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Mobility of Elements in Ashes from a Wood-Fired Heat and Power Plant with a Grate-Fired Furnace

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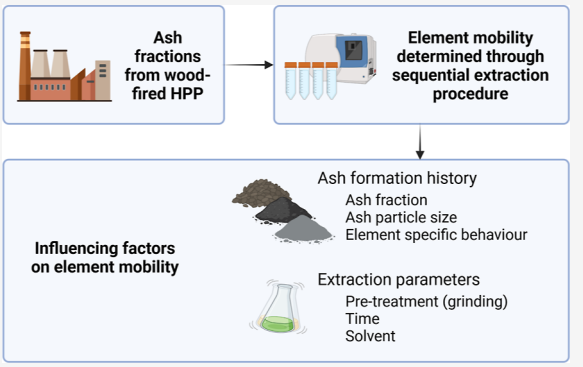
ABSTRACT: The established practice of wood ash disposal in landfills removes valuable elements, such as metals and plant nutrients, from the utilization cycle. In order to use the residual material wood ash as a secondary raw material and to conserve important natural resources (landfill space, mineral, and metallic raw materials), a treatment process must be developed. As a basis for such a process, fundamental knowledge of element solubility is required. Therefore, a sequential extraction process describing the mobility of the ash-forming elements was carried out for three ash fractions from a wood-fired heat and power plant. This work describes the extraction of 24 elements from ash by four sequentially applied extractants. As an aqueous solvent, bidest. water was used, acetic acid was used as the acidic solvent, hydroxylamine hydrochloride was used as the reducing solvent, and ammonium acetate with hydrogen peroxide was used as the oxidizing solvent. Element concentrations in the individual extractants were determined by ICP−OES. We found that the extraction is influenced by the ash fraction, the particle size, and the element-specific behavior during ash formation. Extractability is higher from filter and cyclone ash fractions compared to grate ash as well as from smaller particle size fractions within grate ash compared to coarse grate ash particles. The majority of the metals were acid-soluble. In parameter studies, we found that extractability can be increased by using stronger solvents, grinding the ash, and a longer extraction time. The results provide information on (I) the environmental mobility of the ash-forming elements and (II) suitable solvents and process parameters for the processing of ashes, with the aim of a consistent recycling of valuable substances and nutrients.



1. INTRODUCTION

Ash from industrial-scale wood combustion is usually differentiated in bottom ash, discharged from the combustion chamber, and fly ash that is entrained with the flue gas and discharged by flue gas cleaning systems.[1] Ash fractions that contain high concentrations of potentially hazardous substances such as environmentally critical metals have to be disposed at great expense in suitable landfills or underground.[2,3] However, these ashes are valuable materials that should not be disposed of, but should be used in line with the circular economy concept.[4] The established practice of ash disposal removes valuable elements from the utilization cycle. In order to use these wood ashes as a secondary raw material and to conserve important natural resources (landfill space, mineral, and metallic raw materials), a treatment process to ensure safe utilization must be developed. As basis for the development of such a process, a fundamental understanding of element mobility in wood ashes is required.

1.1. Combustion and Ash Formation. The processes of element release from the fuel and the mineral phase transformation during solid fuel combustion are well researched.[5−10] Element behavior during the combustion process and in flue gas cleaning facilities and thus the element concentrations in the resulting ash fractions are influenced by several factors. First, the fuel composition determines the total amount of elements entering the process. With wood fuel, inorganic elements are fed into the combustion process. They make up the ash content of the fuel which is typically >2 wt % (wf) for wood-derived fuels.[11] These inorganic elements may be present as free mineral particles, mineral inclusions within the fuel particles, or as organically bound elements incorporated into the fuel matrix.[12,13] During combustion, different pathways of element release and transformation are likely to occur. Minerals are released from the fuel matrix, and trace elements are subsequently vaporized. After the flame zone, aerosol particles form through nucleation and coagulation mechanisms and can grow through agglomeration. Another way of fly ash formation is the heterogeneous

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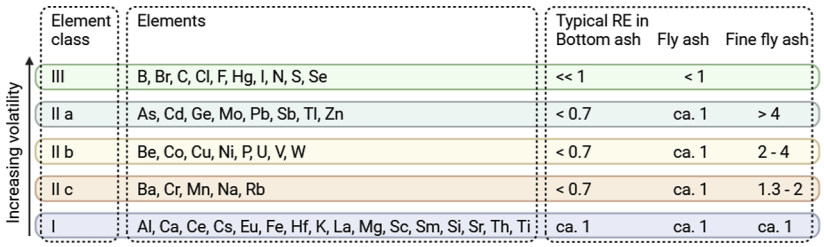

Figure 1. Element classification based on RE calculated for coal bottom, fly and fine fly ashes. Data from ref 19.

condensation of trace element vapor onto fly ash particles. Highly volatile elements may stay gaseous and be emitted in the vapor phase. Next to the gas-phase reaction, ash is formed during char burnout. Within the char, particles undergo mineral fragmentation and especially less volatile trace elements can be found in the resulting ash.[7,12,14]

In wood fired plants, employed combustion technologies range from grate firing to fluidized bed and pulverized fuel boilers,[15,16] while in this paper, it is focused on ashes from grate-fired systems. Ash is typically removed as a coarse fraction (bottom or grate ash) and finer fractions from flue gas cleaning devices such as cyclones, electrostatic precipitators, or fabric filters.[9,17] The fuel type and combustion technology influence the ash particle size distribution. Flue gas cleaning technologies determine the separated ash particle size and the particle separation temperature, which typically decreases downstream the plant.[4] Higher concentrations of metals tend to be found in finer fractions and smaller particle sizes.[18]

The concentration of inorganic elements in the ash is generally a factor of higher than the concentration in the fuel, which is linked to the ash content in the fuel. This relation is described by the relative enrichment factor (RE, eq 1).

$$\mathrm{RE} = \frac{\text{element concentration in ash}}{\text{element concentration in fuel}} \times \frac{\text{ash content in fuel [\%]}}{100} \quad (1)$$

According to ref 19, elements can be classified according to typical behavior into five groups (Figure 1). Previous studies show that the element behavior in wood fired plants is comparable to the behavior on coal fired power stations.[4]

1.2. Ash Utilization and Disposal. The global production of bottom and fly ash from biomass combustion is estimated between 170 Mt/a[20] to 480 Mt/a,[1] depending on the type of feedstock taken into consideration and the degree of utilization of the biomass potential. Few more precise estimates of wood ash production in individual countries can be found. A scenario study for The Netherlands has predicted an ash volume between 2 and 3 Mt/a in the year 2030.[1,21] For the German Federal State of Bavaria (i.e., southeast Germany), market reports indicate a total of 30,000−60,000 t/a of ash from untreated wood from medium-sized plants with an installed capacity >1 MW.[22] Ref 23 estimated the annual ash production from industrial-scale wood energy plants (>20 MW) in the German Federal State of Baden-Wuerttemberg (i.e., southwest Germany) to 67,500 t/a of coarse ash, 20,250 t/a of fly ash, and 5400 t/a of fine fly ash. Assuming 100% nutrient recovery of the P, N, K, and Ca potentials identified in this study, approximately 3.1% of the P, 7.5% of the K, and 22.8% of the Ca fertilizer sales in Baden-Wuerttemberg could be substituted from the total amount of ash from large-scale plants only.[23]

Due to relatively low pollutant levels, biomass ash may be returned directly to soil under certain conditions. Regulatory requirements for ash utilization vary from country to country. Most specifications include limits for organic and inorganic contaminants. To ensure this, there are, e.g., specifications regarding the fuel used (only natural wood, no waste wood) and the origin of the ash (coarse ash from the combustion chamber, no fly ash from the flue gas cleaning section). More details are given in ref 23.

One field of application that has already been well studied is the recycling of the coarse wood ash fraction (bottom or grate ash) to forest soil. The alkaline effect can be used to counter the soil acidification. With the exception of nitrogen, which is mainly released with the flue gas after combustion, the nutrient balance in the forest soil can be maintained by recycling the ash.[24,25] However, the coincineration of waste wood and logging residues which is commonly practiced, leads to high levels of pollutants within the ash that forbids its recycling to forest soils.[26] Furthermore, finer ashes from the flue gas cleaning facilities must be disposed in any case.

Ash can also be used as a fertilizing material in agriculture, providing a liming effect on the soil as well as nutrient elements for plant growth. To evaluate ash characteristics regarding its potential use as fertilizer, the composition and leaching behavior of different biomass ashes was investigated.[27−29] The effect of ash fertilization on plant growth, soil properties, and element accumulation in plants and seeds was evaluated in pot experiments.[30] Besides positive effects through nutrient supply, potential risks of ash application as a fertilizing material are pollutant input and accumulation in soil and plants as well as the alkalinization and salinization of the soil.[31,32] An evaluation of combustion ashes from industrial-scale wood-fired heat and power plants (>20 MW) regarding legal requirements for fertilizers shows that both important plant nutrients (e.g., P, K, Ca) and heavy metals, mainly Cd, Pb and Zn which do not allow an uncontrolled utilization, are contained in the ash in relevant concentrations. In order to make both element groups available for secondary utilization, the ash must be treated to separate the metals from the nutrient fraction.[23]

Another utilization pathway for biomass ash is its use as a secondary raw material in construction. In compliance with certain quality requirements, ash can be applied, e.g., in road construction or as a replacement for cement in concrete production, saving primary raw materials and CO_2 emissions.[33,34] However, even though biomass ash has a potential beneficial use in fertilizer or construction products, this residue is still disposed of in landfills.[3,35] In terms of a circular economy approach, a new process for element recovery from wood ash is needed. As a basis for such a process, fundamental knowledge of the solubility of the individual ash components is required.

