

# Trace Element Concentrations in Firewood and Corresponding Stove Ashes

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**ABSTRACT:** The combustion of natural untreated wood in firewood stoves generates ashes with high contents of minor and trace elements. Those ashes can be disposed via garbage collection. Those ashes can also be used as a fertilizer. This study investigates the elemental composition of four natural untreated wood species (beech, oak, spruce, and fir) and their ashes produced in a firewood stove. In total, 30 minor and trace elements were analyzed using inductively coupled plasma-optical emission spectroscopy. With a complete set of fuel and ash data, possible effects of ashes from untreated wood on the environment are discussed. They contain nutrients in concentrations so that ashes are comparable to commercial fertilizers, but they also contain toxic trace elements in concentrations at or above limits given by relevant German legislation. However, the trace elements are not only potentially harmful but also valuable. Therefore, ashes are also valuable in terms of an urban mining prospectus because they do contain certain elements in comparable concentrations as commercially used ores. It is therefore necessary to separate the trace elements from the ash matrix before it is put on soil, and the separated trace elements need to be processed to crude materials for demanded rare earth elements.

## 1. INTRODUCTION

Wooden biomass is a renewable and CO<sub>2</sub> neutral fuel. According to the world energy council, it is used around the world with a total share of about 10% out of the annual primary energy supply.<sup>1</sup> However, more than half of this energy wood is used in small-scale heating stoves for domestic purposes such as heating and cooking.<sup>2</sup>

The ashes that remain in such stoves after wood combustion are mostly used for fertilizing purposes close to the combustion facility because of their specific composition of macro- and micro-nutrients such as calcium (Ca), magnesium (Mg), potassium (K), and phosphorus (P) with a lack in nitrogen (N).<sup>3</sup> Another application of the compensatory ash fertilization is also to prevent further anthropogenic acidification in forest mineral soils.<sup>4–7</sup>

Besides nutrients, plants take up a large number of different other elements in various amounts, during growth, depending on availability and requirements. Therefore, natural and uncontaminated wood contains also different trace elements such as cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), and arsenic (As). Those elements are mostly heavy metals and can be toxic for the plant itself and for the human body via consumption of agricultural products. The concentrations of trace elements in natural wood is commonly in comparable concentrations as found in uncontaminated soil.<sup>8–10</sup>

Depending on their volatility, during combustion, trace elements are partially released from the wood matrix to the flue gas. As the flue gas cools down after combustion, trace elements end up either in ash fractions or in the emitted flue gas. These mechanisms are depending on condensation and sorption mechanisms taking place in the flue gas of small- and large-scale applications.<sup>10–21</sup>

The concentrations of trace elements in ashes are therefore defined by the fuel composition, combustion/operation conditions, and design of the combustion facility.

An important fuel parameter is the ash concentration in the fuel. For wooden fuels, this is mainly depending on the wood-to-bark ratio and is in general rather low with ash contents below 1.0 wt %. Because all elements that are not emitted with the flue gas end up in the resulting ash fractions such as bottom ash/coarse- and fine fly ash, the individual trace element concentrations in those ashes can be approximately about 100 times higher than the corresponding concentrations in the fuels.

Data on trace element concentrations in wooden fuels are available in the literature<sup>22–24</sup> and summarized in Tables 1 and 2. The differences in the given numbers are often rather high, and the authors of the respective studies do not give any reasons for the differences in the values. Especially often not many different elements are reported and no information on trace elements in the most commonly used firewood in Europe such as beech, oak, fir, and spruce are available.<sup>13,25</sup>

In case of high trace element concentrations, those data imply that those ashes even if they originate from untreated wood, cannot be used for fertilizing purpose but have to be disposed in certified disposal sites. Therefore, trace element concentrations in wood combustion ashes are of special concern. Besides those data, no information on trace element concentrations in ashes from log-wood stoves is available, even though these ashes can be harmful to the environment as well.

Besides the toxicity of the trace elements and their potential to be harmful to the environment and human beings, trace elements in combustion ashes are also valuable materials. This means that because of their significant trace element concentrations, ashes from wood combustion facilities (industrial as

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Table 1. Trace Metal Concentrations from Refs<sup>11,12,26,37</sup> in Beech, Oak, and Corresponding Ashes in mg kg<sup>-1</sup> on Dry Basis (d.b)

fuel substrate on d.b.	beech						oak												
	26	27	28	29	30	31	32	12	33	11	26	34	28	35	34	31	34	36	37
Al				8.0–319.0 354.0		8881.0–15484.0		620.0								57.0–319.0		2600.0	19 000.0
As				1.0 0.07–0.08		1.2–1.7		450.0										2.1	23.0–29.0
B				3.7–5.0														180.0	750.0
Ba				11.0–25.0 20.5				1880.0										1400.0	2700.0
Be																			
Ca	670.6		148.0	955.0	1400.0–3100.0	5114.0–1928.0–3855.0		179 000.0		381.5			68.5			5890.0–6501.0		190 000.0	23 100.0
Cd		0.1	0.06	0.2	0.1	0.04–0.05	0.2–0.4	7.0		7.0		3.5	0.003		0.1	0.04–0.05	3.4	0.47	4.0–61.0
Co		0.5	0.45	3.6	0.5–24.0	0.4–1.3		6.0		3.0		4.3	0.55		0.2	1.4–7.8	10.7	140.0	21.0–77.0
Cr				2.0–8.3	7.0–7.8	0.4–1.3		6.0		3.0		721.0	0.44	10.1	0.2	1.4–7.8	90.9	140.0	16.0–213.0
Cs																			
Cu		1.9	0.51	2.7	1.4–31.7	3.0–3.3	43 191.0	120.0		120.0		147.0	0.25	18.3	2.0	2.4–3.0	69.0	100.0	83.0–244.0
Fe	57.0	38.5	38.5	27.0–100.0	189.0	28.0–71.0	193.0–377.0	380.0		380.0		4703.2	80.5	77.1	16.0	36.0–180.0	5989.89	17 000.0	5500.0
Hg								0.06–1.2		0.06–1.2									
K	761.0		1590.0	1530.0	1150.0–1600.0	1851.0		73 000.0		761.0			720.0			1253.0–1841.0		68 000.0	250 000.0
Li																			
Mg	195.9		40.5	408.0	365.0–503.0	546.0–625.0	304.0–494.0	26 000.0		55.1			11.0			234.0–625.0		17 000.0	54 000.0
Mn	60.2	60.0	61.0	59.9	51.0–94.0	400.0–609.0		5480.0		118.0			29.0			86.0		4900.0	3500.0–15 000.0
Mo								5.0		5.0									
Na			152.0	18.0	8.5–110.0	65.0–75.0	56.0–58.0						61.0			27.0–65.0		3900.0	37 000.0
Ni		0.5	1.7	1.0–4.1		1.2–1.7		90.0		90.0		190.3	1.1	13.0	0.3		95.0	44.0	23.0–69.0
P	69.6		12.5	88.0–110.0	252.0–286.0	250.0–666.0		7300.0		43.7			9.5			229.0–252.0		6000.0	13 000.0
Pb		0.55		1.8	0.9	0.8–9.6	0.5–5.0	24.0		200.0		8.1			0.3	0.5–9.6	21.4	3.1	14.0–62.0
S				60.0				3060.0					0.07					52 000.0	
Se																			
Si			1580.0	70.0–242.0	1959.0–2472.0		9960.0											74 000.0	57 000.0
Sr				10.4–12.0			10.2–12.1						1200.0						
Ti				1.5–4.0				65.0											1.5
V				0.1		1.2												21.0	10.0
W																			
Zn		10.5	32.5	3.9	2.8–11.0	14.0–16.0	11.0–26.3	289.0		190.0		59.4	18.0	23.0	3.0	8.4–15.4	148.6	93.0	1400.0

