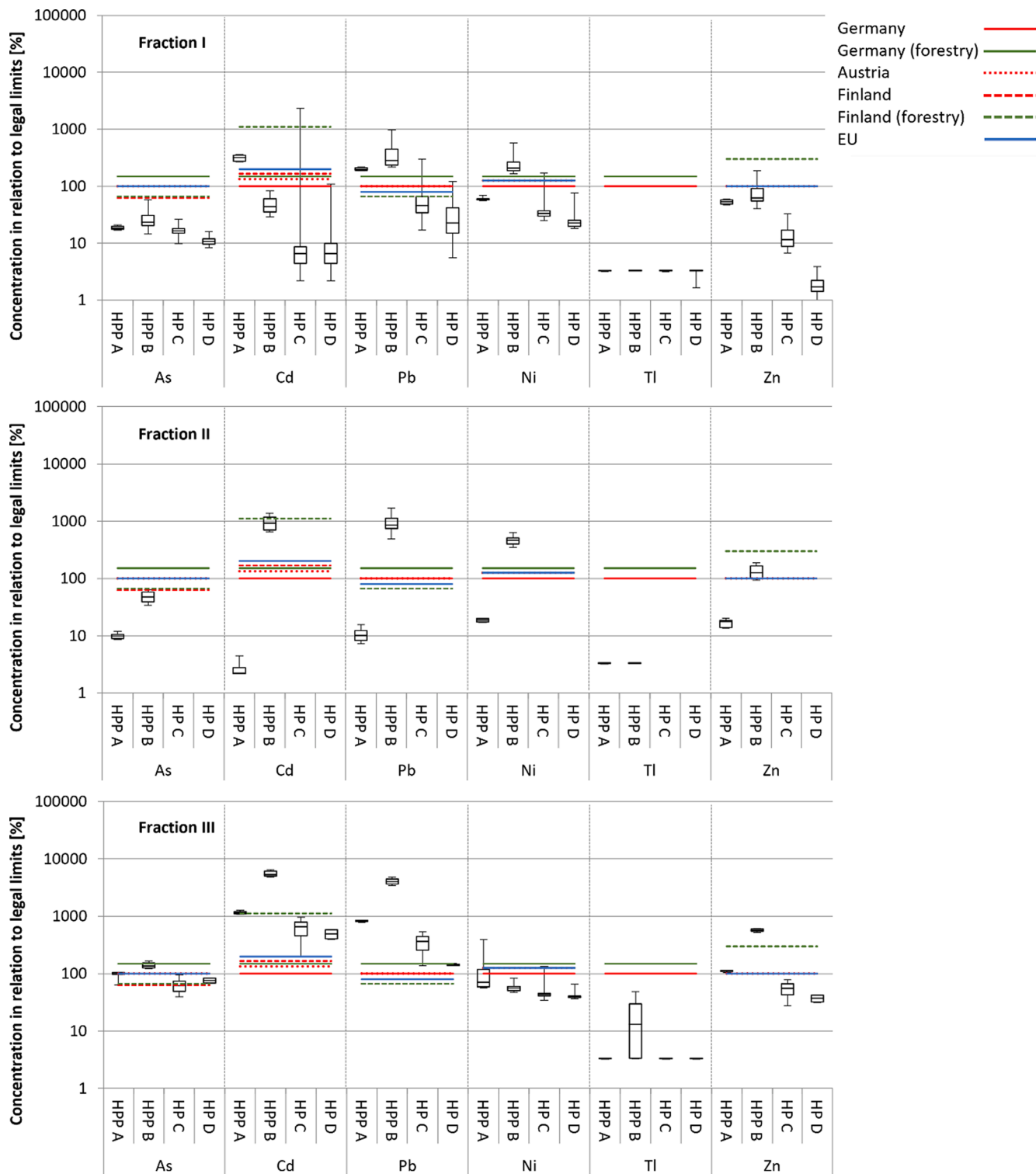
Fig. 3. Concentrations of As, Cd, Pb, Ni, Tl and Zn in bottom ash (fraction I), fly ash (fraction II) and fine fly ash (fraction III) in relation to legal limits. Maximum contents are indicated as 100% (red line - application in agriculture) and 150% (green line - application in forestry). Reference values for 100%, resp. 150% are taken from the German fertilizer ordinance (As, Cd, Pb, Ni, Tl) and the EU fertilizer regulation (Zn). Boxplots with 25% and 75% quantiles (box) and minimum to maximum values (whisker).

