



## Full Length Article

## Trace element behavior in wood-fueled heat and power stations in terms of an urban mining perspective

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## ABSTRACT

Trace elements (TE) occur in natural and waste wood in a broad variety at considerable concentrations. Those TEs end up in different ash fractions (bottom-, fine-, and fly ashes) after combustion in furnaces at heat and power plants (HPP). The ash fractions differ significantly in TE concentrations and are therefore of variable quality. On the one hand they can be a matter of cost intensive disposal due to their toxicity. On the other hand they are a resource of valuable elements demanded by future technologies in an urban mining perspective. By understanding the individual element behavior during combustion and in the flue gas cleaning facilities, it is possible to predict element concentrations in the ash fractions. The results show the differences of TE concentrations in wood fuels as well as in the corresponding ash fractions precipitated in the air pollution control devices (APCDs) of four HPPs. The results from the mass balances show that the behavior of 23 investigated elements in wood fired stations is comparable to the behavior in coal fired stations. The individual element concentrations in the ash fractions are determined by different parameters, i.e. the element concentration in the fuel, the element volatility, and the operation of available flue gas cleaning facilities. The concentration of TE in bottom and especially in fly ashes of wood fired HPP are comparable to those found in economic important ores such as magnetite. The ashes from industrial wood combustion systems can therefore be considered as a valuable resource instead of a hazardous substance.

## 1. Introduction

Investigations on wood fuels and corresponding ashes from small scale combustion facilities have shown, that ashes from combustion of untreated natural wood do have a significant potential regarding urban mining [1]. Looking at the pathways of energy wood starting in the forest, eventually via use as construction wood or in furniture, to the heat and/or power plant, it becomes obvious that high shares of the energy wood are not necessarily used in small scale facilities but in heat and power stations with higher capacities [2]. Besides that, in industrial plants, not only one ash fraction, but up to four different fractions are precipitated and removed from the facility. It is known, that those ashes do differ in terms of their trace element concentrations as well as in their chemical composition regarding the formed element species [3–5]. Therefore it has to be expected that they differ in terms of their

urban mining potential. To evaluate this aspect, samples from four different heat as well as heat and power stations have been analyzed in their pure element content. With those data, it is the aim of this study to evaluate the impact of the combustion and flue gas cleaning technologies on trace element behavior in wood fired heat and power plants. Furthermore, it is aimed to assess the potential of the different ashes gained at wood fired stations regarding their urban mining potential.

## 2. State of knowledge

Concentrations of trace elements (TE) in ashes are influenced by a variety of different parameters, such as wood source, element specific properties, such as volatility, as well as combustion and flue gas cleaning technologies.

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## 2.1. Wood originating from different sources

Trace elements present in soils and soil porewater are being taken up by plants, including trees, during growth. However, the individual concentrations in the tree differ in different parts of the tree. Generally, the concentrations of trace elements are low in wood and higher in bark, leaves or needles [6]. Due to that, TE concentrations in wood fuels delivered to the combustion facilities depend on the mixture of pure wood, bark and leaves or needles. Besides that, element concentrations can also be influenced by other parameters such as soil, water and air quality in the area where the tree was grown [7]. Therefore the individual amounts of elements that are fed to the furnace are, depending on the wood fuel originating from different natural sources. In addition to that, concentrations of certain elements are also influenced by the way the wood product was eventually used before it became waste wood. Therefore, wood fuels originating from different sources like waste wood, road side wood, forest residues and logs, show different concentrations of TE with values in a very wide range [1].

## 2.2. Phase mineral transformation and volatile character of trace elements

The phase mineral transformation of minor and trace elements during coal and biomass combustion are highly complex systems and show similarities. These transformation mechanisms potentially influence the various mineral phases and due to that the volatile character of trace elements [4,5]. However, during combustion, as well as in possibly available air pollution control devices, individual elements undergo specific physico-chemical transformations. When fuel enters the flame zone the devolatilization of organic matter is started. Burning of combustible gases results in the formation of less stable compounds such as oxalates, nitrates, chlorides, hydroxides, carbonates, sulfates and inorganic amorphous material following the conversion in more stable compounds like silicates, phosphates and oxides [4]. With increasing combustion temperatures even minerals with high melting-temperatures start to melt, decompose and even evaporate. During the cooling of those phases in the air pollution devices crystallization of molten material starts and formation of glass as well as salt condensation, hydroxylation, hydration and carbonation of newly formed phases on particles takes place [4]. Numerous studies on this subject have been performed for coal and biofuels [3–5,8–11]. Vassilev et al. [4] generated a broad database displaying compositions and properties of biomass fuels and their solid combustion products regarding the phase mineral transformations and chemical interactions of organic- and inorganic matter during biomass combustion at temperatures from 200 up to 1500 °C. Zhou et al. [9,10] characterized the combustion temperature induced phase transition of trace elements from 500 up to 1200 °C in coal and classified two groups according to their volatile tendencies, high volatile elements (Ni, Cu, Zn, Cd, Sn, Pb, and As). And low volatile elements, (Co, Cr and V). Froment et al. [8] carried out a thermodynamic approach describing the release of all inorganic elements during biomass gasification, stating that a pressure increase favors condensation and decreases the release of condensable species such as KCl. Frandsen et al. [5] observed for the thermal conversion of coal about 800 chemical species of 33 elements under oxidizing conditions in the temperature range from 26.0 up to 1700 °C and divided the trace elements into two groups according to their condensation phase behavior at low temperatures: Sulfate forming elements (Be, Cd, Cr, Hg, Ni, Pb, Sb, Sn, V and Zn) and oxide-hydroxide forming elements (As, B, Ga, Ge, P, Se, and Ti). Even though phase mineral transformation mechanics of trace elements are various and depend on given parameters such as temperature, pressure conditions, and fuel characteristics, as well as the design of the combustion facility, they do follow a certain behavior pattern concerning their distribution within single ash species regardless of their mineral form. The aforementioned literature does not indicate a clear difference between the results obtained from coal combustion and results obtained from biomass

Volatility ↑	Class III	B, Br, C, Cl, F, Hg, I, N, S and Se
	Class IIa	As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
	Class IIb	Be, Co, Cu, Ni, P, U, V and W
	Class IIc	Ba, Cr, Mn, Na and Rb
	Class I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti

Fig. 1. Classification of elements based on research carried out in the Netherlands [12].

combustion concerning the volatile behavior of elements. Instead it is often found an overlap in the volatile categorization regardless the differences of constitution or combustion temperatures between coal and biomass. However the comparison in the volatile element behavior between both fuels is not fully described and therefore available to a lesser extent in the literature. It has been found that biomass is similar to solid fossil fuels in the case of being a complex heterogeneous mixture of organic matter and to a lesser extent inorganic matter e.g. (minerals, and amorphous material) [4]. The common trace element behavior in coal fired power stations is very well characterized [12–14]. Meij classified the elements based on mass balance studies carried out in coal fired power stations in the Netherlands [15,12]. He divided the elements in three classes, while class II is subdivided, as shown in Fig. 1.