Table 2. Trace Metal Concentrations from refs <sup>1,11,12,27,29,33,38,41</sup> in Spruce, Fir, and Corresponding Ashes in mg kg<sup>-1</sup> on Dry Basis (d.b)

fuel substrate on d.b.	spruce												fir					
	wood						ash						wood			ash		
	38	39	32	40	41	27	29	30	31	32	33	12	30	30	11	11	12	
Al				4.8	14.0			53.0–477.0	440.0		1090.0		3090.0	56.0	1710.0	4199.0–9141.0		
As	0.21							0.05–0.5	0.1	0.05–1.1	11.0		0.5	1.0		0.8–1.0		
B								6.0		9.2			308.0			2.0		
Ba		0.58		9.9				40.0–110.0	34.1		3250.0			11.0	830.0			
Be																		
Ca	887.0		5555.0	636.3	705.5		940.0	712.0–10 700	3031.0–3426.0	1928.0–14 942.0	282 000.0		8250.0	893.0	151 000.0			
Cd	0.3	0.005		0.3		0.5	0.3	0.1–0.5	0.26	0.08–0.4	11.0	1.3–3.2	0.2		9.0	0.1–0.2		
Co								0.2–0.6		0.09–0.6				3.0				
Cr	1.1					0.63	2.0	1.6–4.2	18.3–20.7	2.2–24.7	4.0		26.8		3.0	0.6–3.4		
Cs																		
Cu	2.2	0.36		0.1		0.97	0.73	1.4–10.0	3.0	1.4–3.2	133.0	229.0–230.0	90.0	180.0	49.0–53.0			
Fe	41.0		320.0	2.4	49.0	30.33		26.0–670.0	279.0–307.0	85.0–971.0	720.0		1546.0	25.0	760.0	126.0–247.0		
Hg	0.02								0.07									
K	304.0		3915.0	477.14	480.0		841.0	354.0–3600.0	1610.0–1769.0		64 000.0		2370.0	25.0	99 000.0			
Li																		
Mg	103.0	80.95		72.74	148.5		81.0	352.0–830.0	457.0–499.0	304.0–1330.0	26 000.0		825.0	144.0	19 000.0			
Mn	30.0		600.0			208.0		140.0–660.0	28.0–419.0		10 070.0		427.0	55.0	5990.0	86.0–409.0		
Mo								0.1		0.2		1.3			1.3			
Na				100.3	250.0		17.0	54.0–190.0	103.0–114.0	85.7–171.4			1444.0	18.0				
Ni	1.1					0.17	1.2	0.8–3.1		0.85–13.6	30.0	37.0–39.0	10.3	0.6	5.0	0.4–1.5		
P																		
Pb	0.6	0.2	13.7	0.7		5.43	7.2	1.2–5.6	1.5–7.4	0.5–4.4	13.0	47.0–3.2	1.7	12.0	0.5–0.8			
S	49.0			63.0			60.0				2770.0				5449.0			
Se								0.1										
Si				616.7	700.0		1160.0	84.0–9800.0	3212.0–3653.0		1570.0			225.0	1200.0			
Sr			17.25	2.6				15.0–9.0	15.0–20.4					4.0		37.18		
Ti											67.0	91.0–216.0			34.0	0.96–2.7		
V								0.4–1.1										
W																		
Zn	11.0		75.25	14.2	8.3	16.33	7.2	19.0–140.0		13.2–100.0	2350.0	1110.0–1290.0	155.0	14.0	690.0	5.9–10.0		

PA	100%		0%				0%	
SA	100%		100%				70%	
	Batch 1 2 kg	Batch 2 2 kg	Batch 3 2 kg	Batch 4 2 kg	Batch 5 2 kg	Batch 6 2 kg	Batch 7 1 kg	Batch 8 1 kg
	Starting phase		Nominal load				Partial load	

Figure 1. Combustion cycle procedure.

well as household systems) represent also attractive resources in terms of an urban mining prospective. Within this prospective, minor and trace elements from those ashes are recovered and made available as crude materials for demanded rare earth elements and fertilizers.

The main goals of this study are therefore to prepare a broad data basis on trace element concentrations in the tree species oak, beech, fir, and spruce as well as on trace element concentrations in ashes from firewood stoves originating from the combustion of the aforementioned wood species. On the basis of these data, the goal of this study is to evaluate the potential for urban mining and to assess the effect on the environment.

## 2. METHODS AND MATERIALS

All samples were processed and analyzed in the central laboratory of the University of Applied Sciences Rottenburg (HFR).

**2.1. Origin of the Wood Samples.** Four tree species oak (*Quercus robur*), beech (*Fagus sylvatica*), fir (*Abies alba*) and spruce (*Picea abies*) were logged in May 2015 at the municipal forest of Rottenburg a. N. (Rammert). Further treatment was done by cutting up the stem wood in 1 m long cleaved logs. The generated wood logs were stored and air dried to <30.0% of water content in a barn for two years. Standard wood logs for firing purposes were generated by debarking the 1 m logs with a hand axe and cut in smaller units with a total of 33 cm in length by a firewood drag saw. Afterward, these wood logs were cut again to a total length of 30 cm. The generated wood residues were assigned to its standard log and stored. In the last step, the logs were chopped with a hand axe to  $1.0 \pm 0.010$  kg in mass for the hardwood. The softwood logs hold in average  $0.633 \pm 0.010$  kg in mass, compensating the specific higher calorific value to be able to compare both wood types during combustion. Furthermore, the reason for debarking the firewood is also to compare trace element concentrations because in both wood types, concentrations within the bark could be up to three times higher than those in the wood and that might cloud the results.<sup>42</sup>

**2.2. Combustion and Procedure.** All combustion tests were performed with an 8 kW firewood stove (Hark 44 GT ECOplus by Hark GmbH & Co. KG, Germany). It provides combustion air staging with separate manually controlled primary and secondary air. The test facility is described in more detail in ref 43. For each wood species, a test cycle corresponding to real life operation was carried out according to ref 43. This test cycle consisted of eight consecutive combustion batches, as shown in Figure 1. The batches were attributed to a starting phase, nominal load, and partial load operation. The used amount of fuel and the positing of primary (PA) and secondary (SA) combustion air valves were adjusted and kept constant according to the load phase.