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Table 1. Fractions Defined in SE Procedures, Related Extraction Principles, and Indication on Environmental Conditions as Described by[51,53,57,61]

element fraction	extraction principle, indication on environmental conditions
(I) exchangeable (water-soluble)	elements are soluble if the hydration energy is equal to or greater than its lattice energy
(II) bound to carbonates (acid-soluble)	solubility of elements is affected by changes in pH
(III) bound to Fe and Mn oxides (reducible)	compounds are instable under reducing conditions
(IV) bound to organic matter (oxidizable)	compounds are degraded under oxidizing conditions
(V) residual (primary and secondary minerals)	elements are not expected to be released from crystal structure over a reasonable timespan under conditions as encountered in nature

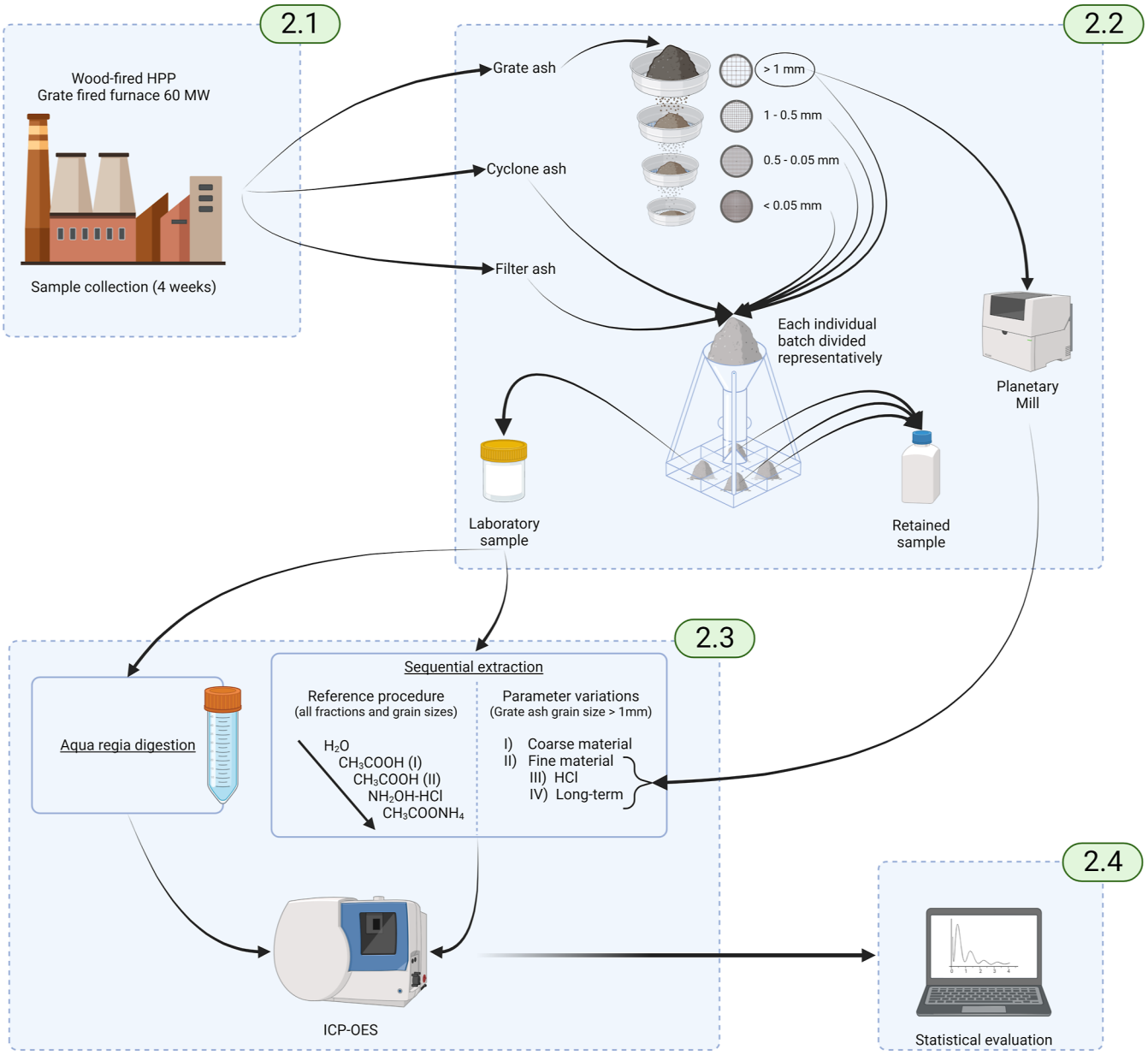

Figure 2. Overview of sample collection, preparation, wet chemical extraction procedure, analysis, and statistical evaluation.

Experience can be drawn from the treatment of MSWI ashes, where washing, chemical stabilization and solidification or thermal treatment prior to disposal in landfills is already being practiced, reducing its hazard potential.[36−38] The removal of metals from MSWI ashes, e.g. through leaching, reduces environmental risks and enables the recovery of resources that would otherwise be discharged from the utilization circle.[39−42] For example, the recovery of high purity zinc from fly ash of waste to energy plants has successfully been demonstrated.[43−45] Also, gold could be recovered from processed MSWI residues via thiourea leaching.[46]

1.3. Description of Element Mobility through Sequential Extraction. Extraction and processing of natural resources as well as waste disposal are linked to numerous

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negative effects on the environment.[47,48] The transition from the current linear economic model, which is associated with increasing resource consumption and waste generation, to a circular economy is necessary for sustainable development.[49] This requires information on the availability of man-made material stocks and flows such as landfills, built infrastructure and waste streams.[50]

For this, not only the total element content (TEC) of a waste stream such as biomass ash but also the mobility of the elements must be taken into account.[1] An analytical method for assessing the ecological risk from potential leaching of metals from environmental samples based on sequential chemical extractions was first developed by ref 51 and is well-known as BCR-protocol (European Community Bureau of Reference) as described by ref 52. The purpose of the procedure is a selective SE for partitioning elements into the chemical forms likely to be released in solution under different environmental conditions.[51,53]

Since its first publication, the SE procedure has been continuously developed for the application with different solid materials (e.g., sediment, soil, sewage sludge and incineration residues) and leaching agents.[54,55] SE procedures were applied to investigate the element solubility from various incineration residues under different conditions. For example, SE was used to investigate the environmental mobility of metals in coal and MSWI fly ashes[56−59] as well as ashes from biomass combustion.[53,60,61]

Due to the high content of alkaline substances in incineration residues,[62] concluded that for the investigated fly ash instead of a single-step, successive acid washing should be carried out in order to extract the full amount of acid-soluble metals. Although the SE process has been adapted to different materials, the fact that modified formulations have been developed limits the comparability of the data within and between different materials.

During SE, elements contained in the solid sample are partitioned into five fractions (Table 1). Ref 63 found a similar solubility behavior in bottom and fly ash samples, except for alkali metals in the bottom ash, which were less soluble than in the fly ash. ref 64 investigated four grain size fractions of processed MSWI residue. Results indicate higher leaching efficiencies of metals in the fine fractions (0−0.5, 0.5−2.0 mm), posing higher risks for the release of toxic compounds than in the coarse fractions (2.0−4.0, 4.0−16.0 mm). Ref 65 used statistical methods to understand heavy metal stability and predict the leaching potential from MSWI fly ash with its compositional variety in order to give recommendations for the management and landfilling of the ash. Element mobility and thus the leaching efficiency was found to depend on the chemical concentration within the ash, extraction time and pH.[66,67]

1.4. Aim of the Study. Element mobility in wood ashes is to be studied by experimental investigations of element solubility in this paper. Therefore, it is aimed to determine the solubility of 24 elements in an SE procedure. The results will contribute to a better understanding of the mobility of elements in wood ash, focusing on four aspects:

(I) Specifically, we will determine the influence of particle size on element solubility in raw, untreated ash fractions that are separated with declining particle sizes downstream the plant, and flue gas cleaning facilities (grain sizes in grate ash > cyclone ash > filter ash) as well as in raw vs manually crushed grate ash.

(II) We aim at evaluating the influence of process engineering parameters (use of different acids, extraction time) on element solubility.

(III) We will determine the relationship between the leachability of elements and the specific behavior of elements during mineral phase transformation in combustion, using the concept of element volatility classes described in the literature. The hypothesis that low volatile elements show a rather low leachability and high volatile elements are easier to leach will be investigated.

(IV) A substance flow analysis will be carried out to (a) quantify the environmental mobility of elements contained in wood ash; (b) demonstrate whether a separation of plant nutrients and potential pollutants in the form of environmentally relevant metals is possible by process engineering solutions; and (c) identify ash fractions and leaching agents that can be used in treatment plants for element recovery.

2. MATERIAL AND METHODS

All samples were analyzed at the laboratory of the University of Applied Forest Sciences Rottenburg (Germany). Figure 2 provides an overview of the sampling, extraction, and analytical methods described in Chapters 2.1−2.4.

2.1. Ash Origin and Sample Collection. Wood ash samples of grate, cyclone, and filter ash were collected over a period of approximately 4 weeks in summer 2022 at a plant installed in southern Germany. All samples were taken from the plant operator.

The wood-fired HPP has a grate-fired furnace with a thermal capacity of approximately 60 MW_{th} using a fuel mixture of forest residues and waste wood category A I−IV according to the German Waste Wood Ordinance.[68] Three ash fractions are removed separately from the plant. Grate ash is removed wet at the end of the grate. Cyclone ash is removed at approximately 173 °C after gravimetric removal of fly ash particles. In addition to the actual ash, the filter ash also contains the loaded sorbents coke and hydrated lime $Ca(OH)_2$, which are added upstream of the fabric filter. The flue gas flows through the fabric filter at approximately 171 °C.

The plant operator provided mixed samples that were collected according to ref 69 each time the ash silo was emptied (cyclone respectively filter ash) or the ash was collected by the waste disposal company (grate ash). The total mixed sample amounts of 1.7 kg (wf) grate ash, 1.3 kg (wf) cyclone ash, and 0.5 kg (wf) filter ash were packed in airtight buckets and sent to the University of Applied Sciences Rottenburg for further analysis.

2.2. Sample Preparation. After arrival at the laboratory, all collected ash samples were dried at 105 °C in a drying oven (UNP 700, Memmert, Schwabach, Germany) for approximately 24 h until constant weight.

The grate ash was sieved into fractions of >1 mm (87.1 wt %), 1−0.5 mm (6.9 wt %), 0.5−0.05 mm (5.6 wt %) and <0.05 mm (0.4 wt %) with a Vibratory Sieve Shaker (Retsch AS 400 control, Haan, Germany).