Elements categorized in Class I are not volatile and are therefore evenly distributed in the different ash fractions. Class II elements are volatile. They are evaporated during combustion and condense or adsorb on fly ash particles during flue gas cleaning. Elements in Class III are highly volatile. They are evaporated during combustion and remain mainly in the gas phase till they reach the chimney. In [12] relative enrichment factors (RE) were calculated according to Equation (1). It describes the enrichment of a certain element *i* in a certain ash fraction, relative to the ash concentration in the fuel. The results of numerous mass balances of trace element volatile behavior in coal fueled heat and power plants are summarized in Table 1.

$$RE = \frac{c_i^{ash}}{c_i^{fuel}} \cdot \frac{A^{fuel}}{100} \quad (1)$$

$c_i^{ash}$  = concentration of element *i* in ash

$c_i^{fuel}$  = concentration of element *i* in fuel

$A^{fuel}$  = ash concentration in the fuel

## 2.3. TE behavior in combustion- and flue gas cleaning technologies

The impact of biomass fuels on TE behavior in a 500 kW<sub>th</sub> coal fired test facility during combustion and flue gas cleaning was investigated in [16]. For pure coal combustion, the general findings of Meij concerning TE behavior were confirmed. Furthermore it was concluded, that the behavior of TE is dominated by a) (fly) ash particle size distribution, b) particle separation temperature and c) particle separation technology [16]. The fuel type, that is classified by origin and the fuel processing technology, as well as the combustion technology, impact on the ash particle size distribution [16,17]. Additionally, the particle sizes formed by combustion, in combination with style of the combustion technology, impact on the TE behavior [16,17]. This aspect is even more relevant during flue gas cleaning. In case of wood combustion, flue gas cleaning means mainly ash precipitation via cyclones, fabric-filters (FF) or electrostatic precipitators (ESP). Generally TE precipitation with ashes increases with a) decreasing mean particle diameter of the ash fraction and b) decreasing temperatures at which the ash fraction is precipitated [16–18]. In industrial flue gas cleaning facilities, mean particle size as well as temperatures decrease from furnace to chimney. So, concentrations of volatile TE are expected to increase from the boiler ash separated directly out of the combustion chamber to the last hopper of the last filter plant. Related to that, the TE precipitation

**Table 1**  
Classification of elements based on their behavior in the furnace and subsequent facilities [12].

Class	bottom ash	ESP ash	fly ash	Behavior in installation
I	≈ 1	≈ 1	≈ 1	Not volatile
IIc	< 0,7	≈ 1	1,3 < ... < 2	Volatile, but condensation within the installation on the ash particles
IIb	< 0,7	≈ 1	2 < ... < 4	
IIa	< 0,7	≈ 1	> 4	
III	≪ 1	< 1		Very volatile, hardly any condensation

efficiency of an ash removal technology is determined by a) the temperature at which it is operated and b) its capability to precipitate fine fly ash particles [16]. Therefore, ashes precipitated in cyclones are expected to show rather low volatile TE concentrations while the concentrations of volatile TE are expected to be rather high in fabric filters and electrostatic precipitators (ESPs). In addition, fabric filters (FFs) can, in combination with potentially Carbon-loaded filter cakes, also act as fixed bed TE ab-/adsorbers [19]. Therefore, even higher volatile TE concentrations be present fabric filters.

**3. Methods and materials**

For this study four plants were selected, differing in terms of their purpose regarding heat and/or power production, combustion technology, flue gas cleaning technology and employed wood fuel. All samples were taken in the plants during several days.

**3.1. Investigated heat and power stations**

There were two heat and power plants named HPP A and HPP B and two heating plants named HP C and HP D investigated. The flow charts of the four plants are displayed in Fig. 2. HPP A possesses a circulating fluidized bed boiler and the other plants possess grate fired furnaces. All four plants are equipped with fabric filters and the plants HPP A, HPP B and HPD possess a cyclone in addition.

In HPP A three ash fractions are removed from the plant. The first fraction is bottom ash out of the furnace at 880 °C. The second is a mixture of ash from a cyclone at 165 °C and ash that is gravimetrically

removed from a vertical duct used as economizer at 165 °C. The third ash fraction is from the fabric filter with an intermediate additive injection consisting of hearth furnace coke (HOK) and calcium hydroxide (CaOH<sub>2</sub>) at 158 °C. Correspondingly in HPP B also three ash fractions are removed. The first is a bottom ash from the end of the grate at 948 °C, the second ash is from a cyclone at 173 °C and the third ash is from a fabric filter at 171 °C with an intermediate active coal injection also consisting of hearth furnace coke (HOK) and calcium hydroxide (CaOH<sub>2</sub>). In the plants HP C and HP D only two ash fractions are removed. The first ash fraction is taken out of the furnace at both plants similar to HPP B (at 840 °C for HP C and 880 °C for HP D). The second ash fraction from both installations is a mixture of ash from a fabric filter (at 150 °C for HP C and 120 to 160 °C for HP D) and a cyclone (at 200 °C for HP C and 120 to 160 °C for HP D). The installation specific flue gas cleaning parameters are summarized in Tables 6–8 in the appendix.

**3.2. Origin of the fuel wood and ash samples**

During the campaigns in the four plants, fuel samples and ash samples were taken in the same time frame so that the fuel samples are corresponding to the ash samples. However, the single installations used different wood fuel sources. For HPP A and B the fuel was composed according to the German waste wood ordinance (AltholzV) [20] in a mixture of 60:40 of forest residues and waste wood of Class A I and A II. HPP C used a fuel mixture of 50:50 road side wood, forest residues and landscape management material with waste wood of Class A I and A II. HPP D used a mixture of 67:33 of landscape management material

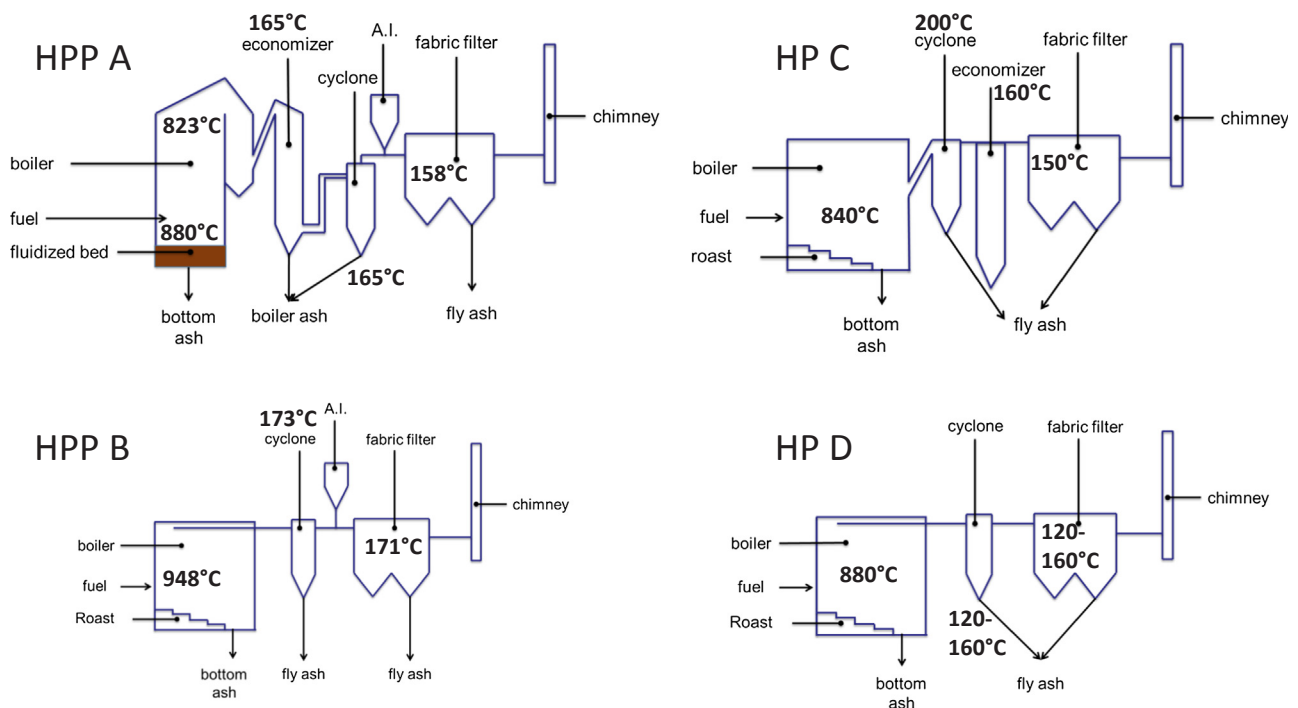


Fig. 2. Investigated heat and power plants.

and forest residues.

### 3.3. Analytics

The fuel and ash samples were taken in the plants during several consecutive days. All analytics were performed at the central laboratory of the University of Applied Sciences Rottenburg (Germany).

#### 3.3.1. Fuel sample preparation and digestion

First, the water content in of the fuel samples was determined according to ref [21]. Therefore the samples were oven dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.) for approx. 24 h until constant weight. Afterwards each dried fuel sample consisting of 4.5 kg in mass was split up via a bulk sample divider in four representative fractions. Two of the four collected fractions were combined and milled to two different particle sizes (1.0 mm and 0.25 mm) by a cutting mill (Pulverisette19 Fritsch Ltd.) with trace element free inlet milling cassettes. For ICP-OES element determination the 0.25 mm particle size material was microwave digested in aqua regia [22,23] (Multivave GO 3000 Anton Paar Ltd.). The digested residues were aliquoted to 50 ml with aqua bi-dest and measured by ICP-OES (Spectro Blue 3000 spectro/Aemtek Ltd.) in six replicates for each fuel sample.