**2.3. Analytics.** **2.3.1. Wood Sample Preparation and Digestion.** Fuel wood samples for analytical purposes were gained out of the wood residues from the standard log preparation. First, the water content was determined according to ref 22. Therefore, they were oven-dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.) for 3 days until constant weight was reached. Afterward, the 1–2 cm thick pieces were cut on both sides by a wood drag saw to prevent contamination with chain oil or soil from the previous treatments. The samples were milled to two different particle sizes holding 1 and 0.25 mm by a cutting mill (Pulverisette19 Fritsch Ltd.) with trace metal free inlet milling cassettes. For inductively coupled plasma-optical emission spectroscopy (ICP-OES) element determination, the

0.25 mm particle size material was microwave digested according to ref 44 with Multiwave GO 3000, Anton Paar Ltd. Therefore,  $300 \pm 1.0$  mg of the fine material was transferred in 50 mL Teflon vessels and combined with 2.5 mL of HNO<sub>3</sub> supra quality (69%) (Merck, Germany) and 7.5 mL of HCL supra quality (35%) (Roth, Germany) and digested at 190 °C for 20 min with a heat ramping by  $12.6$  °C min<sup>-1</sup>. The digested residues were aliquoted to 50 mL with aqua bidest and measured at the ICP-OES system. There were six replications for each wood sample.

**2.3.2. Ash Sample Preparation and Digestion.** Residual ashes were collected after each combustion cycle and stored in a vacuum-sealed plastic bag at 4 °C. Before analysis, the samples were dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.) and milled to 0.25 mm by a cutting mill (Pulverisette19 Fritsch Ltd.). The total ash amounts of the combustion cycles were for beech 57.5 g, oak 36.7 g, spruce 41.3 g, and fir 65.2 g. For ICP-OES element determination, the ashes were microwave digested according to ref 44 with Multiwave GO 3000, Anton Paar Ltd.. Therefore, a representative sample of  $150 \pm 1.0$  mg of the fine material was transferred in 50 mL Teflon vessels and combined with 2.5 mL of HNO<sub>3</sub> supra quality (69%) (Merck, Germany) and 7.5 mL of HCL supra quality (35%) (Roth, Germany) and digested at 190 °C for 20 min with a heat ramping by  $12.6$  °C/min. The digested residues were aliquoted to 50 mL with aqua bidest and measured at the ICP-OES system. There were six replications for each ash sample.

**2.3.3. Calorific Analysis.** The gross calorific value at a constant volume in dry basis was determined according to ref 45. Therefore, the fine material out of the wood sample preparation holding 1 mm in particle size were weighing  $0.5 \pm 0.020$  g and transferred in glass crucibles. Afterward, they were combusted in an (C6000 IKA Ltd.) automated isoperibol calorimeter. There were three replications for each wood sample.

**2.3.4. Proximate Analysis.** The ash content was determined by pyrolysis of 1 g  $\pm$  20 mg of oven-dried sample in a ceramic crucible by a muffle furnace model (AAF 1100 Carbolite Ltd.) at  $550 \pm 10$  °C. All analyses were done in quadruplicate, and the results were expressed on a dry weight basis according to ref 46.

**2.3.5. Ultimate Analysis.** The simultaneous determination of carbon, hydrogen, nitrogen, and sulfur was done by an Elemental vario Macro cube elemental Analysis device using direct oxidation/reduction and detection by thermal conductivity according to ref 47. Each sample of 0.25 mm particle size for wood and dried raw ash was weighing  $20 \pm 1.0$  mg, pressed in a zinc foil coated tablet, and measured at the device with six replications per wood and ash sample.

**2.3.6. Trace Element Analysis.** Quantitative metal analysis on the solutions obtained from the microwave digestion of wood and ash samples were measured with an ICP Optical Emission Spectrometer series Spectro Blue with a model ASX-260 auto sampler.

**2.3.7. Data Evaluation.** All presented results are arithmetic mean values. The results of the combustion tests are also calculated for standard conditions for pressure and temperature (1013 hPa and 273 K) and normalized to volumetric oxygen content (O<sub>2,ref</sub>) of 13 vol % in the flue gas. Student's *t*-test was used to identify statistical differences between element concentrations in the ashes and wood of the different tree species. In this study, the following interpretations are used for the *p*-values from the student's tests:

$p < 0.01$  highly significant difference or correlation.

$p < 0.05$  significant difference or correlation.

$0.32 \leq p \leq 0.05$  no significance, but a clear trend of difference or correlation.

$p > 0.32$  no significance and no trend of difference or correlation.

**Table 3. Measured Wood Properties db: (Dry Basis); ar: (As Received)**

sample	gross calorific value [MJ kg <sup>-1</sup> db]	ash content w [%] db	water content w [%] ar	C/H/N values w [%] db	chloride Cl <sup>-</sup> [mg kg <sup>-1</sup> db]
oak wood	19.31	0.35	14.3	48.51:6.01:0.12	42.56
beech wood	19.42	0.71	13.9	48.14:6.14:0.20	61.93
spruce wood	20.11	0.30	15.1	48.86:6.38:0.07	44.54
fir wood	19.98	0.65	13.8	49.14:6.32:0.08	149.16

### 3. RESULTS

**3.1. Wood Properties.** All results refer to wood without bark.

**3.1.1. Proximate and Ultimate Analysis of Wood.** The fuel properties of all four wood species are shown in Table 3. The gross calorific values of the hardwood types are 19.31 and 19.42 MJ kg<sup>-1</sup>. The softwoods are 19.98 and 20.11 MJ kg<sup>-1</sup>. The ash contents of all wood species are below 1.0 wt %. The water content of all observed wood species are within the air-dry range (10–20%). The measured CHN concentrations within the wood species holding for carbon (C) 48–49%, for hydrogen (H) about 6%, and for nitrogen (N) >0.1% for the hardwood and <0.1% for the softwood. The IC measurements result for chloride (Cl<sup>-</sup>) in hardwood 42.56–61.93 mg kg<sup>-1</sup>. The softwood holds 44.54–149.16 mg kg<sup>-1</sup> chloride (Cl<sup>-</sup>).

**3.1.2. Minor Elements in Wood.** Concentrations of the investigated minor elements in the four wooden fuel species are expected to be in general between 100 and 10 000 mg kg<sup>-1</sup> and are shown in Figure 2. The concentrations of Ca and K are at about 1000 mg kg<sup>-1</sup>. On the other end, the concentrations of Na, P, S, and Si are mainly at about 100 mg kg<sup>-1</sup>. The concentrations of Mg are in between, with average concentrations of about 500 mg kg<sup>-1</sup>.