For each individual batch (filter ash, cyclone ash, grate ash >1 mm, grate ash 1−0.5 mm, grate ash 0.5−0.05 mm and grate ash <0.05 mm), the dried material was separated in a sample divider[70] until 50 g (wf) of each batch remained as a laboratory sample.

The >1 mm fraction was selected for the parameter studies (chapter 2.3.2) due to its high quantitative significance. Therefore, a part of the grate ash coarse fraction (>1 mm) sample was milled in an orbital mono mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany) for aqua regia digestion as well as for SE parameter studies. The other ash fractions were not crushed before further handling. Cyclone ash consists mainly of fine particles (93.6 wt % < 0.5 mm).

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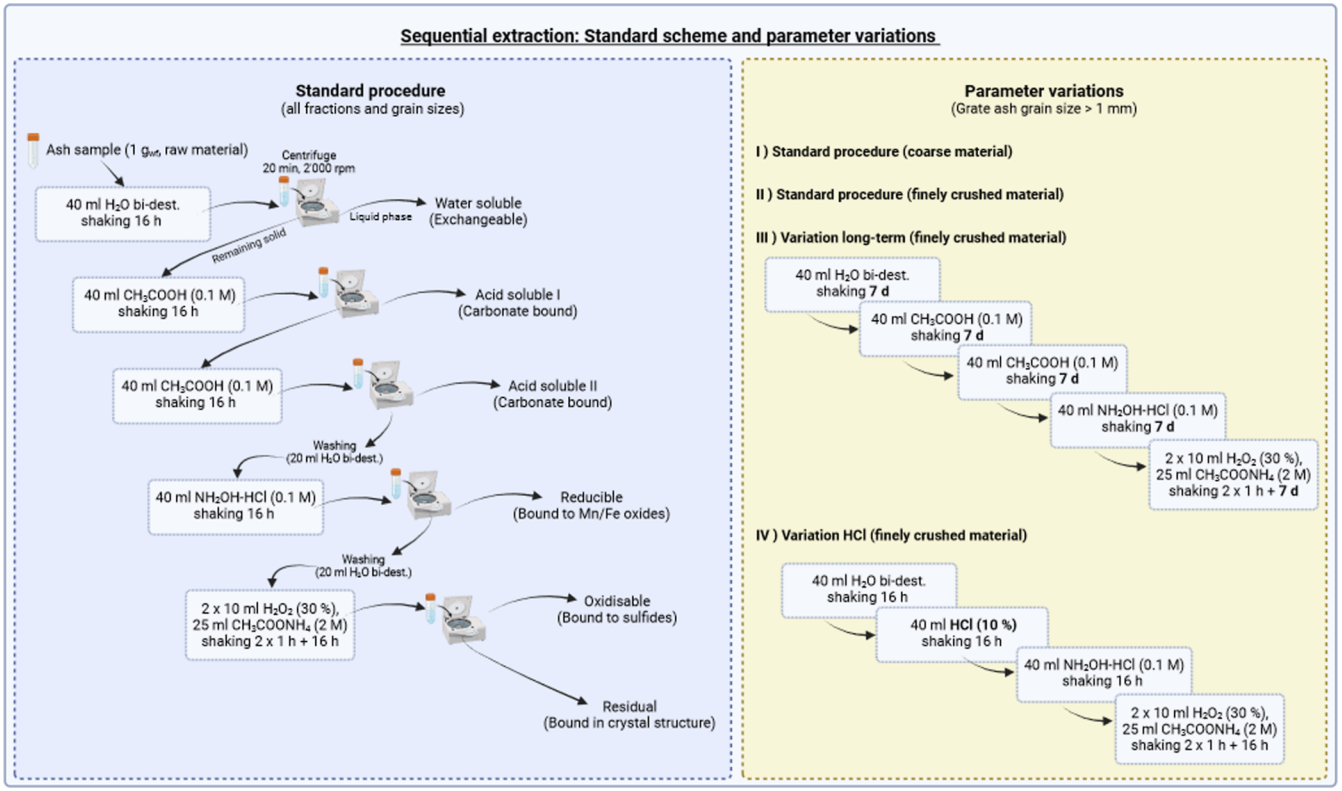

Figure 3. SE procedure.

The >1 mm grate ash fraction (coarse fraction) was both directly used for testing (SE reference procedure) and used after size reduction in parameter studies (fine material, HCl, long-term).

2.3. Wet Chemical Extraction and Analytics. *2.3.1. Aqua Regia Digestion.* Element analysis was carried out in quadruplicate for all three ash fractions removed at filter, cyclone, and grate ash. The grate ash was divided into four grain sizes. For sample preparation, 0.1 g of ash was treated with 1 mL of 30% H_2O_2 (for synthesis, Roth, Karlsruhe, Germany), 4 mL of 69% HNO_3 (Rotipuran Supra, Roth), and 9 mL of 35% HCl (Rotipuran Supra, Roth, Karlsruhe, Germany). Samples were microwave digested (Multiwave GO 3000, Anton Paar, Graz, Austria). The digested residues were diluted to 50 mL with aqua bidest. for further analysis.[71]

2.3.2. Sequential Extraction. For the SE of the elements contained in the wood ash, a modified BCR protocol as described by refs 57, 62 and 64 was used. The standard SE procedure shown in Figure 3 was used to characterize all ash fractions and grain sizes (filter ash, cyclone ash, and grate ash in four grain sizes) that are examined in this study. As an aqueous solvent, bidest. water (H_2O bidest.) was used, acetic acid (CH_3COOH) as acidic solvent, hydroxylamine hydrochloride (NH_2OH−HCl) as reducing solvent, and ammonium acetate (CH_3COONH_4) after application of hydrogen peroxide (H_2O_2) as oxidizing solvent.

Extraction tests in the standard procedure were carried out with grate ash separated into grain size fractions. For comparison of the ash fractions (grate, cyclone, and filter ash), the weighted average of the values for grate ash across all grain sizes was calculated.

Deviating from the standard procedure, the influences of grain size, extraction time, and extractant strength on the extraction process were examined. The standard procedure carried out with a coarse material (variant I) served as a reference. In variant II, finely crushed material was used instead of the raw coarse material. In variant III, in addition to the crushing of the material, the extraction time was increased from 16 h to 7 d for each extraction step. In variant IV, hydrochloric acid was used instead of the relatively weak acetic acid.

2.3.3. Element Analysis in ICP-OES. The element content of digestate and leachate samples was quantified according to refs 72 and 73 with an ICP−OES (Spectro Blue, ASX-260 auto sampler, SPECTRO Analytical Instruments, Kleve, Germany).

2.4. Statistical Evaluation of Results. *2.4.1. Nomenclature and Quantification of Element Solubility.* The TEC is defined as the concentration (c) of element i in aqua regia digestate [mg kg^{-1}]. For a comparison of the individual extraction steps and the relative proportions of the extracted elements, the TEC is defined as 100% (eq 2).

$$\mathrm{TEC}_i = c_{\mathrm{i,aquaregia}} \tag{2}$$

For each extraction step, the soluble fraction (SF) of an element *i* is defined as the element concentration in the respective leachate [mg kg^{-1}] in relation to the TEC (eqs 3−−7).

$$\mathrm{SF}_{\mathrm{i,water}} = c_{\mathrm{i,water}}/c_{\mathrm{i,aquaregia}}\ [\%] \tag{3}$$

$$\mathrm{SF}_{\mathrm{i,aceticacid(I)}} = c_{\mathrm{i,aceticacid(I)}}/c_{\mathrm{i,aquaregia}}\ [\%] \tag{4}$$

$$\mathrm{SF}_{\mathrm{i,aceticacid(II)}} = c_{\mathrm{i,aceticacid(II)}}/c_{\mathrm{i,aquaregia}}\ [\%] \tag{5}$$

$$\mathrm{SF}_{\mathrm{i,reducingagent}} = c_{\mathrm{i,reducingagent}}/c_{\mathrm{i,aquaregia}}\ [\%] \tag{6}$$

$$\mathrm{SF}_{\mathrm{i,oxidizingagent}} = c_{\mathrm{i,oxidizingagent}}/c_{\mathrm{i,aquaregia}}\ [\%] \tag{7}$$

Across all extraction steps, the sum of the element concentrations in the leachates is defined as the total SF (eq 8).

$$\sum \mathrm{SF}_{\mathrm{i,water;i,acetic\ acid(I);}i\mathrm{,acetic\ acid\ (II);}i\mathrm{,reducing\ agent;}i\mathrm{,oxidizing\ agent}} = \mathrm{SF}_{\mathrm{i,total}}\ [\%] \tag{8}$$

The amount of elements that cannot be extracted is defined as the residual fraction (RF) that is calculated according to (eq 9).

$$\mathrm{RF}_i = \mathrm{TEC}_i - \mathrm{SF}_{\mathrm{i,total}}\ [\%] \tag{9}$$

The extraction efficiency (EE) of the SE procedure of element i in standard and parameter variants is defined as the ratio of extracted elements to the total content in the raw ash (eq 10).