3.3. Potential of wood ash for nutrient recovery with a focus on phosphorus

As shown in chapter 3.2, wood ash has a high nutrient content that can partly be compared to mineral fertilizers. These nutrients will be lost when the ash is landfilled and disposed of. The average amount of ash

produced per ash fraction I-III was estimated based on the distribution of bottom and fly ashes as described by Obernberger et al. (1997) and scaled up to the estimated annual ash production from industrial scale wood energy plants in the German federal state of Baden-Wuerttemberg. The mean nutrient content within these fractions and substitution potentials were calculated based on the determined P, resp. N, K, and Ca
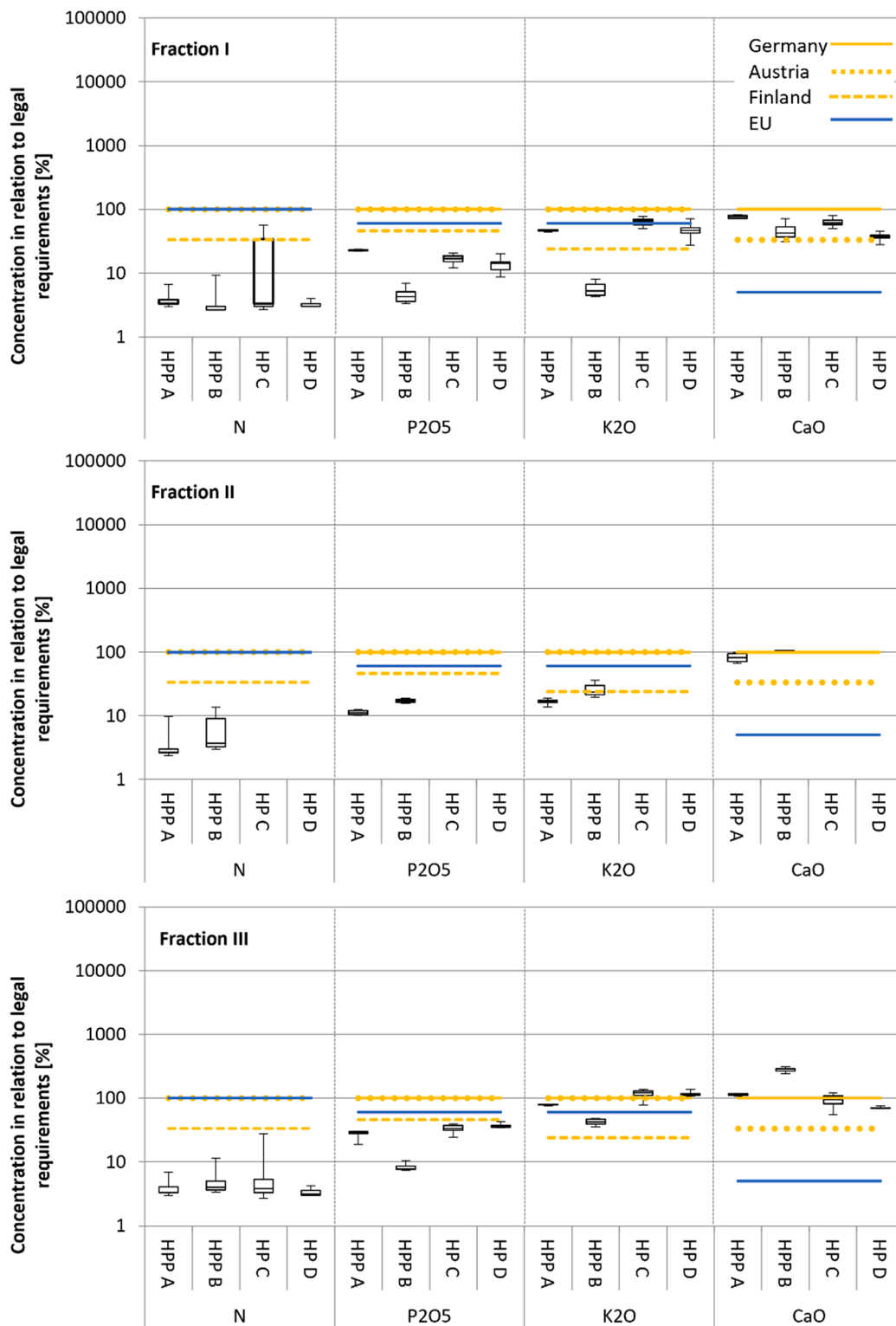
Fig. 4. Calculated concentrations of N, P_2O_5, K_2O and CaO in bottom ash (fraction I), fly ash (fraction II) and fine fly ash (fraction III) in relation to minimum concentrations for commercial solid mineral compound fertilizers and lime fertilizer. The reference value for minimum content is taken from the German fertilizer ordinance and indicated as 100% (yellow line). Boxplots with 25% and 75% quantiles (box) and minimum to maximum values (whisker).

concentrations (Table 4).

Considering the different ash contents of the fuels used together with P, N, K and Ca concentrations determined in the sampled fractions, it is estimated that on average 306 t/a P, resp. 136 t/a N, 1507 t/a K and 23 t/a Ca leave the HP(P)s with the ash. Due to relatively high P, N, K and Ca concentrations and the highest quantitative relevance, fraction I

shows the highest potential, followed by fraction II, fraction III. This seems beneficial, as fraction I also has the lowest content of heavy metals (Table 3).