In general, the diagram does not show any tendency that would suggest any impact of the four tree species on minor element concentrations for Ca, Na, S, and Si. However, their *p*-values given in Table 4 show partially significant differences, but partially only a clear trend of difference (*p* > 0.01) to (*p* < 0.32). But the concentrations are still in the same region. However, an impact on the tree species is observed within K, Mg, and P; here, beech shows a highly significant difference (*p* < 0.01) in concentration to all other tree species. Furthermore, the partially wide ranges of concentrations that are reported in the literature and summarized in Table 1 cannot be seen for the four wood species samples that have all been grown in the same region.

**3.1.3. Trace Elements in Wood.** The concentrations of the investigated trace elements that are in general below 100 mg kg<sup>-1</sup> are shown in Figure 3 and *p*-values given in Table 8. For As, Cd, Pb, Se, Ti, and V, the concentrations are mainly between 0.1 and 1 mg kg<sup>-1</sup>. For Be, Co, Cr, Li, Mo, and Zn, the concentrations are mainly in the range of 1–10 mg kg<sup>-1</sup>. In addition, the concentrations of Al, B, Ba, Co, Fe, Mn, and Sr are in the range of 10–100 mg kg<sup>-1</sup>. As for the minor elements, the results from the trace elements do not suggest any impact of the tree species on trace element concentrations (Table 5).

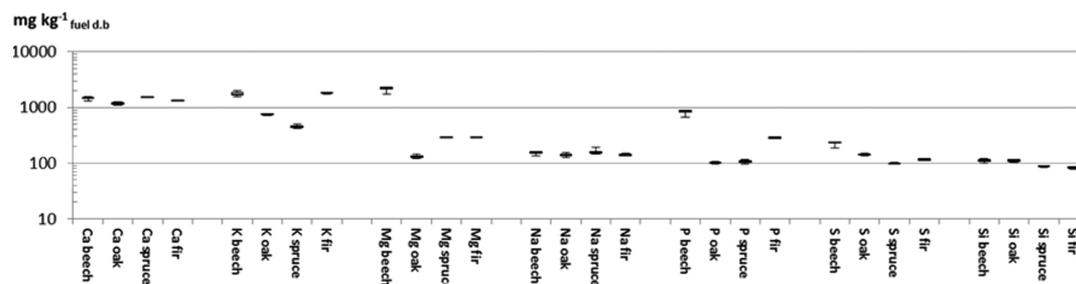
**3.2. Ash Properties.** **3.2.1. Combustibles and Relevant Ions.** The ash concentrations of the four tree species are with 0.3–0.7% compared with other solid fuels, rather low. This means that enrichment factors for elements that are not volatilized during combustion are rather high. With respect to that, the combustion was good for all other samples, except for oak. This is shown in detail in the flue gas analysis in Table 6. However, the concentrations in the ashes can differ for carbon between 8 and 16 wt %, for hydrogen between 0.59 and 0.76 wt % and for nitrogen between 0.07 and 0.23 wt % as shown in Table 7. The chloride concentration ranges from 492 to 956 mg kg<sup>-1</sup>.

**3.2.2. Minor Elements in Wood Ash.** Concentrations of minor elements in wood ashes from firewood stoves from the combustion of beech, oak, spruce, and fir are shown in Figure 4. Those elements are expected to be volatilized during combustion only partially and end up mainly in the ashes. The concentrations of those elements found in the ashes are therefore expected. An element mass balance cannot fully be closed because the elements are also partially released with the flue gas.

With respect to that, the concentrations of Ca and K are at about 100 000 mg kg<sup>-1</sup>. The concentrations of Na, P, S, and Si are around 10 000 mg kg<sup>-1</sup>, where the volatilization of Na is rather high. The concentrations of Mg are with about 50 000 mg kg<sup>-1</sup> in between the aforementioned elements.

**3.2.3. Trace Elements in Wood Ash.** As discussed for the minor elements, the concentrations of trace elements are determined by the element and the ash concentration in the fuel as well as the volatilization of the individual element during combustion. With respect to that, the concentrations of the investigated trace elements that are displayed in Figure 5 are in the range that would have been expected based on the fuel analysis.

The concentrations of the elements As, Be, Cd, Co, Cr, Li, Pb, Se, Ti, and W are in the range of 1–10 mg kg<sup>-1</sup>. The concentrations of the elements Mo, Ni, and V are in the range of 10–100 mg kg<sup>-1</sup>. The concentrations found for Al, Cu, Fe, Sr, and Zn are in the range of 100–1000 mg kg<sup>-1</sup> and the highest concentrations are found for B, Ba, Cs, and Mn (Tables 8–10).



**Figure 2.** Minor element concentrations (mg kg<sup>-1</sup>) measured in wood species on dry basis (d.b.). Range of error bars are min/max concentration values.

Table 4. *p*-Values for Minor Element Concentrations in Compared Wood Species

element	beech/oak	beech/spruce	beech/fir	oak/spruce	oak/fir	fir/spruce
Ca	<0.01	>0.05	<0.05	<0.01	<0.01	<0.01
K	<0.01	<0.01	>0.32	<0.01	<0.01	<0.01
Mg	<0.01	<0.01	<0.01	<0.01	<0.01	>0.32
Na	>0.05	>0.32	>0.05	>0.05	>0.32	>0.05
P	<0.01	<0.01	<0.01	>0.05	<0.01	<0.01
S	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	>0.32	<0.01	<0.01	<0.01	<0.01	<0.01

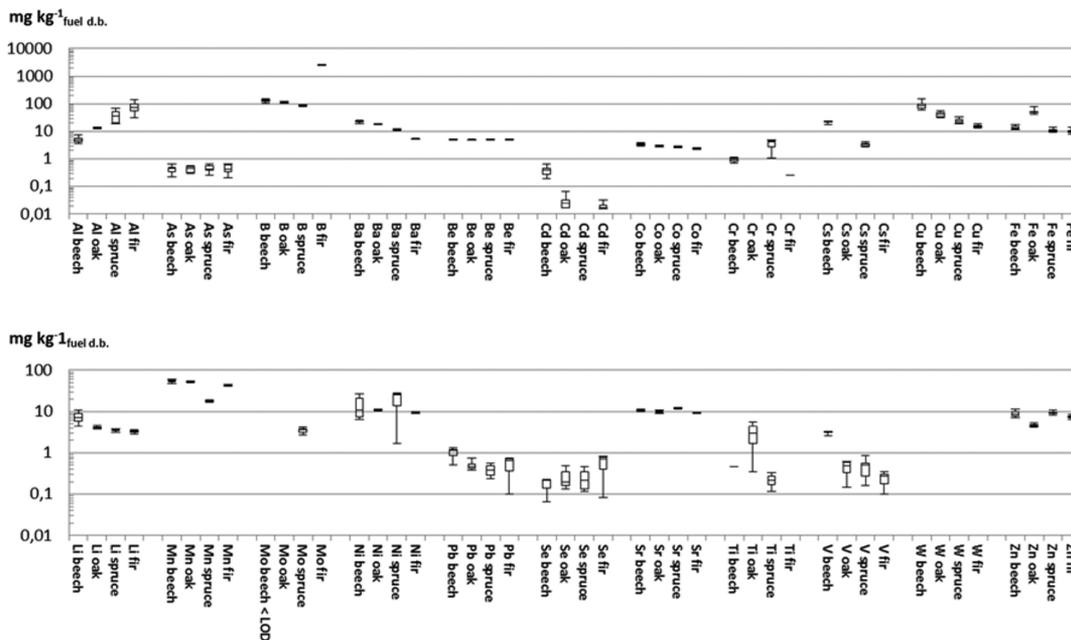


Figure 3. Trace metal concentrations (mg kg<sup>-1</sup>) measured in beech, oak, spruce, and fir wood on dry basis (d.b.).