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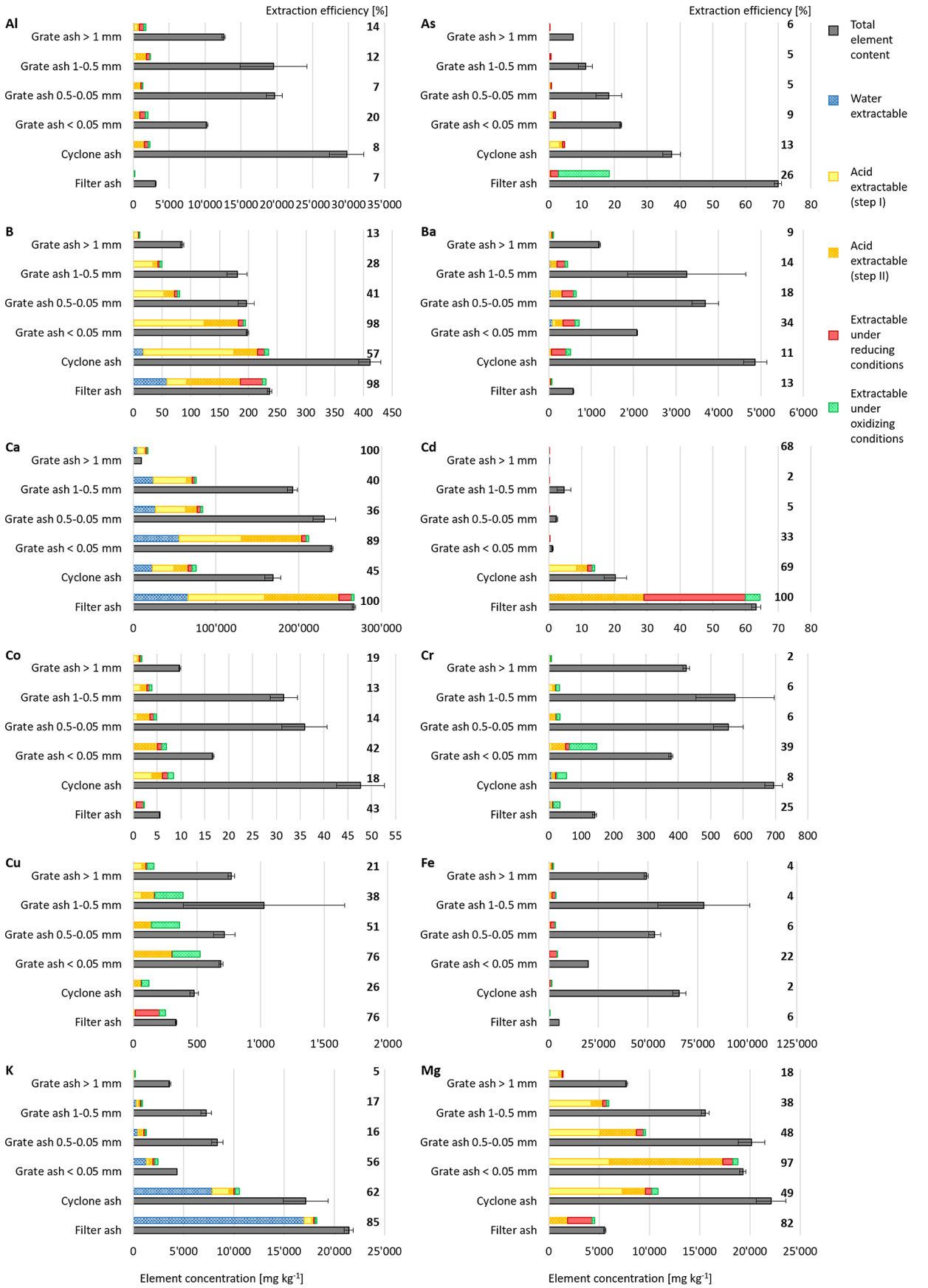

Figure 4. continued

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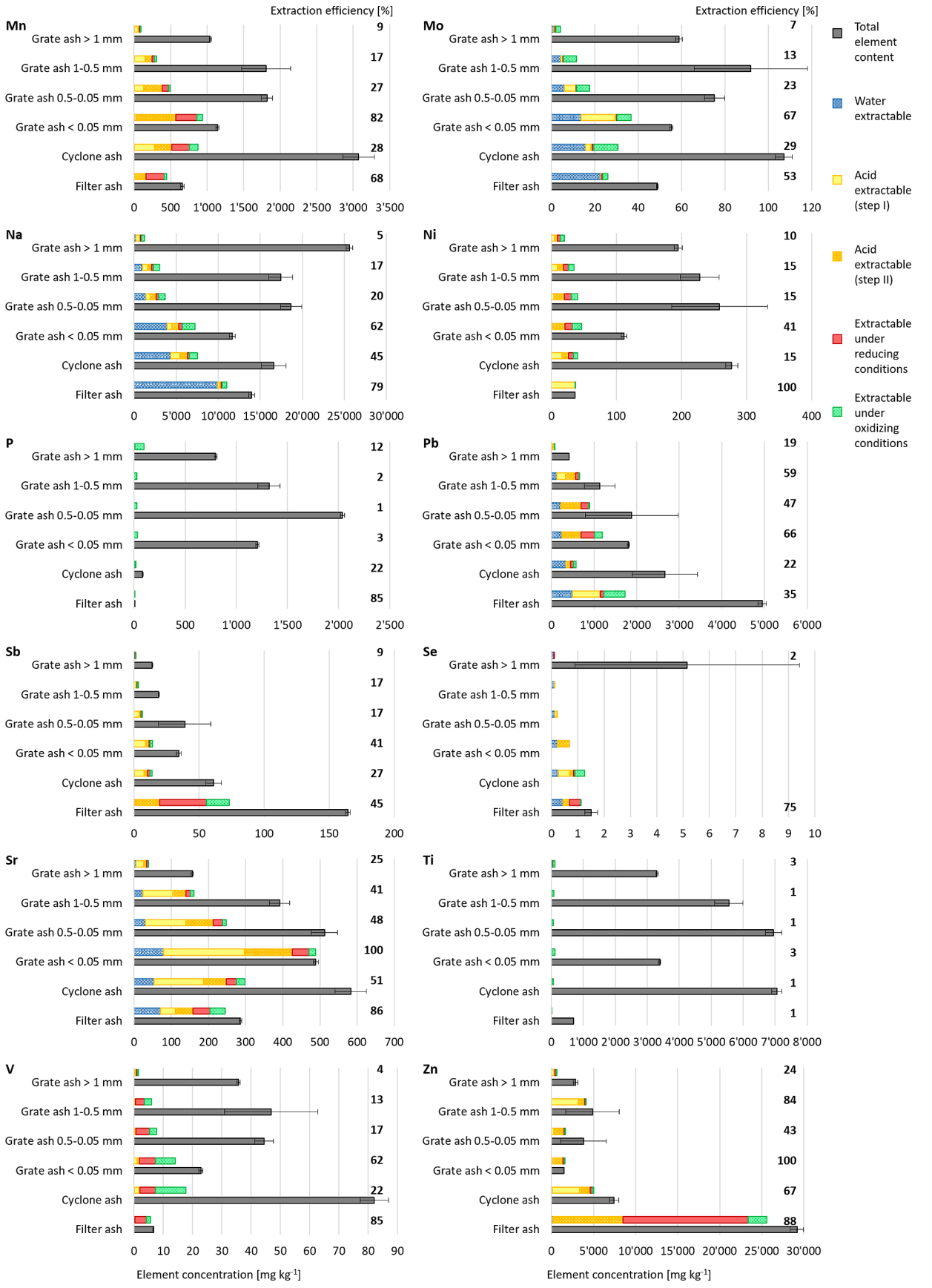

Figure 4. TEC [mg kg^{-1}], extractability in aqueous, acidic, reducing and oxidizing leaching agents [mg kg^{-1}] per element across grate ash particle size fractions, cyclone ash, and filter ash. The EE [%] for each is given next to each bar for each ash respective to the particle size fraction.

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Table A1. Mean Values (±SD) of the pH Value (n = 4) in Leachates from Different Ash Fractions in Water, Acid, Reducing and Oxidizing Extractants[a]