Assuming 100% nutrient recovery of the identified P, N, K and Ca potentials, approx. 3.1% of the P, 7.5% of the K and 22.8% of the Ca fertilizer sales in Baden-Wuerttemberg (Federal Statistical Office of

Table 4
Estimation of element accumulation (N, P, K and Ca) within wood ash from HPP and HP > 20 MW in southwestern Germany and substitution potential of N, P, K and Ca fertilizer products. Calculation based on an esteemed annual fuel input (wf) of 1.000.000 t/a for plants > 20 MW in Baden-Wuerttemberg and a presumed ash content of 9 w.-%.

		Fraction I Mean value (Range 60–90%) *	Fraction II Mean value (Range 10–35%)*	Fraction III Mean value (Range 2–10%)*
Ash accumulation [t/a]		67,500 (54,000–81,000)	20,250 (9,000–31,500)	5,400 (1,800–9,000)
Therein contained	N [t/a]	103 (82–123)	26 (12–41)	7 (2–11)
	P [t/a]	212 (169–254)	63 (28–98)	31 (10–52)
	K [t/a]	1,132 (905–1,358)	177 (79–275)	198 (66–331)
	Ca [t/a]	8,079 (6,463–9,695)	4,005 (1,780–6,230)	1,614 (538–2,691)
Substitution potential [% of annual use in Baden-Wuerttemberg]	N	–	–	–
	P	2.18 (1.74–2.62)	0.65 (0.29–1.00)	0.32 (0.11–0.54)
	K	5.65 (4.52–6.78)	0.88 (0.39–1.37)	0.99 (0.33–1.65)
	Ca	13.42 (10.74–16.11)	6.66 (2.96–10.35)	2.68 (0.89–4.47)

Germany, 2020) could be substituted.

Phosphorus in phosphate is an essential nutrient for all living organisms and, as raw material in agriculture, cannot be substituted by any other substance. Its mining is associated with increasing challenges, leading to a growing interest in the development of secondary sources such as biomass ashes (Cruz-Paredes et al., 2017; Tan and Lagerkvist, 2011). In this context, closing the P cycle becomes important in the future utilization of biomass and its residues. Nutrient-rich biomass-ashes should be returned to the soil as fertilizer as far as possible. Concerning the reuse of P as fertilizer, the chemical composition of P is critical for plant availability. However, previous research have shown that P in ashes is mainly present as phosphate in combination with Ca, Mg or K, e.g., as apatite phases with low solubility in soil (Boström et al., 2012). This also applies to other plant nutrients such as K and Ca. Whether recycling, resp. nutrient recovery from wood ashes, could be a component of an integrated approach to a bio-based circular economy requires further investigation.

Combined recycling processes for different sources for element recovery, e.g., municipal sewage sludge or sewage sludge ash could increase this amount (Herzel et al., 2016). Thus, wood ash recycling could be one component of an integrated approach towards a circular, bio-based economy.

4. Conclusions

This study evaluates the quality of wood combustion ashes from four industrial wood-fired heat and power plants (>20 MW) with regard to utilization potentials as fertilizer according to legal requirements on European level and from selected countries. Wood ashes contain important plant nutrients but also heavy metals (mainly Cd, Pb and Zn) which do not allow an uncontrolled utilization. According to current legislation, only ashes from the combustion of untreated wood are suitable for use as fertilizer. In some countries, wood ashes are exempt from use altogether. In addition, ashes from the combustion of waste wood are produced in industrial-scale wood energy plants. These ash quantities are currently primarily landfilled, and nutrients are thus removed from the natural cycle. An estimation of the nutrient recovery

potential from industrial wood energy plants in southwest Germany shows that approx. 3.1% (P), 7.5% (K) and 22.8% (Ca) of raw material for fertilizers could be substituted by ash.

Inconsistencies between the EU-wide and national specifications are shown. Furthermore, the allocation of ash fractions towards utilization possibilities depending on the employed fuel and method of separation (combustion chamber, cyclone or filter ash) as made in the regulatory framework does not seem to be suitable. The present study shows that certain ash fractions should not generally be excluded from utilization as fertilizer. For example, the incineration of contaminated waste wood also produces ash fractions that would be suitable for use as fertilizer based on their heavy metal content. Moreover, the actual heavy metal load within a fuel mixture and not the simple definition as waste wood should be used to derive possible applications of combustion residues. Finally, also ashes from natural wood combustion exceed legal limits depending on the employed wood fuel and ash fraction. Nevertheless, the legal limit values serve as an orientation and should be respected in order to preserve soil quality, taking into account the precautionary principle. While the combination of heavy metals and plant nutrients in ash is challenging, both groups of elements are valuable in a closed material circle. In order to develop these quantities for secondary use, investigations are necessary to develop a suitable treatment process for the targeted separation of the heavy metals from the nutrient fraction, taking into account the plant availability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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