Table 5. Measured Element Concentrations in Wood Species and Corresponding Ashes

Element mg kg <sup>-1</sup>	Beech		Oak		Spruce		Fir	
	wood	ash	wood	ash	wood	ash	wood	ash
Al	5,1	227,2	13,2	938,7	38,0	399,4	78,4	420,8
As	<0,16	<0,30	<0,15	<0,30	<0,16	<0,30	<0,16	<0,30
B	129,0	2655,7	108,9	5468,7	86,2	2408,1	73,8	1427,2
Ba	22,6	1910,5	18,1	3649,3	11,3	3030,1	5,2	285,5
Be	4,8	9,7	4,8	11,5	157,3	9,4	4,8	9,3
Ca	1473,4	124580,0	1179,4	209514,2	1552,1	283365,3	1341,3	111365,2
Cd	0,4	0,7	<0,08	0,9	<0,083	0,3	<0,08	0,4
Co	3,4	2,8	2,9	2,5	2,7	2,4	2,3	0,3
Cr	0,9	2,5	<0,083	2,2	3,5	1,7	0,3	6,2
Cs	21,1	2452,9	<0,38	4132,9	3,4	3138,0	<0,96	334,4
Cu	90,5	412,2	41,6	226,6	24,5	140,0	15,6	97,7
Fe	13,9	291,2	52,6	445,7	11,2	283,7	10,4	148,3
K	1784,5	50869,6	745,5	41244,5	451,6	26186,7	1828,6	61162,6
Mg	2176,0	124131,8	129,8	10338,0	287,5	38183,1	288,9	22575,1
Mn	53,9	6117,4	52,4	16453,2	17,8	8588,7	43,2	1517,8
Mo	<0,15	<0,30	<0,15	<0,30	3,4	<0,30	<0,15	14,1
Na	151,2	864,4	137,9	1167,6	157,3	632,7	140,7	463,4
Ni	14,2	59,5	10,9	45,1	18,7	3,0	9,4	81,8
P	832,4	91221,3	101,8	7899,5	107,1	9637,1	282,3	7427,5
Pb	1,0	3,0	0,5	7,3	0,4	2,2	0,5	2,8
S	222,4	8578,2	139,3	12716,0	97,2	6657,4	114,1	4094,2
Sr	10,6	435,6	9,8	928,6	12,1	1299,5	9,0	224,1
Ti	0,5	5,0	3,0	22,1	0,2	5,8	<0,11	8,1
V	3,1	242,8	0,4	18,6	0,5	76,3	0,2	42,9
W	<0,65	1,8	<0,65	<1,3	<0,65	8,0	<0,65	<1,30
Zn	8,9	193,5	4,6	79,3	9,2	702,5	7,4	156,6

4. DISCUSSION

4.1. Impacts of Firewood Ashes on the Environment.

The composition of ashes from firewood stoves depends on combustion conditions as well as on the fuel composition. Depending on its composition, it can be a valuable fertilizer,

hazardous waste, or source of valuable elements in terms of an urban mining prospectus.

4.1.1. Ash as Fertilizer. Ash is a fertilizer that has been used since centuries. This is due to the concentrations of nutrients like P, Na, K, Mg, and Ca. The concentrations of those

Table 6. Results of the Combustion Tests

phase	batch	CO [mg/m <sub>13vol %O<sub>2</sub><sup>3</sup>]</sub>	C <sub>tot</sub> [mg/m <sub>13vol %O<sub>2</sub><sup>3</sup>]</sub>	NO [mg/m <sub>13vol %O<sub>2</sub><sup>3</sup>]</sub>	O <sub>2</sub> [vol %]	T <sub>FG</sub> [°C]	m <sub>fuel</sub> [g]
<b>Beech</b>							
all batches	16	3272	347	186	16.3	213.6	1727.3
starting phase	4	4251	424	192	17.4	164.3	1980.8
nominal load	8	2323	309	194	15.7	239.3	1966.3
partial load	4	4189	345	165	16.4	211.3	996.0
<b>Oak</b>							
all batches	16	7102	1156	158	17.4	202.9	1787.9
starting phase	4	8049	2092	189	18.5	172.2	1994.0
nominal load	8	7549	1027	156	17.1	212.8	1981.0
partial load	4	4852	299	137	16.7	222.1	998.0
<b>Spruce</b>							
all batches	16	2621	162	81	15.2	252.4	1663.1
starting phase	4	4225	195	75	16.4	210.2	1900.0
nominal load	8	1989	161	85	14.8	271.9	1878.8
partial load	4	2282	128	79	14.7	255.3	995.0
<b>Fir</b>							
all batches	16	3593	306	100	15.1	247.4	1692.7
starting phase	4	5021	967	88	16.0	184.2	1929.0
nominal load	8	2697	94	108	14.4	277.6	1923.4
partial load	4	3957	69	97	15.5	250.4	995.0

Table 7. Measured Ash Properties on Dry Basis

sample	C/H/N values w [%]	chloride Cl <sup>-</sup> [mg kg <sup>-1</sup> ]
oak ash	15.87:0.60:0.23	492.00
beech ash	8.50:0.61:0.07	503.50
spruce ash	10.44:0.59:0.11	544.20
fir ash	10.66:0.76:0.11	956.25

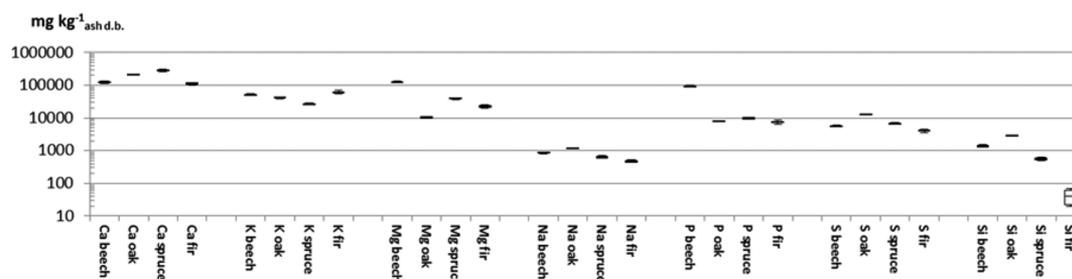
elements in the investigated samples are shown in Figure 6 and additional *p*-values given in Table 11. The figure shows in addition the usual concentrations of those elements in specific synthetic mineral fertilizers in comparison to measured wood ash.