	water extractable	acid extractable (step I)	acid extractable (step II)	extractable under reducing conditions	extractable under oxidizing conditions	total
			Grate Ash > 1 mm			
pH	11.84 (±0.05)	3.95 (±0.19)	3.43 (±0.09)	4.22 (±0.06)	6.57 (±0.13)	
Al [mg kg^{-1}]	121.04 (±64.82)	414.71 (±142.66)	320.54 (±155.04)	614.67 (±482.08)	287.88 (±260.45)	12574.27 (±186.66)
As [mg kg^{-1}]	0.05 (±0.02)	0.05 (±0.05)	0.03 (±0.03)	0.28 (±0.07)	0.00 (±0.00)	7.35 (±0.06)
B [mg kg^{-1}]	1.26 (±0.18)	7.70 (±5.06)	0.07 (±0.10)	1.78 (±1.03)	0.23 (±0.13)	84.66 (±2.91)
Ba [mg kg^{-1}]	10.05 (±1.10)	38.27 (±4.90)	30.77 (±7.17)	17.48 (±1.98)	10.17 (±5.32)	1192.63 (±20.70)
Ca [mg kg^{-1}]	4950.33 (±453.96)	8182.81 (±1006.59)	2168.88 (±604.73)	1561.96 (±203.55)	676.30 (±163.62)	9789.00 (±114.12)
Cd [mg kg^{-1}]	0.01 (±0.01)	0.04 (±0.04)	0.00 (±0.00)	0.12 (±0.03)	0.00 (±0.00)	0.23 (±0.03)
Co [mg kg^{-1}]	0.00 (±0.00)	0.87 (±0.77)	0.41 (±0.33)	0.31 (±0.17)	0.25 (±0.15)	9.76 (±0.19)
Cr [mg kg^{-1}]	0.47 (±0.08)	2.89 (±0.77)	1.06 (±0.38)	0.83 (±0.11)	2.32 (±0.69)	423.54 (±10.09)
Cu [mg kg^{-1}]	1.88 (±0.47)	66.71 (±62.85)	30.50 (±22.63)	11.26 (±5.49)	51.24 (±18.70)	769.72 (±25.24)
Fe [mg kg^{-1}]	23.68 (±10.37)	932.26 (±789.37)	549.22 (±218.15)	478.97 (±81.70)	33.19 (±5.28)	49098.61 (±1044.76)
K [mg kg^{-1}]	60.29 (±6.12)	69.73 (±5.29)	31.25 (±18.07)	0.00 (±0.00)	19.00 (±19.53)	3608.81 (±97.22)
Mg [mg kg^{-1}]	0.00 (±0.00)	982.62 (±267.95)	308.48 (±87.74)	132.34 (±36.33)	0.00 (±0.00)	7736.18 (±95.53)
Mn [mg kg^{-1}]	2.31 (±0.74)	48.33 (±10.77)	24.22 (±7.49)	13.17 (±2.77)	6.40 (±2.58)	1042.88 (±14.02)
Mo [mg kg^{-1}]	1.10 (±0.43)	0.33 (±0.12)	0.10 (±0.10)	0.56 (±0.08)	1.97 (±0.66)	58.84 (±1.42)
Na [mg kg^{-1}]	192.44 (±17.15)	413.64 (±73.27)	134.41 (±36.09)	125.51 (±10.78)	348.05 (±28.50)	25597.98 (±383.83)
Ni [mg kg^{-1}]	0.09 (±0.07)	4.58 (±1.32)	4.10 (±0.85)	4.88 (±0.81)	6.26 (±1.63)	194.84 (±6.00)
P [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	10.05 (±17.41)	0.00 (±0.00)	84.88 (±62.49)	796.80 (±13.80)
Pb [mg kg^{-1}]	7.03 (±2.20)	30.39 (±8.46)	26.11 (±17.37)	7.66 (±4.41)	8.00 (±2.68)	414.46 (±2.54)
Sb [mg kg^{-1}]	0.15 (±0.05)	0.25 (±0.06)	0.39 (±0.37)	0.22 (±0.18)	0.21 (±0.13)	13.97 (±0.30)
Se [mg kg^{-1}]	0.09 (±0.02)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	5.15 (±4.26)
Sr [mg kg^{-1}]	4.38 (±0.55)	20.77 (±4.11)	8.48 (±2.98)	4.08 (±0.89)	1.61 (±0.86)	156.79 (±2.63)
Ti [mg kg^{-1}]	1.89 (±0.67)	8.78 (±4.26)	14.56 (±4.31)	18.06 (±1.73)	59.46 (±27.45)	3305.76 (±34.67)
V [mg kg^{-1}]	0.04 (±0.04)	0.34 (±0.07)	0.35 (±0.13)	0.33 (±0.16)	0.35 (±0.15)	35.69 (±0.49)
Zn [mg kg^{-1}]	4.02 (±1.78)	272.16 (±126.92)	158.18 (±151.90)	141.69 (±43.78)	96.17 (±14.36)	2857.46 (±288.70)
			Grate Ash 1−0.5 mm			
pH	12.47 (±0.01)	4.96 (±0.03)	3.89 (±0.01)	3.99 (±0.07)	6.84 (±0.06)	
Al [mg kg^{-1}]	0.00 (±0.00)	413.21 (±49.89)	1415.46 (±119.16)	461.08 (±95.00)	77.64 (±20.68)	19539.56 (±4667.27)
As [mg kg^{-1}]	0.02 (±0.02)	0.17 (±0.03)	0.16 (±0.05)	0.23 (±0.02)	0.00 (±0.00)	11.18 (±2.16)
B [mg kg^{-1}]	0.27 (±0.02)	33.83 (±2.18)	8.50 (±1.55)	3.97 (±1.11)	3.07 (±0.89)	180.61 (±17.42)
Ba [mg kg^{-1}]	42.22 (±1.71)	20.31 (±2.90)	128.66 (±9.54)	190.20 (±14.16)	55.90 (±9.37)	3250.75 (±1394.00)
Ca [mg kg^{-1}]	24359.60 (±455.57)	39922.78 (±679.37)	7056.24 (±259.88)	2845.46 (±120.46)	2110.53 (±137.45)	192384.87 (±5803.71)
Cd [mg kg^{-1}]	0.00 (±0.00)	0.03 (±0.02)	0.01 (±0.02)	0.06 (±0.01)	0.00 (±0.00)	4.63 (±2.10)
Co [mg kg^{-1}]	0.00 (±0.00)	1.52 (±0.29)	1.33 (±0.29)	0.53 (±0.09)	0.56 (±0.10)	31.54 (±2.85)
Cr [mg kg^{-1}]	0.58 (±0.10)	10.28 (±0.78)	9.17 (±0.27)	2.43 (±0.17)	10.66 (±0.40)	575.35 (±121.40)
Cu [mg kg^{-1}]	1.07 (±0.09)	63.25 (±7.41)	100.39 (±18.18)	6.75 (±3.57)	219.23 (±123.36)	1025.48 (±633.89)
Fe [mg kg^{-1}]	13.13 (±4.01)	381.41 (±134.10)	1302.67 (±300.51)	1675.86 (±208.04)	58.36 (±16.48)	77997.02 (±23219.46)
K [mg kg^{-1}]	315.96 (±15.01)	168.46 (±10.75)	216.93 (±13.58)	78.17 (±0.93)	136.44 (±12.78)	7245.04 (±521.31)
Mg [mg kg^{-1}]	0.00 (±0.00)	4200.16 (±227.32)	1184.98 (±35.86)	392.66 (±47.55)	198.51 (±16.30)	15566.75 (±380.77)
Mn [mg kg^{-1}]	1.36 (±0.30)	146.67 (±7.86)	94.89 (±5.95)	37.91 (±1.54)	26.02 (±2.20)	1809.59 (±337.00)
Mo [mg kg^{-1}]	4.41 (±0.16)	0.77 (±0.29)	0.03 (±0.05)	0.30 (±0.09)	5.97 (±0.90)	92.02 (±26.09)
Na [mg kg^{-1}]	1012.07 (±52.25)	592.37 (±45.71)	456.55 (±17.39)	235.87 (±8.98)	742.16 (±25.15)	17457.07 (±1409.00)

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Table A1. continued

	water extractable	acid extractable (step I)	acid extractable (step II)	extractable under reducing conditions	extractable under oxidizing conditions	total
Ni [mg kg^{-1}]	0.00 (±0.01)	9.41 (±2.76)	8.82 (±3.16)	7.63 (±1.14)	9.12 (±0.88)	227.75 (±29.92)
P [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	25.56 (±26.05)	1318.71 (±110.80)
Pb [mg kg^{-1}]	132.32 (±71.55)	200.10 (±181.97)	234.97 (±200.40)	79.46 (±50.35)	19.69 (±4.48)	1135.61 (±364.36)
Sb [mg kg^{-1}]	0.02 (±0.03)	1.51 (±0.46)	0.58 (±0.22)	0.48 (±0.13)	0.68 (±0.23)	18.93 (±0.34)
Se [mg kg^{-1}]	0.10 (±0.02)	0.02 (±0.02)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)
Sr [mg kg^{-1}]	23.39 (±0.66)	81.28 (±0.83)	35.24 (±0.91)	12.04 (±0.79)	9.02 (±0.59)	391.77 (±27.27)
Ti [mg kg^{-1}]	0.00 (±0.00)	3.53 (±0.62)	7.65 (±0.99)	5.63 (±0.61)	51.77 (±6.34)	5552.62 (±438.41)
V [mg kg^{-1}]	0.01 (±0.01)	0.26 (±0.06)	0.26 (±0.03)	3.11 (±0.16)	2.39 (±0.21)	46.86 (±15.96)
Zn [mg kg^{-1}]	9.93 (±1.67)	3139.05 (±202.79)	812.13 (±342.38)	81.19 (±8.13)	44.50 (±26.26)	4889.21 (±3172.87)
			Grate Ash 0.5−0.05 mm			
pH	12.51 (±0.00)	7.16 (±0.30)	4.36 (±0.04)	4.26 (±0.05)	6.75 (±0.02)	
Al [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	1036.75 (±129.92)	247.91 (±38.81)	77.64 (±20.68)	19667.81 (±1117.79)
As [mg kg^{-1}]	0.00 (±0.01)	0.30 (±0.06)	0.35 (±0.02)	0.21 (±0.01)	0.00 (±0.00)	18.33 (±3.93)
B [mg kg^{-1}]	0.25 (±0.11)	52.93 (±1.96)	18.87 (±1.33)	5.17 (±0.34)	3.07 (±0.89)	196.34 (±13.88)
Ba [mg kg^{-1}]	48.75 (±1.04)	36.37 (±0.93)	231.26 (±19.64)	271.59 (±17.94)	55.90 (±9.37)	3685.37 (±311.90)
Ca [mg kg^{-1}]	26951.42 (±641.80)	36355.39 (±860.37)	13744.30 (±1043.26)	4679.71 (±441.34)	2110.53 (±137.45)	230842.47 (±13836.25)
Cd [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.06 (±0.01)	0.06 (±0.00)	0.00 (±0.00)	2.39 (±0.28)
Co [mg kg^{-1}]	0.00 (±0.00)	0.87 (±0.15)	2.57 (±0.17)	0.85 (±0.09)	0.56 (±0.10)	35.91 (±4.72)
Cr [mg kg^{-1}]	0.79 (±0.11)	1.41 (±0.30)	19.32 (±0.73)	2.86 (±0.14)	10.66 (±0.40)	554.69 (±45.83)
Cu [mg kg^{-1}]	0.89 (±0.42)	6.00 (±2.05)	134.51 (±7.84)	1.86 (±0.13)	219.23 (±123.36)	713.93 (±84.39)
Fe [mg kg^{-1}]	9.38 (±3.43)	32.54 (±8.23)	730.04 (±151.57)	2289.21 (±180.76)	58.36 (±16.48)	53306.12 (±3008.67)
K [mg kg^{-1}]	438.45 (±15.66)	153.74 (±5.43)	452.24 (±21.52)	147.15 (±5.95)	136.44 (±12.78)	8345.15 (±589.93)
Mg [mg kg^{-1}]	0.00 (±0.00)	5054.83 (±223.57)	3680.17 (±267.01)	663.79 (±72.24)	198.51 (±16.30)	20167.72 (±1326.69)
Mn [mg kg^{-1}]	1.03 (±0.42)	130.61 (±17.37)	252.87 (±16.46)	87.49 (±12.32)	26.02 (±2.20)	1819.22 (±73.69)
Mo [mg kg^{-1}]	5.89 (±0.36)	5.45 (±1.12)	0.10 (±0.04)	0.11 (±0.03)	5.97 (±0.90)	75.26 (±4.71)
Na [mg kg^{-1}]	1421.12 (±48.78)	477.19 (±19.74)	691.59 (±28.91)	343.73 (±4.03)	742.16 (±25.15)	18657.94 (±1267.76)
Ni [mg kg^{-1}]	0.02 (±0.03)	3.85 (±0.61)	16.25 (±2.16)	10.56 (±1.09)	9.12 (±0.88)	258.28 (±73.72)
P [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	25.56 (±26.05)	2039.01 (±19.12)
Pb [mg kg^{-1}]	223.08 (±83.74)	11.72 (±4.83)	458.18 (±138.64)	180.34 (±40.83)	19.69 (±4.48)	1885.10 (±1087.70)
Sb [mg kg^{-1}]	0.01 (±0.01)	3.69 (±0.49)	1.38 (±0.23)	0.75 (±0.32)	0.68 (±0.23)	38.98 (±20.19)
Se [mg kg^{-1}]	0.13 (±0.02)	0.08 (±0.01)	0.01 (±0.01)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)
Sr [mg kg^{-1}]	30.69 (±1.30)	108.52 (±1.43)	74.12 (±2.65)	25.65 (±0.72)	9.02 (±0.59)	512.44 (±35.04)
Ti [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	12.51 (±3.93)	2.60 (±0.29)	51.77 (±6.34)	6954.49 (±251.51)
V [mg kg^{-1}]	0.00 (±0.01)	0.26 (±0.03)	0.42 (±0.14)	4.61 (±0.32)	2.39 (±0.21)	44.47 (±3.22)
Zn [mg kg^{-1}]	7.92 (±2.11)	271.92 (±164.83)	1206.76 (±273.67)	115.25 (±32.84)	71.50 (±26.26)	3810.38 (±2684.07)
			Grate Ash < 0.05 mm			
pH	12.51 (±0.00)	9.01 (±0.83)	4.71 (±0.15)	4.01 (±0.15)	6.65 (±0.05)	
Al [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	904.55 (±370.45)	798.22 (±571.68)	365.01 (±54.62)	10257.28 (±114.02)
As [mg kg^{-1}]	0.02 (±0.02)	1.02 (±0.56)	0.42 (±0.09)	0.57 (±0.31)	0.00 (±0.00)	21.94 (±0.32)
B [mg kg^{-1}]	0.74 (±0.04)	122.54 (±22.22)	59.23 (±18.84)	8.40 (±4.95)	3.66 (±1.34)	198.12 (±2.14)
Ba [mg kg^{-1}]	82.98 (±4.07)	77.87 (±11.42)	180.24 (±29.90)	274.46 (±156.10)	95.97 (±19.96)	2079.04 (±11.48)
Ca [mg kg^{-1}]	55251.59 (±1688.19)	75293.91 (±3489.91)	72922.03 (±4500.26)	5535.59 (±3254.79)	3193.98 (±534.04)	239831.54 (±2013.11)
Cd [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.28 (±0.01)	0.09 (±0.05)	0.00 (±0.00)	1.11 (±0.17)