#### 3.3.2. Ash fraction sample preparation and digestion

Ash fractions from the sampled power stations 3–10 kg were dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.). The dried ash fractions such as boiler and bottom ash, holding coarse material were broken and milled to the particle sizes of 1.00 mm and 0.25 mm by a Jawbreaker (Pulverisette 1 Mod. II classic line Fritsch Ltd.) and an orbital mono mill (Pulverisette 6 Fritsch Ltd.). The milling units of both devices consist of zirconium oxide, preventing sample contamination with trace elements. For ICP-OES element analysis, the ashes with a particle size of 0.25 mm were microwave digested in aqua regia [22,23] (Multivave GO 3000 Anton Paar Ltd.). The digested residues were aliquoted to 50 ml with aqua bi-dest and measured by ICP-OES in six replicates each.

#### 3.3.3. Calorific analysis

The gross calorific value at constant volume in dry basis was determined according to ref. [24]. The 1.0 mm particle sized fuel samples,  $0.5 \pm 0.020$  g were transferred into a 15.0 ton press to gain fuel tablets. The fuel tablets were transferred to glass crucibles and combusted in an automated isoperibol calorimeter (C6000 IKA Ltd.) in three replicates for each fuel sample.

#### 3.3.4. Proximate analysis

The ash content was determined by pyrolysis of  $1.0 \text{ g} \pm 20.0$  mg of the 1.00 mm particle sized fuel samples in a ceramic crucible by a muffle furnace (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 [25].

#### 3.3.5. Ultimate analysis

The determination of carbon, hydrogen and nitrogen of the fuel and the ash fractions was done by an elemental analysis device (vario macro cube Elementar Ltd.) [26]. The water-free 0.25 mm particles of both sample materials (fuel and ash) was weighed to  $20 \pm 1.0$  mg, pressed in a zinc foil tablet, and analyzed in six replications per fuel and ash sample.

## 4. Results

### 4.1. Proximate and ultimate analysis of fuel

The fuel properties of all installations are shown in Table 2. The gross calorific values ranged from 17 to 19 MJ kg<sup>-1</sup> on dry basis. The

ash contents of the single fuels were between 5 and 12 w% on dry basis. The water contents of the observed fuels as received were between 33 and 39 w%. The C:H:N ratios of all fuels on dry basis were in the typical ranges of wood: the concentrations of Carbon (C) in all fuels ranged from 43 to 47 % and the concentrations of H lie between 5.5 and 6.0 %. The concentrations of N in the fuels ranged from 0.5 to 2.0%. The concentrations of Cl within all fuels were about 0.7–1.0 mg kg<sup>-1</sup>.

### 4.2. Volatile trace elements in fuel and corresponding ashes

The concentrations of the investigated trace elements in the wooden fuels as well as in their corresponding ashes are listed in Tables 3–5 in the appendix. To show the specific element behavior in the flue gas cleaning sections of the single installations, the elements (Fe, Mn, Co, Cd and B) were chosen being representative for their volatility class. For the element Fe which is categorized to the low volatile class I Fig. 3 show for HPP A a concentration of 3000 mg kg<sup>-1</sup> in the fuel. Within the bottom ash a concentration of about 16,000 mg kg<sup>-1</sup> was detected. Following the pathway of the flue gas, the concentrations in the boiler and filter ash are in a comparable range from 22,000 to 21,000 mg kg<sup>-1</sup>. In HPP B the concentration of Fe in the fuel is at 2000 mg kg<sup>-1</sup> whereas the concentration in the bottom ash is about 47,000 mg kg<sup>-1</sup> and the cyclone ash up to 74,000 mg kg<sup>-1</sup>. The concentration in the filter ash is situated lower around 7900 mg. In HP C and D the concentrations of Fe in the fuels are ranging from 1000 to 2400 mg kg<sup>-1</sup>. The bottom ashes are also found in comparable ranges from 18,000 up to 20,000 mg kg<sup>-1</sup>. The investigated fly ashes from those installations do also show a similar range of 24,000 to 28,000 mg kg<sup>-1</sup>.

For the element Mn which belongs to the more volatile subclass 2c, Fig. 4 show for all observed installations concentrations in the fuel the range from 160 to 200 mg kg<sup>-1</sup>. The bottom ashes do show concentration ranges five times higher than in the fuel, but are in comparable ranges from 770 up to 1000 mg kg<sup>-1</sup>. In HPP A the concentrations of Mn in the boiler ash is at 1200 mg kg<sup>-1</sup> followed by 2300 mg kg<sup>-1</sup> in the accompanying filter ash. In HPP B the concentrations in the cyclone ash is at 3700 mg kg<sup>-1</sup> whereas the concentration in the filter ash is below 1600 mg kg<sup>-1</sup> situated. The fly ashes in HP C and D are at identical concentrations about 2000 mg kg<sup>-1</sup>.

The element Co is categorized to the medium volatile subclass IIb and displayed in Fig. 5. The concentrations in all observed fuels range from 1.0 to 1.6 mg kg<sup>-1</sup>. The concentrations in the bottom ashes are eight to twenty times higher (8.0 to 20.0 mg kg<sup>-1</sup>). However the boiler ash from HPP A shows a lower concentration of 6.2 mg kg<sup>-1</sup> compared to the following filter ash with a notable concentration of 22.0 mg kg<sup>-1</sup>. Whereas in HPP B the cyclone ash is noticed with a peak concentration of 50 mg kg<sup>-1</sup> compared to the lower concentration in the followed filter ash stating 10 mg kg<sup>-1</sup>. The fly ashes of HP C and D do also show the highest concentrations found in both installations in the range of 13.0–18.0 mg kg<sup>-1</sup>.

Stating one of the most volatile element subclass IIa the element Cd is represented in Fig. 6. Concentrations in all observed fuels are found at low ranges from 0.1 to 0.4 mg kg<sup>-1</sup>. Also in the bottom ashes of the single installations concentrations below 1.0 mg kg<sup>-1</sup> (0.05 to 0.8 mg kg<sup>-1</sup>) were detected. However considerable concentrations could be found in the boiler- and cyclone ash of HPP A and B with 2.0 and 17.0 mg kg<sup>-1</sup> as well as in their filter ashes with 20.0 up to 90.0 mg kg<sup>-1</sup>. Even in the installations HP C and D the concentrations in the fly ashes are about 10.0 mg kg<sup>-1</sup>.

The high volatile elements of Class III are represented by B. The results for B are displayed in Fig. 7. With a concentration range from 6.0 to 13.0 mg kg<sup>-1</sup> B is detected in fuels from all observed installations. In the bottom ashes also comparable concentrations could be found from 60.0 up to 80.0 mg kg<sup>-1</sup>. The boiler ash of HPP A shows a lower concentration at 50 mg kg<sup>-1</sup> whereas the concentration in the

**Table 2**  
Measured fuel wood properties on dry basis (d.b.) and as received (a.r.).

fuel wood	gross calorific value [MJ kg <sup>-1</sup> ] d.b.	ash content w[%] d.b.	Water content w[%] a.r.	C:H:N values w[%] d.b.	Chloride Cl <sup>-</sup> [mg kg <sup>-1</sup> ] d.b.
HPP A	17.10	11.90	38.99	43.50:5.50:2.08	0.99
HPP B	19.02	5.31	32.81	47.60:5.99:1.26	0.85
HP C	17.89	10.90	37.85	44.85:5.56:1.53	0.74
HP D	17.24	10.57	39.18	43.46:5.54:0.54	0.94