The comparison of ash and fertilizers from ref 48 show that the relevant elements are generally contained in the measured firewood ashes in comparable concentrations as in commercially available fertilizers. As expected, nitrogen is mainly volatilized during combustion and therefore contained in ashes in rather low concentrations. As nitrogen (N), also sulfur (S) is volatilized during combustion and is therefore partially emitted with the flue gas. The concentrations in the ashes are therefore about 10 times lower than the concentrations in fertilizers. The phosphorus (P) concentrations in the ashes are in the range of 10 000–100 000 mg kg<sup>-1</sup> which is right in the range of the concentrations in fertilizers. The potassium (K) concentrations in ashes are below 100 000 mg kg<sup>-1</sup> which is twice as low as the concentration of potassium (K) in fertilizers that are mainly about 200 000 mg kg<sup>-1</sup>. For Mg and Ca, the concentrations in the ashes are within the range of the concentrations

in the fertilizers. For Mg, the concentrations are at about 8000 mg kg<sup>-1</sup> and for Ca, the concentrations are at about 11 000 mg kg<sup>-1</sup>. Besides those macronutrients, there are also micronutrients such as Al, Fe, or Mn. Those are also very important for the growth of the plant because they are required for pathways within their metabolism. However, those elements are also toxic trace elements. Whether those elements are toxic or valuable depends on the individual concentration and the amount of ash that is put on the soil.

**4.1.2. Toxic Elements in Ashes.** Besides the valuable nutrients in ashes, there are also potentially toxic elements. The uptake of some of those elements to agricultural soils needs to be limited. Therefore, legislative bodies tend to limit those elements in the environment. In Germany there are three different acts: the fertilizer ordinance,<sup>49</sup> biological waste ordinance,<sup>50</sup> and soil protection ordinance.<sup>51</sup> Those acts limit the concentrations of Cu, Cr, Ni, Cd, Pb, and Zn in fertilizers. The individual limits for the six different elements are given in Figure 7 with respect to the element concentrations measured in the different ashes.

The limit values given in the three acts differ partially by several magnitudes. For instance for chromium, the limit value in the fertilizer ordinance is 2 mg kg<sup>-1</sup> while the corresponding limit in the soil protection ordinance is 200 mg kg<sup>-1</sup>. This can also be found the other way round as seen for Zn. Here, the limit value in the fertilizer ordinance is 1000 mg kg<sup>-1</sup> while the corresponding value in the soil protection ordinance is 200 mg kg<sup>-1</sup>.

Figure 4. Minor element concentrations (mg kg<sup>-1</sup>) measured in wood ashes on dry basis (d.b.).

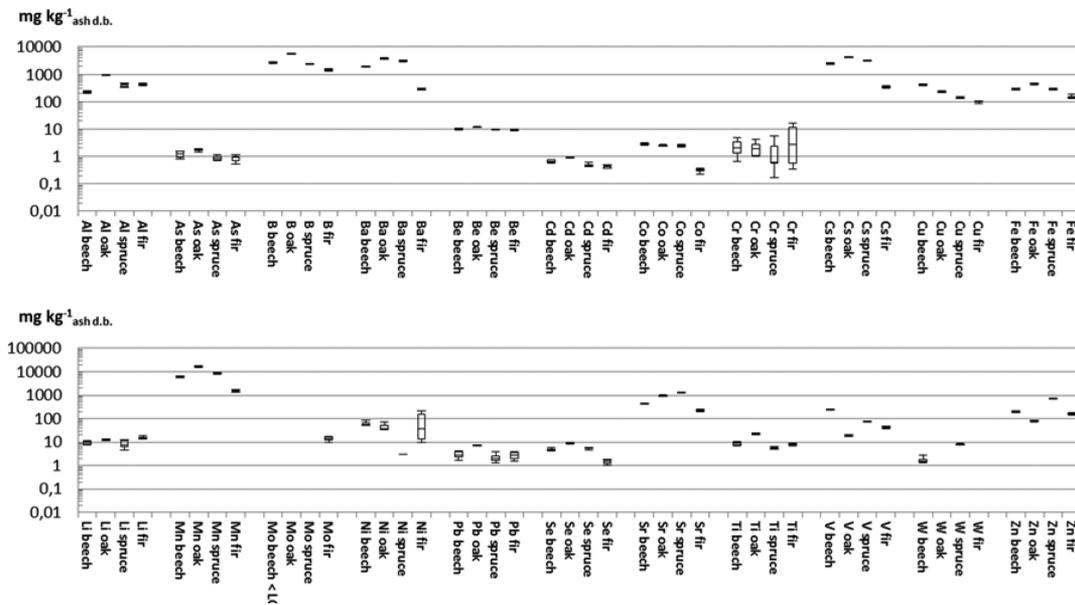


Figure 5. Trace metals concentrations ( $\text{mg kg}^{-1}$ ) measured in beech, oak, spruce, and fir ash on dry basis (d.b.).

Table 8. *p*-Values for Trace Element Concentrations in Compared Wood Species

element	<i>p</i> -value					
	beech/oak	beech/spruce	beech/fir	oak/spruce	oak/fir	fir/spruce
Al	<0.01	<0.01	<0.01	<0.05	<0.05	>0.05
As	>0.32	>0.32	>0.32	>0.32	>0.32	>0.32
B	<0.05	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Be	>0.32	>0.32	>0.32	>0.32	>0.05	>0.05
Cd	<0.01	n.a.	<0.01	n.a.	<0.32	n.a.
Co	<0.05	<0.01	<0.01	<0.05	<0.01	<0.01
Cr	n.a.	>0.05	n.a.	n.a.	n.a.	n.a.
Cs	n.a.	<0.01	n.a.	n.a.	n.a.	n.a.
Cu	<0.05	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.01	<0.05	<0.05	<0.01	<0.01	>0.32
Li	<0.05	<0.05	<0.01	<0.05	<0.01	<0.05
Mn	>0.32	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ni	>0.32	>0.32	>0.05	>0.32	<0.01	>0.32
Pb	<0.05	<0.01	>0.05	<0.32	>0.32	>0.32
Se	>0.32	>0.32	<0.32	>0.32	>0.32	>0.32
Sr	>0.05	<0.01	<0.01	<0.01	<0.05	<0.01
Ti	n.a.	n.a.	n.a.	>0.32	n.a.	n.a.
V	<0.01	<0.01	<0.01	>0.32	>0.05	>0.05
W	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Zn	<0.01	>0.32	>0.05	<0.01	<0.01	<0.01