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Table A1. continued

	water extractable	acid extractable (step I)	acid extractable (step II)	extractable under reducing conditions	extractable under oxidizing conditions	total
Co [mg kg^{-1}]	0.00 (±0.00)	0.07 (±0.08)	4.94 (±0.24)	1.05 (±0.61)	0.86 (±0.12)	16.70 (±0.21)
Cr [mg kg^{-1}]	2.60 (±0.06)	7.51 (±2.02)	41.09 (±12.05)	12.66 (±7.86)	84.54 (±2.75)	376.87 (±6.90)
Cu [mg kg^{-1}]	1.35 (±0.13)	1.89 (±0.10)	301.99 (±65.41)	3.69 (±2.15)	215.55 (±25.49)	689.19 (±15.63)
Fe [mg kg^{-1}]	13.99 (±3.64)	24.76 (±2.39)	234.68 (±83.67)	3926.34 (±447.74)	207.27 (±20.85)	19755.56 (±176.31)
K [mg kg^{-1}]	1287.40 (±17.70)	245.44 (±12.82)	426.18 (±31.15)	174.39 (±100.71)	306.48 (±91.72)	4353.56 (±19.23)
Mg [mg kg^{-1}]	0.00 (±0.00)	6029.08 (±3055.64)	11297.75 (±672.24)	987.65 (±678.20)	479.13 (±247.78)	19296.99 (±282.32)
Mn [mg kg^{-1}]	1.62 (±0.21)	24.71 (±20.78)	546.86 (±17.86)	291.20 (±14.66)	71.20 (±15.77)	1141.38 (±17.75)
Mo [mg kg^{-1}]	13.65 (±0.33)	15.58 (±1.65)	0.77 (±0.43)	0.19 (±0.11)	6.62 (±0.33)	55.26 (±0.70)
Na [mg kg^{-1}]	3904.50 (±35.02)	569.82 (±66.70)	864.09 (±28.48)	402.85 (±234.33)	1479.36 (±120.69)	11663.16 (±331.25)
Ni [mg kg^{-1}]	0.02 (±0.03)	1.33 (±1.00)	19.49 (±0.22)	11.30 (±6.63)	13.97 (±1.41)	111.54 (±4.23)
P [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	30.84 (±53.41)	1205.20 (±13.90)
Pb [mg kg^{-1}]	245.26 (±9.52)	5.75 (±0.92)	444.18 (±64.59)	319.07 (±185.47)	181.53 (±37.52)	1805.96 (±20.76)
Sb [mg kg^{-1}]	0.00 (±0.00)	8.91 (±2.02)	2.45 (±1.03)	1.02 (±0.64)	1.63 (±0.30)	34.48 (±1.72)
Se [mg kg^{-1}]	0.23 (±0.05)	0.00 (±0.00)	0.45 (±0.03)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)
Sr [mg kg^{-1}]	79.58 (±1.24)	217.45 (±10.34)	128.36 (±2.19)	45.40 (±26.18)	18.04 (±2.84)	488.97 (±6.58)
Ti [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	6.33 (±3.02)	3.20 (±1.90)	95.05 (±20.28)	3386.25 (±36.59)
V [mg kg^{-1}]	0.00 (±0.00)	0.98 (±0.22)	0.79 (±0.12)	5.64 (±3.16)	6.62 (±0.60)	22.82 (±0.71)
Zn [mg kg^{-1}]	10.23 (±0.24)	4.04 (±0.69)	1381.81 (±101.93)	138.19 (±29.13)	68.33 (±22.73)	1511.47 (±22.69)
			Cyclone Ash			
pH	12.36 (±0.01)	5.24 (±0.06)	4.22 (±0.03)	4.08 (±0.06)	6.54 (±0.02)	
Al [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	1549.53 (±87.30)	559.26 (±23.21)	180.70 (±7.75)	29737.97 (±2373.91)
As [mg kg^{-1}]	0.25 (±0.05)	3.08 (±0.28)	0.79 (±0.07)	0.72 (±0.03)	0.00 (±0.00)	37.44 (±2.68)
B [mg kg^{-1}]	17.66 (±0.83)	157.38 (±3.68)	40.42 (±3.97)	12.54 (±1.20)	7.30 (±0.55)	410.94 (±19.54)
Ba [mg kg^{-1}]	1.16 (±0.75)	8.08 (±1.69)	53.99 (±13.98)	339.92 (±53.19)	109.58 (±9.91)	4864.42 (±271.34)
Ca [mg kg^{-1}]	23256.38 (±1455.10)	26152.85 (±1162.76)	16867.28 (±1421.40)	4836.18 (±517.71)	5158.66 (±377.98)	168756.16 (±9631.15)
Cd [mg kg^{-1}]	0.06 (±0.03)	8.41 (±0.88)	3.31 (±0.25)	1.44 (±0.48)	0.71 (±0.04)	20.31 (±3.46)
Co [mg kg^{-1}]	0.00 (±0.00)	3.90 (±0.37)	2.24 (±0.08)	1.19 (±0.06)	1.13 (±0.07)	47.68 (±5.00)
Cr [mg kg^{-1}]	10.16 (±1.00)	2.90 (±0.88)	7.62 (±0.43)	3.93 (±0.09)	29.76 (±1.56)	694.23 (±27.53)
Cu [mg kg^{-1}]	0.69 (±0.17)	8.63 (±1.99)	54.20 (±2.32)	4.04 (±0.30)	55.37 (±4.76)	477.48 (±33.80)
Fe [mg kg^{-1}]	19.71 (±5.35)	22.15 (±15.02)	160.96 (±3.97)	1209.78 (±74.69)	61.63 (±1.98)	65758.09 (±3265.02)
K [mg kg^{-1}]	7860.01 (±1743.06)	1650.58 (±334.39)	508.64 (±55.44)	150.65 (±6.43)	398.40 (±51.14)	17149.32 (±2228.21)
Mg [mg kg^{-1}]	0.00 (±0.00)	7317.99 (±443.50)	2307.22 (±161.67)	630.50 (±65.84)	628.12 (±63.64)	22095.62 (±1480.31)
Mn [mg kg^{-1}]	2.93 (±0.77)	277.58 (±15.80)	233.72 (±10.10)	243.11 (±4.90)	115.29 (±10.42)	3075.96 (±214.56)
Mo [mg kg^{-1}]	15.86 (±0.82)	2.26 (±0.47)	0.67 (±0.07)	0.73 (±0.07)	11.09 (±0.34)	107.20 (±3.95)
Na [mg kg^{-1}]	4339.40 (±921.52)	1077.64 (±102.40)	912.31 (±46.65)	263.85 (±11.02)	918.65 (±51.88)	16591.37 (±1443.07)
Ni [mg kg^{-1}]	0.04 (±0.03)	15.90 (±1.23)	10.17 (±0.52)	7.84 (±0.82)	6.33 (±0.58)	277.16 (±9.23)
P [mg kg^{-1}]	0.11 (±0.03)	1.61 (±0.20)	0.26 (±0.05)	5.45 (±0.38)	10.31 (±0.51)	82.08 (±4.84)
Pb [mg kg^{-1}]	341.23 (±67.07)	30.80 (±4.65)	75.09 (±8.87)	72.97 (±7.06)	60.07 (±6.67)	2665.04 (±760.80)
Sb [mg kg^{-1}]	0.21 (±0.08)	7.46 (±0.18)	2.78 (±0.21)	1.93 (±0.11)	1.46 (±0.09)	61.17 (±6.02)
Se [mg kg^{-1}]	0.26 (±0.03)	0.42 (±0.02)	0.15 (±0.02)	0.06 (±0.04)	0.37 (±0.11)	0.00 (±0.00)
Sr [mg kg^{-1}]	53.93 (±4.45)	133.39 (±5.74)	61.20 (±3.70)	26.67 (±0.50)	23.64 (±1.57)	583.06 (±41.89)
Ti [mg kg^{-1}]	1.73 (±1.55)	0.10 (±0.18)	8.41 (±0.50)	5.60 (±0.28)	44.06 (±5.59)	7056.59 (±159.69)
V [mg kg^{-1}]	0.11 (±0.03)	1.61 (±0.20)	0.26 (±0.05)	5.45 (±0.38)	10.31 (±0.51)	82.08 (±4.84)