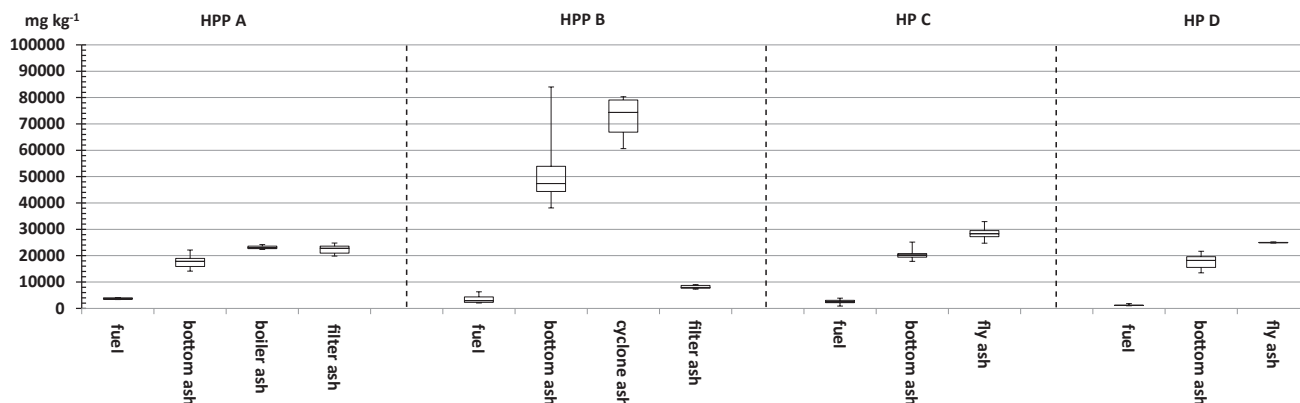


Fig. 3. Class I Fe concentrations mg kg<sup>-1</sup> in fuel and accompanying ashes from selected heat and power plants A, B, C and D on dry basis (d.b.).

corresponding filter ash displays at 400 mg kg<sup>-1</sup>. These considerable concentrations could be also found in the cyclone ash of HPP B with 400 mg kg<sup>-1</sup> and 300 mg kg<sup>-1</sup> in the accompanying filter ash as well as in the fly ashes of HP C and D.

**5. Discussion**

*5.1. Element behavior during wood combustion in heat and power plants*

With all results of the element concentrations in fuel and corresponding ashes given in sections 4.2 it is possible to calculate the relative enrichment factor (RE) for each investigated element according to Eq. (1). In Fig. 8 the relative enrichment factors (RE) for the elements of class 1 (Al, Ca, Fe, K, Mg, Sr, and Ti) in bottom- and fly ash are shown and summarized by their mean value. The (RE) mean value for Class 1 elements in bottom ash is calculated to be 0.89 and for fly ash 1.27 which is comparable to the class 1 element behavior according to Meij [12] with a RE factor for Class 1 of ≈ 1.0 in bottom and fly ash.

The RE factors for Class 2c elements (Ba, Cr, Mn, and Na) in bottom- and fly ash are shown in Fig. 9. The mean value for bottom ash is 0.67 and for fly ash it is 1.60. Comparing to the RE factors calculated by Meij (bottom ash (< 0.7) and fly ash (1.3 ≪ 2)), it is seen that the behavior of

those elements in wood fired facilities is comparable to their behavior in coal fired power stations. Therefore those elements show a volatile behavior, meaning that they are partially evaporated during combustion but condense within the installation and are contained in slightly higher concentrations in the fly ash.

The mean of RE factors calculated for the 2b elements (Co, Cu, Ni, and V) are shown in Fig. 10. With average values of 0.73 for bottom ash and 1.96 for fly ash, these values are also comparable to the values calculated by Meij (< 0.7 for bottom ash and 2 < ... ≪ 4.0 for fly ash). Overall these, data show, that the class 2b elements are evaporated to a higher extent than the class 2c elements.

The RE factors calculated for class 2a elements are shown in Fig. 11. The average of the enrichment factors for the elements As, Cd, Mo, Pb, Sb, and Zn in bottom ash is 0.41 and therefore again lower as their upper limit according to Meij (< 0.7 for bottom ash) and in fly ash 4.47 higher than the upper limit (> 4.0 for fly ash). This correlates very well with the findings of Meij. Therefore, from our results it can be concluded that these elements are evaporated during combustion to a great extent and condense on fly ash particles during cooling of the flue gas.

Out of the Class 3 elements in this study there is only boron (B) considered. The RE factors for B in the bottom ashes are in average at 0.65 (Fig. 12), which is in line with the values of RE ≪ 1, reported by

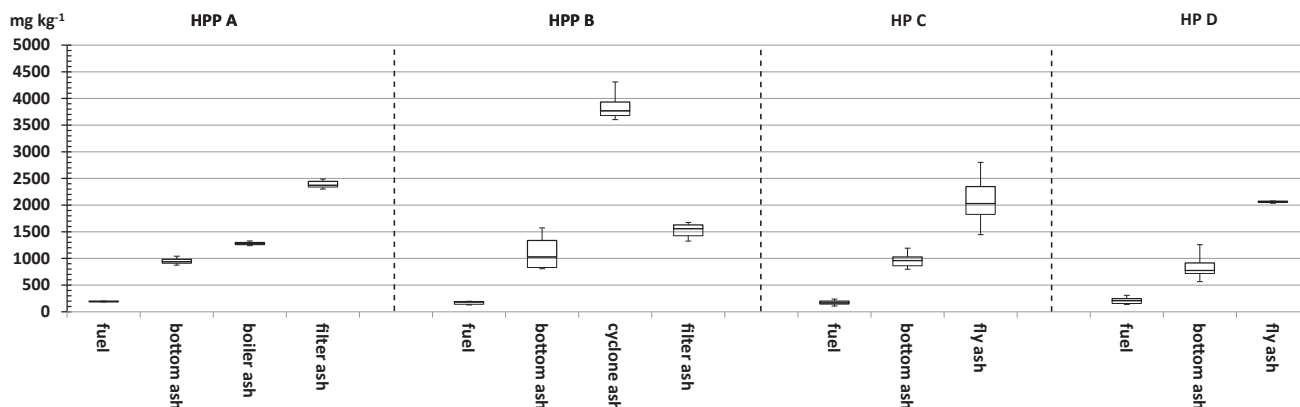


Fig. 4. Class IIc Mn concentrations mg kg<sup>-1</sup> in fuel and accompanying ashes from selected heat and power plants A, B, C and D on dry basis (d.b.).

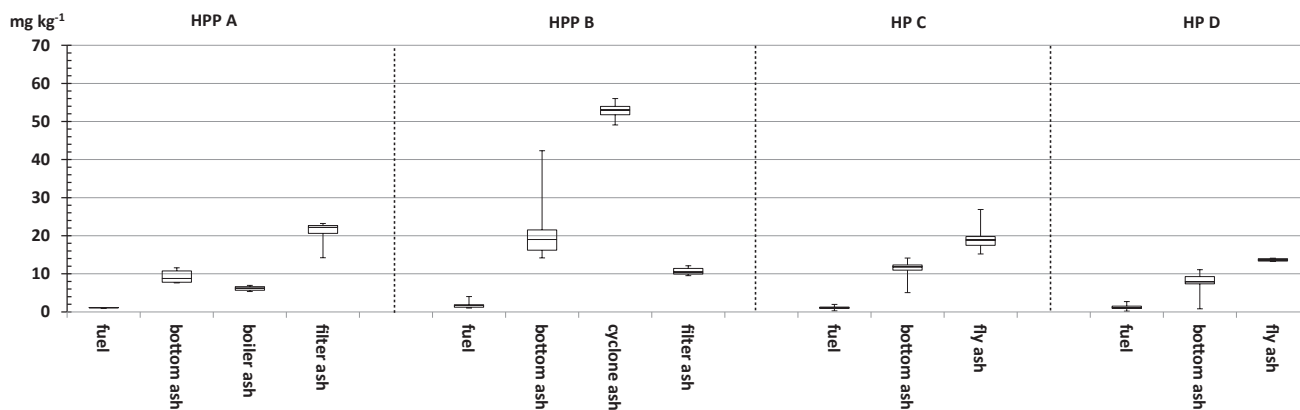


Fig. 5. Class IIB Co concentrations  $\text{mg kg}^{-1}$  in fuel and accompanying ashes from selected heat and power plants A, B, C and D on dry basis (d.b.).