Table 9. *p*-Values for Minor Element Concentrations in Compared Wood Ashes

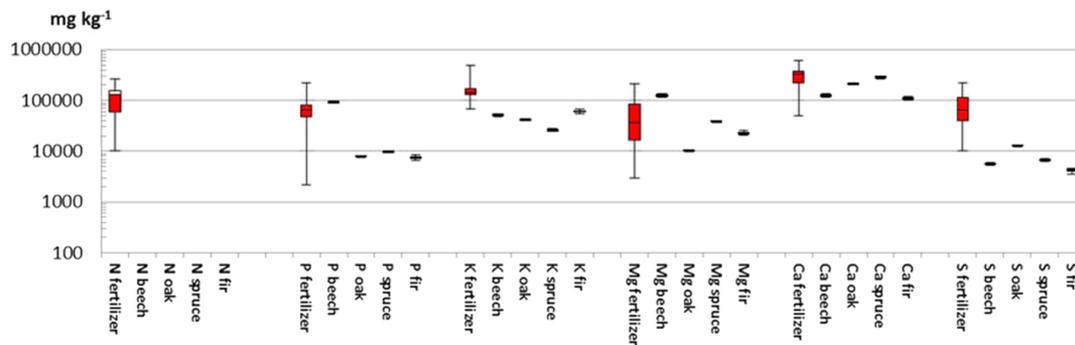
element	<i>p</i> -value					
	beech/oak	beech/spruce	beech/fir	oak/spruce	oak/fir	fir/spruce
Ca	<0.01	<0.01	<0.05	<0.01	<0.01	<0.01
K	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
P	<0.01	<0.01	<0.01	<0.01	<0.05	<0.01
S	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Si	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

In addition, as in case of Ni, the limit values of the three acts are closely together between 50 and 90  $\text{mg kg}^{-1}$ . Considering

these partially wide ranges, the measured values in firewood ashes are safely under the limits as in case of Pb or Cd. They

Table 10. *p*-Values for Trace Element Concentrations in Compared Wood Ashes

element	<i>p</i> -value					
	beech/oak	beech/spruce	beech/fir	oak/spruce	oak/fir	fir/spruce
Al	<0.01	<0.01	<0.01	<0.01	<0.01	<0.32
As	<0.05	>0.05	>0.05	<0.01	<0.01	>0.32
B	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Be	<0.01	<0.01	<0.01	<0.01	<0.01	>0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	>0.05
Co	<0.01	<0.01	<0.01	>0.32	<0.01	<0.01
Cr	>0.32	>0.32	<0.32	>0.32	<0.32	<0.32
Cs	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.01	>0.32	<0.01	<0.01	<0.01	<0.01
Li	<0.01	>0.32	<0.01	>0.05	<0.05	<0.01
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ni	<0.05	n.a.	>0.05	n.a.	>0.32	n.a.
Pb	<0.01	<0.05	>0.32	<0.01	<0.01	<0.32
Se	<0.01	<0.05	<0.01	<0.01	<0.01	<0.01
Sr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ti	<0.01	<0.01	>0.32	<0.01	<0.01	<0.01
V	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W	n.a.	<0.01	n.a.	n.a.	n.a.	n.a.
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Figure 6. Nutrient element concentrations N, P, K, Mg, Ca, and S contained in wood ashes in comparison to concentrations in common fertilizers.<sup>48</sup>Table 11. *p*-Values for Element Concentrations in Fertilizer Compared to Wood Ashes

element	<i>p</i> -value			
	fert./beech	fert./oak	fert./spruce	fert./fir
N	n.a.	n.a.	n.a.	n.a.
P	0.79	0.06	0.07	0.06
K	0.07	0.05	0.04	0.08
Mg	0.13	0.12	0.39	0.21
Ca	0.05	0.20	0.65	0.04
S	0.04	0.05	0.04	0.04

can be mainly under the limits as for Cr, Ni, or Zn. The third option is that the concentrations in the ashes are mainly above the limits given in the relevant legislation. This is the case for Cu. For Cu, all measured values are above the limits of the soil protection ordinance; two values are above the fertilizer ordinance. In addition, one value is even above the limit of the biological waste ordinance.

**4.2. Urban Mining.** For the individual elements such as aluminum (Al) or iron (Fe) that are mined and processed to a usable raw material, it is aimed to mine pure ores that contain

high concentrations of the target element. For instance, if the target element is aluminum, bauxite consisting of the aluminum minerals gibbsite  $\gamma\text{-Al}(\text{OH})_3$ ; boehmite  $\gamma\text{-AlO}(\text{OH})$ ; diasporite  $\alpha\text{-AlO}(\text{OH})$ ; and two iron minerals goethite and hematite is mined. If the target element is iron, magnetite  $\text{Fe}_3\text{O}_4$ , hematite  $\text{Fe}_2\text{O}_3$ , or pyrite  $\text{FeS}_2$  are mined. During the metallurgical process, several pretreatments are performed to concentrate and refine the target elements within the ore. But these ores also contain other trace elements at lower concentrations. These elements are recovered in the same pretreatment steps. One of these aforementioned methods is the roasting process of the ore. During this process, trace elements like arsenic, cadmium, selenium, tellurium, and antimony vaporize as volatile oxides and are collected to gain the raw element in further treatment. Figure 8 gives the concentrations of trace elements in magnetite.<sup>52,53</sup> In comparison, the concentrations of the elements in the analyzed firewood ashes are given. Al is contained in magnetite in concentrations between 30 and 5000  $\text{mg kg}^{-1}$ . With 500  $\text{mg kg}^{-1}$ , the concentrations of Al in ash are in the same region. The concentrations of chromium in the ashes are at about 2  $\text{mg kg}^{-1}$ . This is about 5% the concentration found

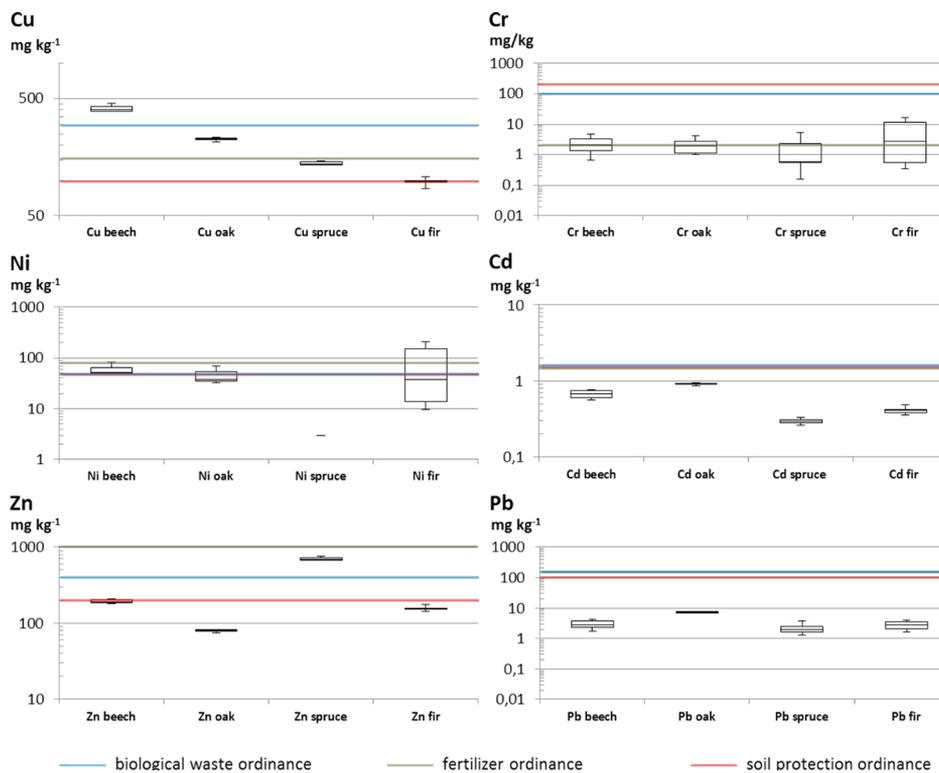


Figure 7. Copper, chrome, nickel, cadmium, lead, and zinc concentrations in beech, oak, spruce, and fir ash in comparison to legal limits.