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Table A1. continued

	water extractable	acid extractable (step I)	acid extractable (step II)	extractable under reducing conditions	extractable under oxidizing conditions	total
Zn [mg kg^{-1}]	97.37 (±12.65)	3261.18 (±252.27)	1243.54 (±109.64)	242.79 (±18.05)	159.00 (±12.99)	7457.36 (±553.49)
				Filter Ash		
pH	12.41 (±0.00)	12.27 (±0.01)	7.27 (±0.42)	5.35 (±0.11)	6.73 (±0.08)	
Al [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	159.80 (±44.27)	63.19 (±9.50)	3111.97 (±52.68)
As [mg kg^{-1}]	0.25 (±0.05)	0.13 (±0.03)	0.14 (±0.11)	2.43 (±0.62)	15.49 (±1.93)	69.90 (±1.02)
B [mg kg^{-1}]	58.68 (±4.97)	33.81 (±4.32)	93.92 (±4.88)	38.25 (±4.54)	6.25 (±0.70)	236.51 (±4.13)
Ba [mg kg^{-1}]	0.87 (±0.08)	26.45 (±1.46)	7.57 (±1.24)	22.17 (±2.70)	19.11 (±0.63)	578.13 (±10.59)
Ca [mg kg^{-1}]	66381.11	92234.53	89726.56	15676.78	2774.77	266805.12 (±2293.61)
Cd [mg kg^{-1}]	0.21 (±0.02)	0.13 (±0.02)	28.75 (±16.39)	30.95 (±10.66)	4.35 (±1.40)	63.26 (±1.37)
Co [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.62 (±0.25)	1.46 (±0.15)	0.29 (±0.01)	5.56 (±0.11)
Cr [mg kg^{-1}]	5.48 (±0.72)	4.87 (±1.03)	0.98 (±0.68)	2.57 (±0.10)	20.81 (±1.25)	141.47 (±6.39)
Cu [mg kg^{-1}]	1.98 (±0.26)	1.84 (±0.09)	10.44 (±6.36)	192.58 (±7.24)	48.21 (±1.86)	335.69 (±4.38)
Fe [mg kg^{-1}]	2.98 (±1.02)	2.17 (±0.34)	4.21 (±3.03)	289.32 (±32.04)	4.18 (±1.31)	5232.87 (±85.02)
K [mg kg^{-1}]	17010.90 (±993.31)	749.39 (±96.48)	181.97 (±9.68)	174.82 (±33.62)	127.12 (±12.59)	21432.58 (±468.52)
Mg [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	1885.90 (±265.69)	2451.32 (±218.17)	240.59 (±24.80)	5575.76 (±136.73)
Mn [mg kg^{-1}]	0.91 (±0.26)	1.05 (±0.07)	158.96 (±75.09)	247.76 (±54.70)	40.48 (±0.72)	662.65 (±23.20)
Mo [mg kg^{-1}]	22.83 (±1.92)	0.00 (±0.00)	0.45 (±0.07)	0.42 (±0.09)	2.36 (±0.10)	48.85 (±0.43)
Na [mg kg^{-1}]	9917.93 (±581.76)	284.73 (±39.83)	141.00 (±6.22)	153.17 (±26.80)	528.53 (±37.52)	13963.52 (±354.17)
Ni [mg kg^{-1}]	0.00	35.99	0.14	0.41	0.12	36.66 (±0.38)
P [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.19 (±0.11)	4.01 (±0.19)	1.42 (±0.13)	6.62 (±0.19)
Pb [mg kg^{-1}]	493.85 (±39.68)	636.96 (±53.17)	21.85 (±10.11)	77.99 (±16.35)	491.18 (±24.19)	4944.90 (±94.84)
Sb [mg kg^{-1}]	0.53 (±0.12)	0.68 (±0.07)	18.47 (±5.13)	36.20 (±1.90)	17.47 (±1.38)	164.50 (±1.73)
Se [mg kg^{-1}]	0.43 (±0.04)	0.02 (±0.02)	0.22 (±0.08)	0.44 (±0.08)	0.01 (±0.02)	1.51 (±0.24)
Sr [mg kg^{-1}]	71.51 (±4.80)	39.95 (±1.52)	47.27 (±3.77)	45.29 (±4.63)	40.76 (±5.08)	286.41 (±3.31)
Ti [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	2.47 (±0.27)	1.91 (±0.18)	698.66 (±7.55)
V [mg kg^{-1}]	0.00 (±0.00)	0.00 (±0.00)	0.19 (±0.11)	4.01 (±0.19)	1.42 (±0.13)	6.62 (±0.19)
Zn [mg kg^{-1}]	153.61 (±18.05)	150.46 (±7.43)	8219.43 (±4946.97)	14878.51 (±2259.67)	2211.74 (±200.50)	29189.21 (±773.12)

[a]TEC [mg kg^{-1}], extractability in aqueous, acidic, reducing and oxidizing leaching agents [mg kg^{-1}] per element across grate ash particle size fractions, cyclone ash, and filter ash.

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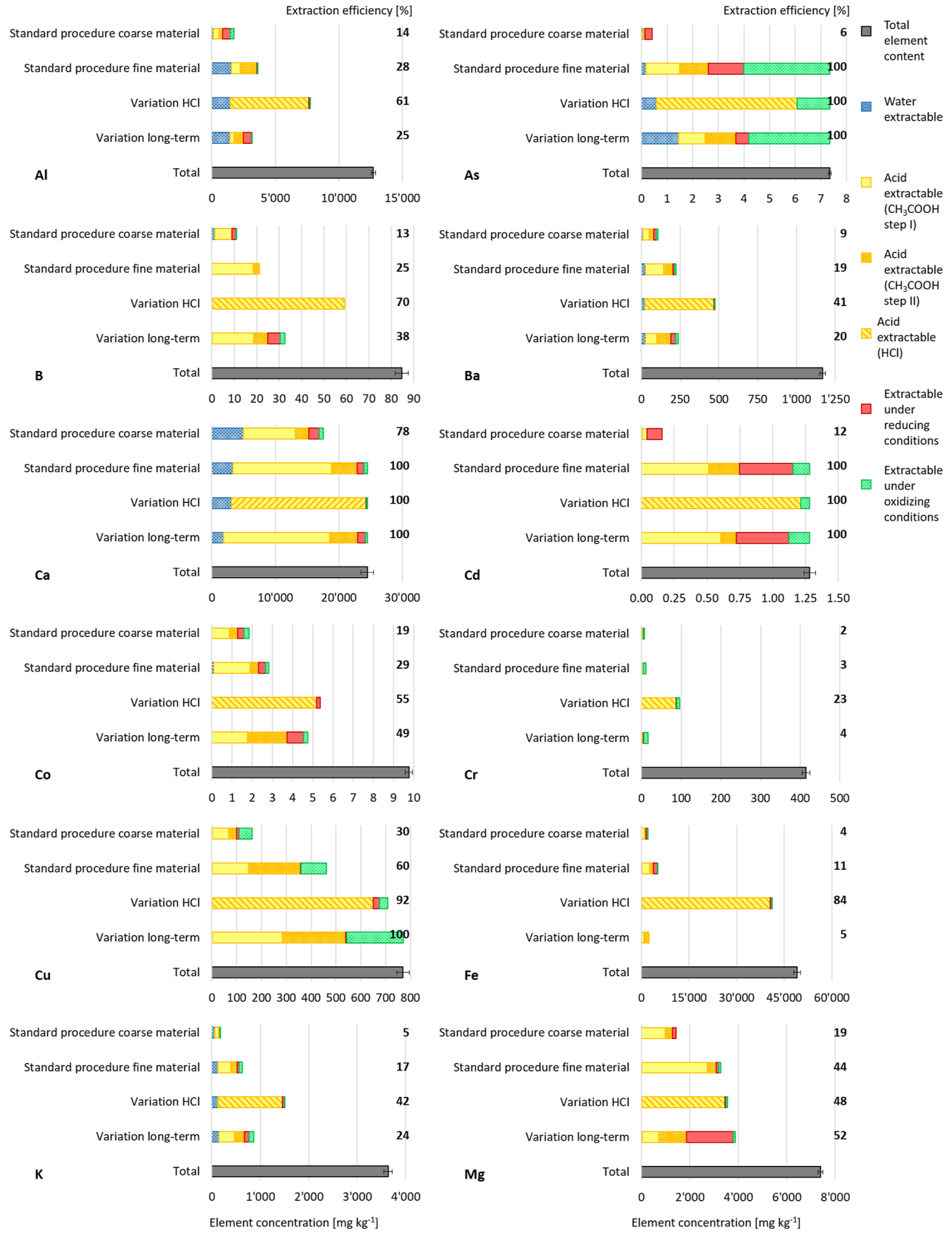