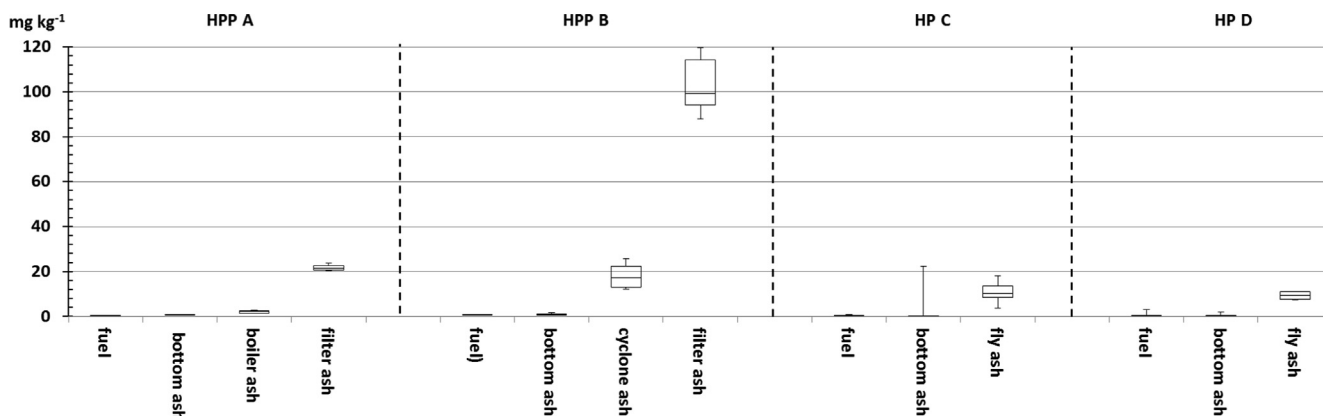


Fig. 6. Class IIA Cd concentrations  $\text{mg kg}^{-1}$  in fuel and accompanying ashes from selected heat and power plants A, B, C and D on dry basis (d.b.).

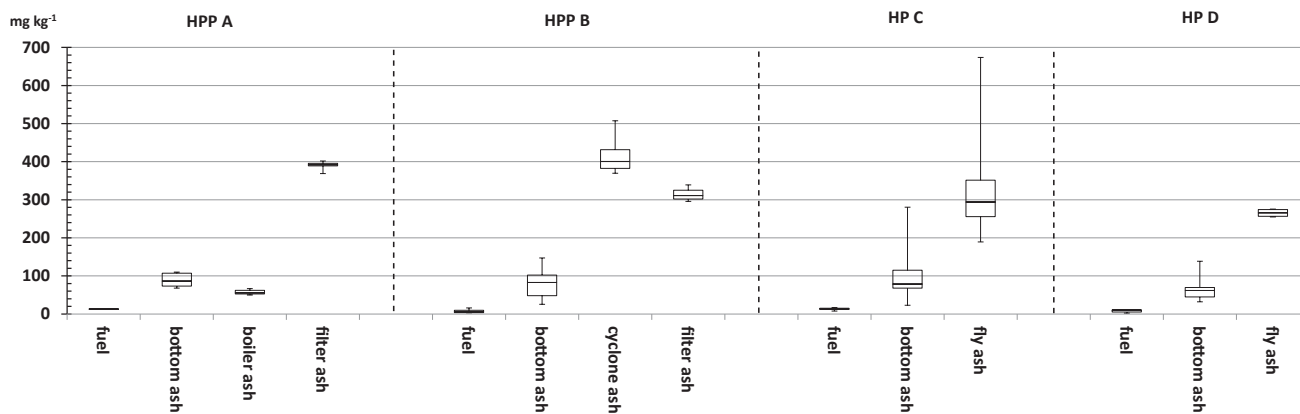


Fig. 7. Class III B concentrations  $\text{mg kg}^{-1}$  in fuel and accompanying ashes from selected heat and power plants A, B, C and D on dry basis (d.b.).

Meij. For the fly ashes, the RE factors in the wood ashes are calculated to be 3.0.

Summarizing the comparison of the presented data from the wood combustion facilities to the data presented by Meij [12], Fig. 13 shows the average enrichment factors for the discussed element classes. For the bottom ashes the highest enrichment factors are found for the Class 1 elements at about 1.0. All the other enrichment factors are below 1.0. This shows that for coal as well as for wood combustion, Class 2 and Class 3 elements are evaporated during combustion and are therefore found in lower concentrations the higher the volatility of the respective element is. Correspondingly, the enrichment factors in fly ashes begin at about 1.0 for Class 1 elements and increase to about 5.0 for class 2a elements. This shows that the higher the volatility of an element is, the later it condenses and the higher is its enrichment in the fly ashes

separated at lower temperatures. The enrichment factors of the Class 3 elements are for wood as well as for coal combustion lower than the RE factors of the Class 2a elements. The reason for that is that the Class 3 elements are still present in the gas phase and are only partially condensed on the ashes.

### 5.2. Potential of ashes from wood combustion for urban mining

Trace elements that are investigated in this work are industrially used for various applications [27]. Today many of those elements are extracted from specific ores that are mined in specific areas around the world [28–34]. As example, magnetite ( $\text{Fe}_3\text{O}_4$ ) is mined to extract iron, chalcopyrite ( $\text{CuFeS}_2$ ) is mined to extract copper or chromite ( $\text{Fe}^{2+}\text{Cr}_2\text{O}_4$ ) is mined to extract chromium [29,35,36]. Other elements,

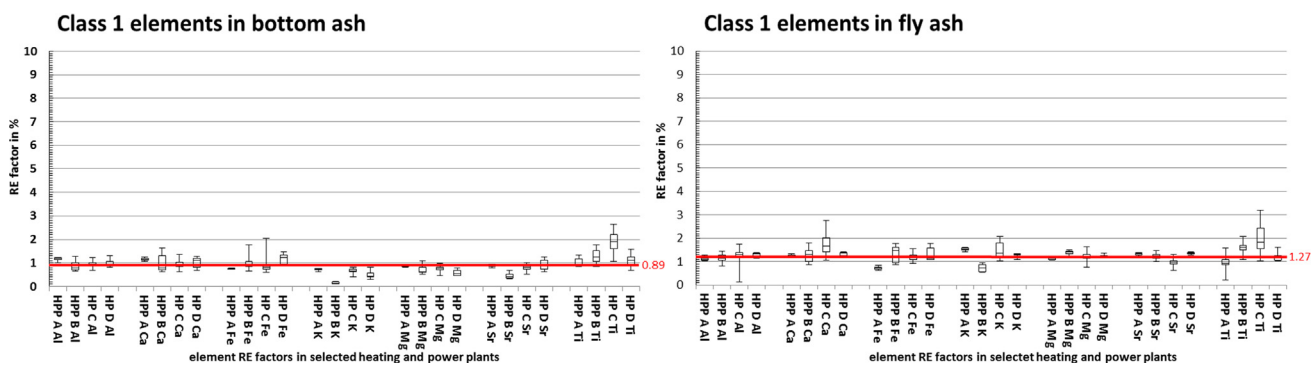


Fig. 8. Class 1 element RE factors in bottom and fly ash.

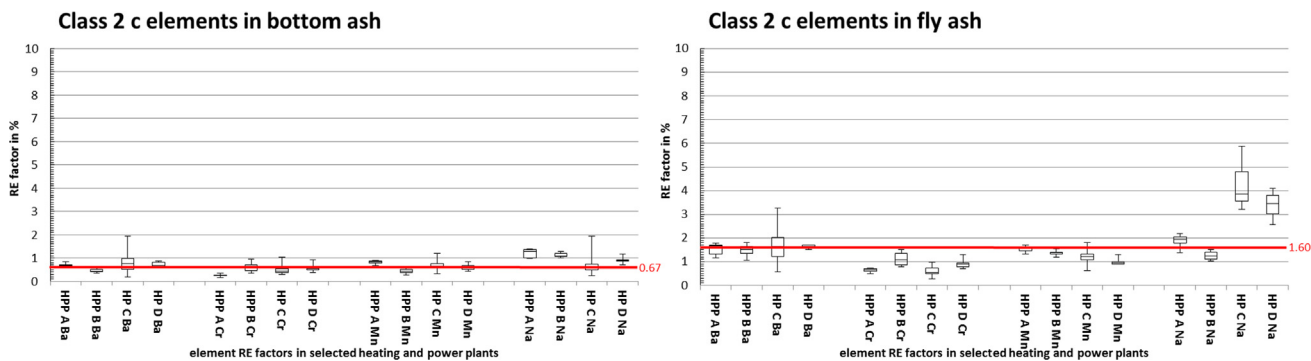


Fig. 9. Class 2c element RE factors in bottom and fly ash.