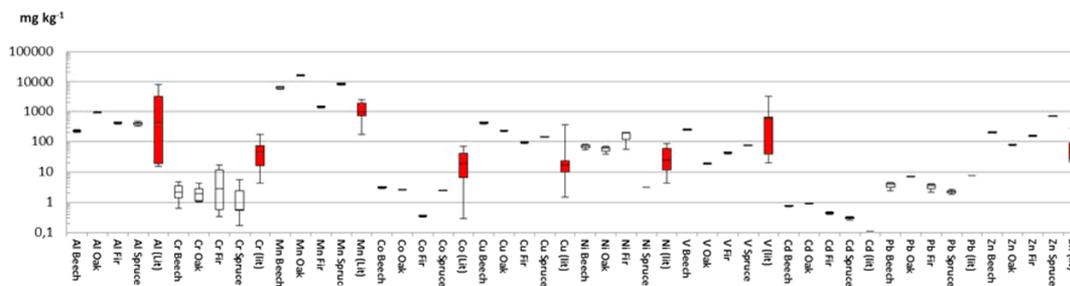


Figure 8. Trace elements from log-wood ashes in comparison to trace elements found in magnetite ore.

in magnetite. Although Mn is contained in magnetite in concentrations of about 1000 mg kg<sup>-1</sup>, the concentrations within ashes with about 10 000 mg kg<sup>-1</sup> are much higher. The concentrations of cobalt in magnetite are about 12 mg kg<sup>-1</sup> and therefore higher than those in the ashes with about 0.5–5 mg kg<sup>-1</sup>. The Cu concentrations in the ore are about 12 mg kg<sup>-1</sup>, whereas the concentrations in the ashes are much higher with a maximum of about 500 mg kg<sup>-1</sup>. The same circumstance reflects in the concentration of Ni. Here, the concentration in the ore is about 13 mg kg<sup>-1</sup> and therefore much lower than the concentrations in the ashes which are about 100 mg kg<sup>-1</sup>. The concentration of V in the ore is about 700 mg kg<sup>-1</sup> while the concentrations found in the ashes are ranging from 12 to 600 mg kg<sup>-1</sup> and are comparable throughout the elemental distribution in the ore. The concentrations of Cd in the ashes are 0.2–1.0 mg kg<sup>-1</sup> and are higher than those in the ore with concentrations lower 0.1 mg kg<sup>-1</sup>. Also, the concentrations of Pb in the ashes ranging from 2.0 to 9.0 mg kg<sup>-1</sup> are comparable to the concentration in the ore. Zn is also higher distributed in the ashes 90–900 mg kg<sup>-1</sup> than in the ore with 50 mg kg<sup>-1</sup>. Additional *p*-values are given in Table 12.

Table 12. *p*-Values for Element Concentrations in Ore Compared to Wood Ashes

element	<i>p</i> -values			
	ore/beech	ore/oak	ore/spruce	ore/fir
Al	<0.32	<0.32	<0.32	<0.32
Cr	<0.05	<0.05	>0.05	<0.05
Mn	<0.01	<0.01	>0.32	<0.01
Co	<0.05	<0.05	<0.05	<0.05
Cu	<0.01	<0.05	>0.32	>0.32
Ni	>0.05	>0.32	<0.32	n.a
V	>0.05	<0.05	>0.05	>0.05
Cd	<0.32	<0.05	>0.32	<0.32
Pb	<0.32	>0.05	>0.32	>0.32
Zn	<0.32	>0.32	<0.32	<0.01

5. CONCLUSIONS

Even though the element concentrations for different tree species reported in the literature show a wide range, this large variety is not determined only by the tree species. Results reported in the present work show that the element concentrations in the four tree species beech, oak, spruce, and fir are

partially all in the same range, whereas there are highly significant differences in concentration found only in beech for the minor elements K, Mg, and P ( $p < 0.01$ ) and for trace elements Cd and V ( $p < 0.01$ ) compared with the other samples. There are also differences between softwood and hardwood. This is noticeable in the concentrations of the elements Mg, Al, Fe, and Pb where the  $p$ -values in the comparison of the softwood types show no significant difference ( $p > 0.32$ ), but the comparison with both hardwood types show highly significant difference in concentration ( $p < 0.01$ ). However, because all wood samples are observed without bark and represent pure wood samples without clouding effects in element concentrations, the soil properties also play a major role in this context.

Assuming comparable combustion conditions, the element concentrations in ashes are dominated by the ash concentration of the individual fuel. In addition, there is no general impact of the tree species found within all observed elements.

If ashes originating from the combustion of untreated natural wood are put on soil, it is impacting on the soil itself as well as on the plants that are grown on that soil. On the one hand, it is a valuable fertilizer because it contains the relevant nutrients in comparable concentrations as commercial fertilizers. An exception is nitrogen which is released during combustion and is therefore contained in low concentration within the ashes. On the other hand, it is potentially harmful to the environment because it contains toxic trace elements in concentrations at or above certain limits given in different relevant German acts. This means that it is no contravention, if those firewood ashes are used for fertilizing purposes. However, it could be better for the health of a user, if the toxic elements from the firewood stove ashes would not be put on fields to produce food.

It is therefore necessary to separate the toxic elements from the nutrients before the ash is put onto a field. Doing so, the main share by mass of the ash material can be used as a fertilizer. The other, minor share, trace elements however are not to be disposed but are usable in terms of an urban mining prospectus. Because those elements are except for iron, found in comparable concentrations as in mined magnetite ore. Moreover, all observed wood ashes show a great variety in different elements that is not found in common ores. Therefore wood ashes could be a valuable resource which is available in large quantities, considering also the industrial combustion of wood. Using wood ashes as resource for fertilizer and valuable elements could also be interesting in case of reducing greenhouse gas emissions and energy consumption in the common fertilizer and mining industry. For this urban mining approach with wood ashes, a method must be established to separate the fertilizer and trace elements. Also, it is necessary to analyze wood ashes from industrial furnace on their elemental composition in case of an urban mining prospectus.

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### Notes

The authors declare no competing financial interest.

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