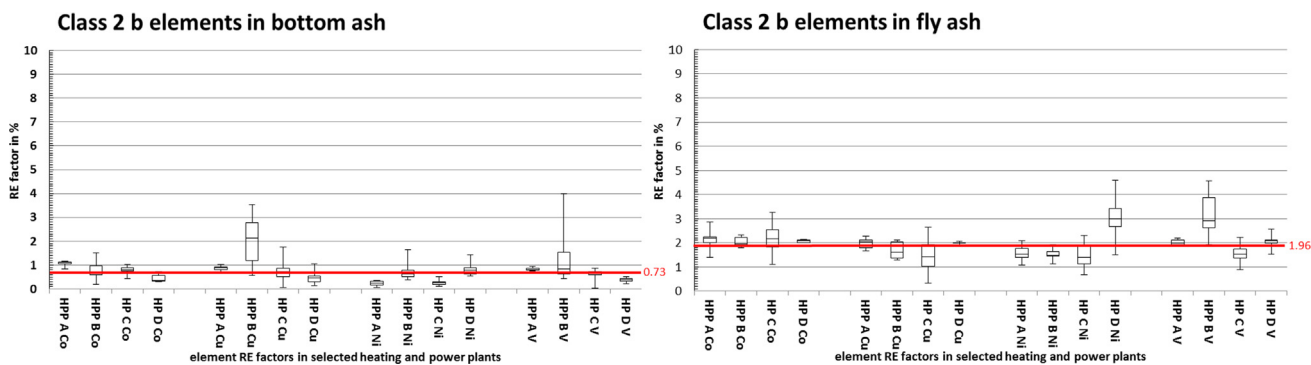


Fig. 10. Class 2b element RE factors in bottom and fly ash.

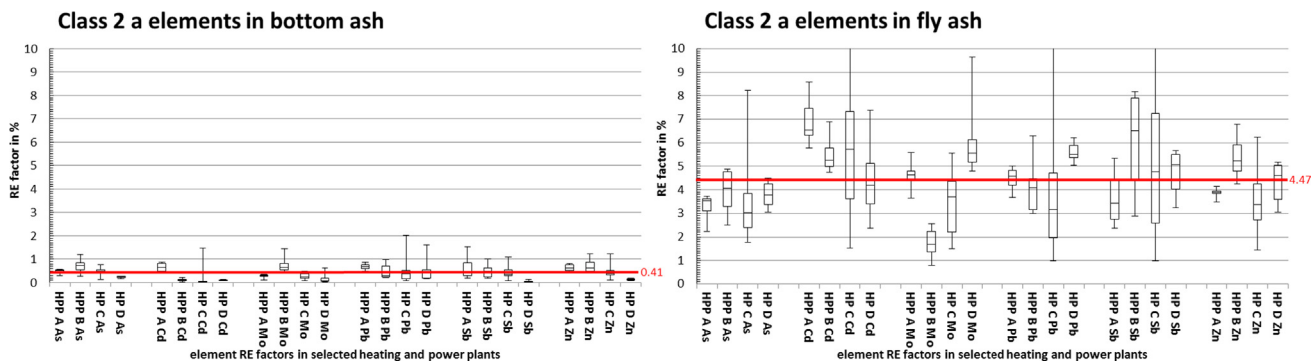


Fig. 11. Class 2a element RE factors in bottom and fly ash.

such as vanadium or cobalt are gained as side products from other industrial processes or by extracting from ores such as magnetite or chalcopyrite as trace elements within the refining process [37–44]. In such cases the co-extraction of additional elements besides the main

element of interest helps to make the extraction process more economic. In a first approach, the extraction of a certain element from a material such as ash is potentially attractive as soon as the element concentration is comparable to the concentrations in ores. Therefore,

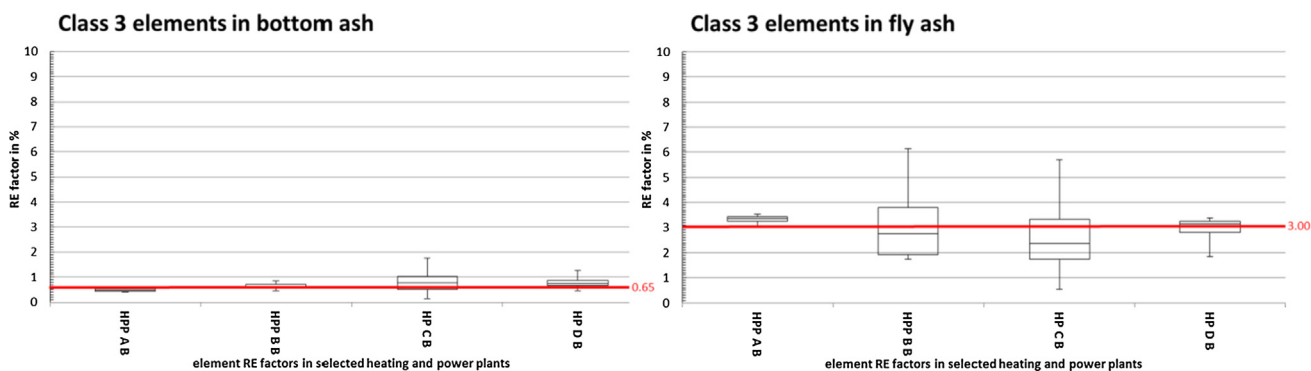


Fig. 12. Class 3 element RE factors in bottom and fly ash.

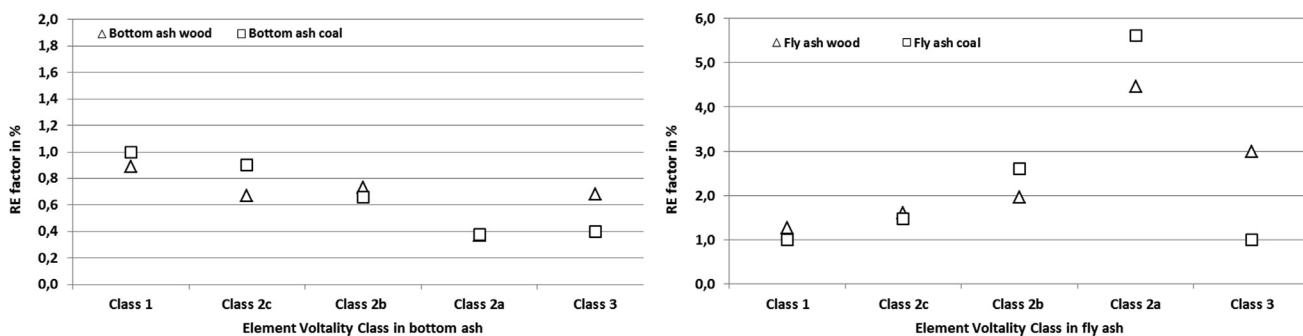


Fig. 13. RE factors in bottom and fly ash from wood and coal.

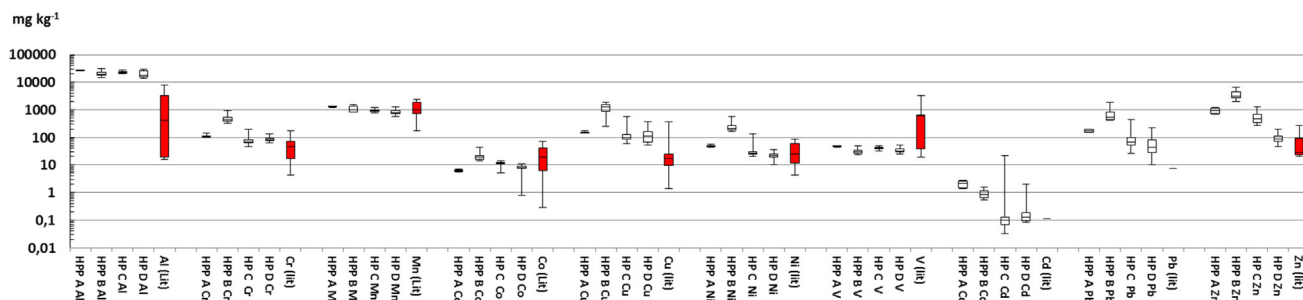


Fig. 14. Trace elements  $\text{mg kg}^{-1}$  in bottom ash from selected heat and power plants in comparison to trace element concentrations found in magnetite ore highlighted in red [45,46].

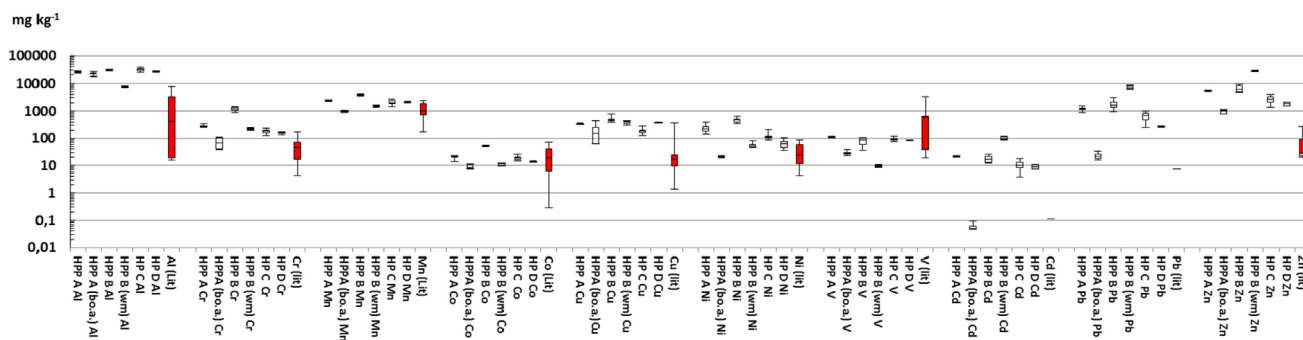


Fig. 15. Trace elements  $\text{mg kg}^{-1}$  in fly ash from selected heat and power plants in comparison to trace element concentrations found in magnetite ore highlighted in red [45,46].

pure trace element concentrations in bottom and fly ashes are compared to concentrations in magnetite ore (Fig. 14 and Fig. 15) regardless of their mineral forms, in order to gain a fundamental overview.

This comparison shows that the concentrations of Al, Cr, Cu, Cd, Pb and Zn in ashes are about ten to 100 times higher than in magnetite ore. The concentrations of Mn, Co, Ni, and V in the investigated ashes are

comparable to the concentrations in the magnetite ore. This means that even though the trace element concentrations in the ashes do vary for instance between bottom ash and fly ash, the element concentrations are in a potentially attractive range for urban mining. Specifically, fly ashes from industrial furnaces show trace element concentrations comparable to economic important ores. Therefore, their potential as a



resource of valuable trace elements might currently be underestimated.

## 6. Conclusions

Within this study a fuel and ash screening for four heat and power plants was carried out. At the investigated facilities, the used fuels, the applied combustion technology as well as the implemented flue gas cleaning facilities are different. Therefore, the investigated fuels and ashes show in total a wide range of trace element concentrations from  $< 0.1$  to  $10,000 \text{ mg kg}^{-1}$ . There is a variety of factors that can impact the concentrations of certain elements in different ash fractions collected at industrial wood fired heat and power stations. First, the results show that the higher the element concentration in the fuel, the higher is the element concentration in the ashes. Second, the results do not show a clear impact of the combustion technology. Third, the flue gas cleaning technology and especially the temperature at which the individual separation technology is operated has an important impact on the TE concentrations in the separated ashes. However, due to the design and operation of the investigated facilities, the temperatures in the different plant are comparable. Therefore, the impact of the temperatures is not observed in this work. TE concentrations in ashes depend on TE concentrations in the used fuel and the design and operation of the available flue gas cleaning technologies. The higher the volatility of a certain element and the lower the particle diameters of the separated ash as well as the lower the separation temperature, the higher the concentrations of trace elements in ash fractions. The comparison of the element enrichment in wood combustion ashes in our study to the element enrichment in coal combustion ashes reported by Meij [12] shows a very similar behavior for most elements. From this comparison we conclude that besides the aforementioned impact of the individual element concentrations in the fuel, it is insignificant whether coal or wood is burned. So far, in Germany especially fly ashes from industrial wood combustion facilities have to be disposed and cannot be used as fertilizer due to their high trace element concentrations. However, our results show that those concentrations could be high enough to consider those ashes as a source for the industrial extraction of certain valuable elements, because in some cases they are present in the same concentration ranges as in magnetite ore.

## CRedit authorship contribution statement

**Julian Tejada:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Jürgen Wiedenmann:** Resources, Conceptualization, Validation, Funding acquisition. **Bernd Gall:** Resources, Conceptualization, Validation, Funding acquisition. **Bernd Kaiser:** Resources, Conceptualization, Validation, Funding acquisition. **Oliver Greißl:** Resources, Conceptualization, Validation, Funding acquisition. **Sven Unterberger:** Resources, Conceptualization, Validation, Funding acquisition. **Andreas Kappler:** Conceptualization, Validation, Resources, Writing - review & editing, Supervision. **Harald Thorwarth:** Conceptualization, Validation, Resources, Writing - review & editing, Supervision, Project administration.

## 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.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.116887>.

## References

- [1] Tejada J, Grammer P, Kappler A, Thorwarth H. Trace element concentrations in firewood and corresponding stove ashes. *Energy Fuels* 2019;33:2236–47. <https://doi.org/10.1021/acs.energyfuels.8b03732>.
- [2] *Energie aus Biomasse: Grundlagen, Techniken und Verfahren*. 3rd ed. Berlin, Heidelberg: Springer Vieweg; 2016.
- [3] Vassilev SV, Vassileva CG, Song Y-C, Li W-Y, Feng J. Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. *Fuel* 2017;208:377–409. <https://doi.org/10.1016/j.fuel.2017.07.036>.
- [4] Vassilev SV, Baxter D, Vassileva CG. An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel* 2013;112:391–449. <https://doi.org/10.1016/j.fuel.2013.05.043>.
- [5] Frandsen F, Dam-Johansen K, Rasmussen P. Trace elements from combustion and gasification of coal—an equilibrium approach. *Prog Energy Combust Sci* 1994;20(2):115–38. [https://doi.org/10.1016/0360-1285\(94\)90007-8](https://doi.org/10.1016/0360-1285(94)90007-8).
- [6] Thorwarth H, Gerlach H, Rieger L, Schroth M, Kirchof R, Tejada J. *Natürliche Einflüsse auf die Qualität von Holzbrennstoffen und deren Auswirkungen auf den Betrieb von Holz-Heizkraftwerken*. *VGB Power Tech* 2018;11:42–9.
- [7] Shahid M, Dumat C, Khalid S, Schreck E, Xiong T, Niazi NK. Foliar heavy metal uptake, toxicity and detoxification in plants: a comparison of foliar and root metal uptake. *J Hazard Mater* 2017;325:36–58. <https://doi.org/10.1016/j.jhazmat.2016.11.063>.
- [8] Froment K, Defoort F, Bertrand C, Seiler JM, Berjonneau J, Poirier J. Thermodynamic equilibrium calculations of the volatilization and condensation of inorganics during wood gasification. *Fuel* 2013;107:269–81. <https://doi.org/10.1016/j.fuel.2012.11.082>.
- [9] Zhou C, Liu G, Fang T, Wu D, Lam PKS. Partitioning and transformation behavior of toxic elements during circulated fluidized bed combustion of coal gangue. *Fuel* 2014;135:1–8. <https://doi.org/10.1016/j.fuel.2014.06.034>.
- [10] Zhou C, Liu G, Yan Z, Fang T, Wang R. Transformation behavior of mineral composition and trace elements during coal gangue combustion. *Fuel* 2012;97:644–50. <https://doi.org/10.1016/j.fuel.2012.02.027>.
- [11] Zhang Y, He F, Gao Z, You Y, Sun P. Effects of ash-forming temperature on recycling property of bottom ashes from rice residues. *Fuel* 2015;162:251–7. <https://doi.org/10.1016/j.fuel.2015.09.025>.
- [12] Meij R. Trace elements behaviour in coal fired power plants. *Fuel Process Technol* 1994;39:199–217.
- [13] Fahlke J. Analysis of the behaviour of trace elements in coal-fired steam generators including flue gas cleaning systems. *VGB Kraftwerkstech* 1993;73(3):254–6.
- [14] Martel C, Rentz O. Comprehensive analysis of heavy metal streams in pulverized coal-fired boilers taking into account different operating conditions. *VGB Kraftwerkstechnik und VGB PowerTech* 1998;10:134–40.
- [15] Meij R, van der Kooij J, Van der Sluys JLG, Siepmann PGC, Van der Sloot HA. Emission of fly ash and trace species from pulverized coal fired utility boilers. Keuring van Elektrotechnische Materialen N.V., Arnhem, Netherlands. 1983:10.
- [16] Thorwarth H. Trace element behaviour in pulverised fuel fired power plants: impact of fuels and emission control technologies. 1st ed. Göttingen: Cuvillier Verlag; 2007.
- [17] Gehrig M, Jaeger D, Pelz SK, Weissinger A, Groll A, Thorwarth H, et al. Influence of firebed temperature on inorganic particle emissions in a residential wood pellet boiler. *Atmos Environ* 2016;136:61–7. <https://doi.org/10.1016/j.atmosenv.2016.04.018>.
- [18] Saqib N, Bäckström M. Trace element partitioning in ashes from boilers firing pure wood or mixtures of solid waste with respect to fuel composition, chlorine content and temperature. *Waste Manage* 2014;34(12):2505–19. <https://doi.org/10.1016/j.wasman.2014.08.025>.
- [19] Hilber T, Thorwarth H, Stack-Lara V, Schneider M, Maier J, Scheffknecht G. Fate of mercury and chlorine during SRF co-combustion. *Fuel* 2007;86(12–13):1935–46. <https://doi.org/10.1016/j.fuel.2006.12.014>.
- [20] BGGI. Verordnung über Anforderungen an die Verwertung und Beseitigung von Altholz (Altholzverordnung - AltholzV): AltholzV; 2002.
- [21] DIN Deutsches Institut für Normung e. V. – Solid biofuels – Determination of moisture content – Oven dry method – Part 1: Total moisture – Reference method (ISO 18134-1:2015); German version EN ISO 18134-1:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2015.
- [22] DIN Deutsches Institut für Normung e. V. Solid biofuels – Determination of minor elements (ISO 16968:2015); German version EN ISO 16968:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2015.
- [23] DIN Deutsches Institut für Normung e. V. Solid biofuels – Determination of major elements – Al, Ca, Fe, Mg, P, K, Si, Na and Ti (ISO 16967:2015); German version EN ISO 16967:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2015.
- [24] DIN Deutsches Institut für Normung e. V. Solid biofuels – Determination of calorific value (ISO/DIS 18125:2015); German and English version prEN ISO 18125:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2015.
- [25] DIN Deutsches Institut für Normung e. V. Solid biofuels – Determination of ash content (ISO 18122:2015); German version EN ISO 18122:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2016.
- [26] DIN Deutsches Institut für Normung e. V. Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen (ISO 16948:2015); German version EN ISO 16948:2015;75.160.10. 10772 Berlin: Beuth Verlag GmbH; 2015.
- [27] Brandenburg T, Buchholz P, Dorner U, Huy D, Liedtke M, Schmidt M et al. Angebotskonzentration bei mineralischen Rohstoffen und Zwischenprodukten – potenzielle Preis- und Lieferisiken: DERA-Rohstoffliste 2016. 2016th ed. Hannover: DERA; 2017.
- [28] Michael Schmidt. Rohstoffrisikobewertung Lithium. 33rd ed. Berlin; 2017.

- [29] Dorner U. Rohstoffrisikobewertung Kupfer: Kurzbericht. 2013rd ed. Berlin: Deutsche Rohstoffagentur (DERA) in der Bundesanstalt für Geowissenschaften und Rohstoffe; 2013.
- [30] Elsner H. Bismut – ein typisches Sondermetall. 2015th ed. Berlin: Deutsche Rohstoffagentur (DERA) in der Bundesanstalt für Geowissenschaften und Rohstoffe; 2015.
- [31] Dorner U. Rohstoffrisikobewertung – Zink. 2014th ed. Berlin: DERA; 2015.
- [32] Liedtke M, Schmidt M. Rohstoffrisikobewertung – Wolfram. 2013rd ed. Berlin: DERA; 2014.
- [33] Marscheider-Weidemann F, Langkau S, Hummen T, Erdmann L, Tercero Espinoza LA, Angerer G et al. Rohstoffe für Zukunftstechnologien 2016: Auftragsstudie. 2016th ed. Berlin: Deutsche Rohstoffagentur (DERA) in der Bundesanstalt für Geowissenschaften und Rohstoffe (BGR); 2016.
- [34] Schmidt M. Rohstoffrisikobewertung – Antimon. 2013rd ed. Berlin: DERA; 2013.
- [35] BGR. Rohstoffwirtschaftlicher Steckbriefe – Chrom (2013). Hannover; 2013.
- [36] BGR- Bundesanstalt für Geowissenschaften und Rohstoffe. Deutschland-Rohstoffsituationenbericht 2017. Hannover; 2018.
- [37] Lopez-Arce P, Garcia-Guinea J, Garrido F. Chemistry and phase evolution during roasting of toxic thallium-bearing pyrite. *Chemosphere* 2017;181:447–60. <https://doi.org/10.1016/j.chemosphere.2017.04.109>.
- [38] Yang C, Chen Y, Peng P, Li C, Chang X, Wu Y. Trace element transformations and partitioning during the roasting of pyrite ores in the sulfuric acid industry. *J Hazard Mater* 2009;167(1–3):835–45. <https://doi.org/10.1016/j.jhazmat.2009.01.067>.
- [39] Mpinga CN, Eksteen J, Aldrich C, Dyer L. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Miner Eng* 2017;110:153–65. <https://doi.org/10.1016/j.mineng.2017.04.019>.
- [40] Singh V, Biswas A. Physicochemical processing of low grade ferruginous manganese ores. *Int J Miner Process* 2017;158:35–44. <https://doi.org/10.1016/j.minpro.2016.11.013>.
- [41] Li J, Bunney K, Watling HR, Robinson DJ. Thermal pre-treatment of refractory limonite ores to enhance the extraction of nickel and cobalt under heap leaching conditions. *Miner Eng* 2013;41:71–8. <https://doi.org/10.1016/j.mineng.2012.11.002>.
- [42] Parirenyatwa S, Escudero-Castejon L, Sanchez-Segado S, Hara Y, Jha A. Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals. *Hydrometallurgy* 2016;165:213–26. <https://doi.org/10.1016/j.hydromet.2015.08.002>.
- [43] Zhang M, Zhu G, Zhao Y, Feng X. A study of recovery of copper and cobalt from copper–cobalt oxide ores by ammonium salt roasting. *Hydrometallurgy* 2012;129–130:140–4. <https://doi.org/10.1016/j.hydromet.2012.06.014>.
- [44] Pickles CA, Forster J, Elliott R. Thermodynamic analysis of the carbothermic reduction roasting of a nickeliferous limonitic laterite ore. *Miner Eng* 2014;65:33–40. <https://doi.org/10.1016/j.mineng.2014.05.006>.
- [45] Canil D, Grondahl C, Lacourse T, Pisiak LK. Trace elements in magnetite from porphyry Cu–Mo–Au deposits in British Columbia, Canada. *Ore Geol Rev* 2016;72:1116–28. <https://doi.org/10.1016/j.oregeorev.2015.10.007>.
- [46] Lau LL, de Castro LFA, Dutra FdC, Cantarino MV. Characterization and mass balance of trace elements in an iron ore sinter plant. *J Mater Res Technol* 2016;5(2):144–51. <https://doi.org/10.1016/j.jmrt.2015.10.007>.