Figure 5. continued

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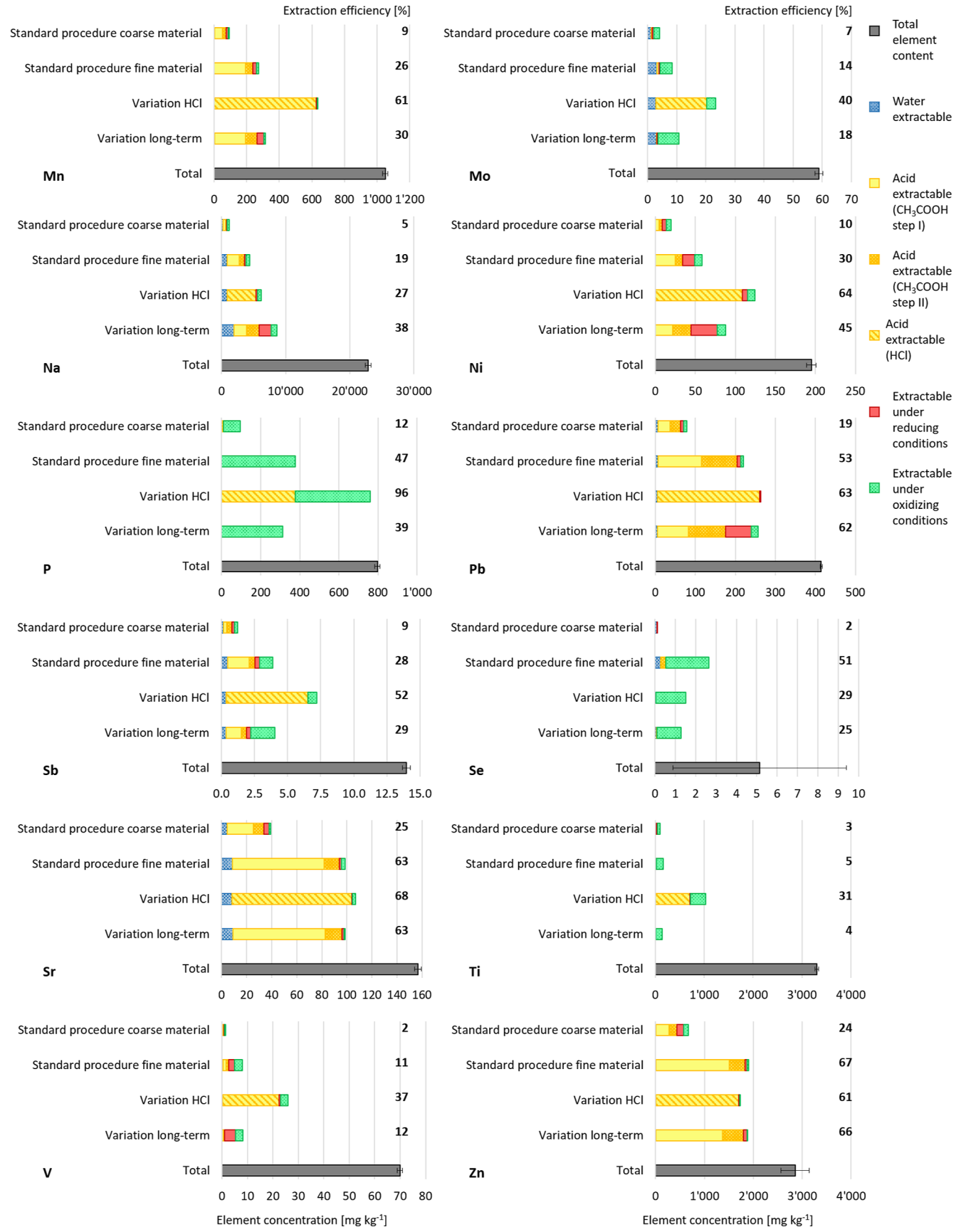

Figure 5. TEC [mg kg^{-1}]; extractability in water, acid, reducing and oxidizing leaching agents [mg kg^{-1}] for (I) the standard SE-procedure using coarse material, (II) the standard SE-procedure using fine milled material, (III) a modified SE-procedure using HCl instead of CH_3COOH as acidic leaching agent, (IV) a modified SE-procedure with extraction time of 1 week instead of 16 h; and EE [%] per element.

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$$EE_i = SF_{i,total}/TEC_i \quad (10)$$

2.4.2. Analysis of Variance. A single-factor analysis of variance (ANOVA) with Tukey posthoc test was performed (IBM SPSS Statistics for Windows, Version 29.0. Armonk, NY: IBM Corp.). The aim of the ANOVA was to test whether there is or is not a statistically significant difference between the EE (dependent variable) and (I) the factor grate ash grain size fraction, (II) the factor ash fraction (grate, cyclone, and filter ash), and the (III) factor element class (grouped according to element volatility), with the null hypothesis (H_0) that all population means are equal along the considered factor levels.

ANOVA tested the mean values for the EE of individual elements for significant differences. The significance level is defined as $p \leq 0.05$.

3. RESULTS AND DISCUSSION

3.1. Extraction Efficiency in Standard Sequential Extraction Procedure. Figure 4 shows the total content of 24 elements in six ash fractions, which differ according to place of origin (grate, cyclone, and filter ash) and grain size (grate ash fractionated in four size classes). Next to the total element concentrations, the leachable amount is presented, differentiated according to extraction conditions. The EE (value in %) is defined as the sum of the leached concentrations in relation to the total element concentration (eq 10). Actual values of element concentrations in extractants including the end pH values after extraction are listed in the appendix (Table A1).

The average EE across all elements ranged from 14.6% in grate ash >1 mm to 64% in filter ash. Within the grate ash particle size fractions, EE increased from 14.6−61% with decreasing particle sizes. The highest extraction efficiencies were found in filter ash and grate ash <0.05 mm. This is in line with ref 64 who also found higher solubility in smaller particle sizes.

Across all ash fractions, we found the plant macronutrients Ca, K, P, and Mg. Ca concentrations in grate ash increased with smaller particle sizes. Ca was predominantly soluble in water and acid−based leaching agents with extraction efficiencies ranging from 36−100%. As a result of the flue gas cleaning technology applied at the HPP providing the ash samples, the filter ash mainly consisted of the loaded sorbents coke and hydrated lime $Ca(OH)_2$, which are added upstream of the fabric filter. Therefore, no conclusions on the recovery of Ca originating from the fuel can be drawn.

Alkaline and alkaline earth metals Na, K, Mg, Sr, and Ba were present in concentrations up to 25,000 mg kg^{-1} with different distributions in the examined ash fractions.

EE of K and Na was highest in filter (85 respectively 79%) and cyclone ash (62 respectively 45%) with the majority soluble in water. Mg and Sr were fully extractable from grate ash <0.05 mm (EE approximately 100%) and showed high mobility in the other fractions. Mg and Sr from grate and cyclone ashes were mainly acid-soluble. Ba was the least mobile element within this group (EE 9−34%).

P was mainly contained in the grate ash (800−2000 mg kg^{-1}), but with low extractability under oxidizing conditions (1.3−12%). Higher extraction efficiencies were found in cyclones and filter ash, but these fractions showed only low total P concentrations.

The highest initial concentrations of Fe were found in the coarse to medium size fractions of grate ash and the cyclone ash (20,000−78,000 mg kg^{-1}). Fe concentrations were lower in the finest fraction of the grate ash (<20,000 mg kg^{-1}) and the filter ash (5000 mg kg^{-1}). Measured in terms of leachability, the general mobility of elements in most fractions was low (2−6%) with the exception of grate ash <0.05 mm (22%).

Plant micronutrients were present in all of the ash fractions. The highest concentrations were found in cyclone ash for Mn (3000 mg kg^{-1} in cyclone ash, 500−2000 mg kg^{-1} in other fractions), B (400 mg kg^{-1}, 100−250 mg kg^{-1}), Mo (110 mg kg^{-1}, 50−90 mg kg^{-1}), Co (50 mg kg^{-1}, 5−35 mg kg^{-1}). Only medium extraction efficiencies were achieved from cyclone ash (28% Mn, 18% Co, 29% Mo, 57% B). Grate ash <0.05 mm and filter ash showed higher element mobility, but due to smaller initial concentrations the total amount that could be recovered was smaller or comparable to cyclone ash.

Cu was contained predominantly in the grate ash (700−1000 mg kg^{-1}) and with lower concentrations in cyclone and filter ash (500 respectively 300 mg kg^{-1}). EE increased from 21 to 76% in cyclone and grate ash with decreasing particle size (acid and oxidizing solvents). From filter ash, 76% of Cu could be extracted, mainly under reducing conditions.

Metals were contained in a wide range of concentrations across the investigated ash fractions and showed very different mobility. Initial concentrations of As, Cd, Pb, Sb and Zn in the ash fractions can be described as filter ≫ cyclone > grate ash, with a decrease of concentrations in grate ash with increasing particle size. The extractability of these five elements was also highest in filter ash, but on different levels for each element. Summed up over all extraction steps, between 26% (As), 35% (Pb), 45% (Sb), 88% (Zn), and 100% (Cd) of the metal content in the filter ash was extractable. In the grate ash size fractions and the cyclone ash, EE ranged from 5 to 13% (As), 19−66% (Pb), 9−41% (Sb), 24−100% (Zn), and 2−69% (Cd). For Al, Cr, Ni, V and Ti, the initial concentration followed the pattern cyclone > grate > filter ash, within the grate ash the finest particles showed the lowest concentrations in contrast to the distribution observed for other elements. As for the before mentioned elements, EE for Ni and V was highest in filter ash (100 respectively 85%). Cyclone ash showed small to medium mobility (V 22%, Ni 15%, Cr 8%, Al 8%). Generally, EE in grate ash increased with decreasing particle size. The element with the lowest solubility was Ti, of which only 1−3% could be extracted.

3.2. Parameter Studies during Extraction. Figure 5 shows the TEC of 24 elements in grate ash fraction >1 mm as shown in chapter 3.1. In addition to the total element concentrations, the leachable amounts under varying extraction parameters is presented. Next to the reference variant (standard SE procedure carried out with coarse, untreated material), three variants were investigated. First, the influence of reducing the particle size through crushing the material (standard SE procedure carried out with finely milled material), second the influence of the acid leaching agent (CH_3COOH vs HCl), and third, the influence of the reaction time (overnight vs 1 week). The EE (value in %) is defined as the sum of the leached concentrations in relation to the total element concentration.

The average EE across all elements was 13.8% in the reference variant (standard procedure with coarse material). All parameter variations led to an increased EE, ranging from 39.6% (standard procedure with fine material), 43.6% (long-term) to 60.2% (HCl). Varying the acid solvent had the greatest effect, quadrupling the EE compared to the reference (average across all elements). Especially the transition metals

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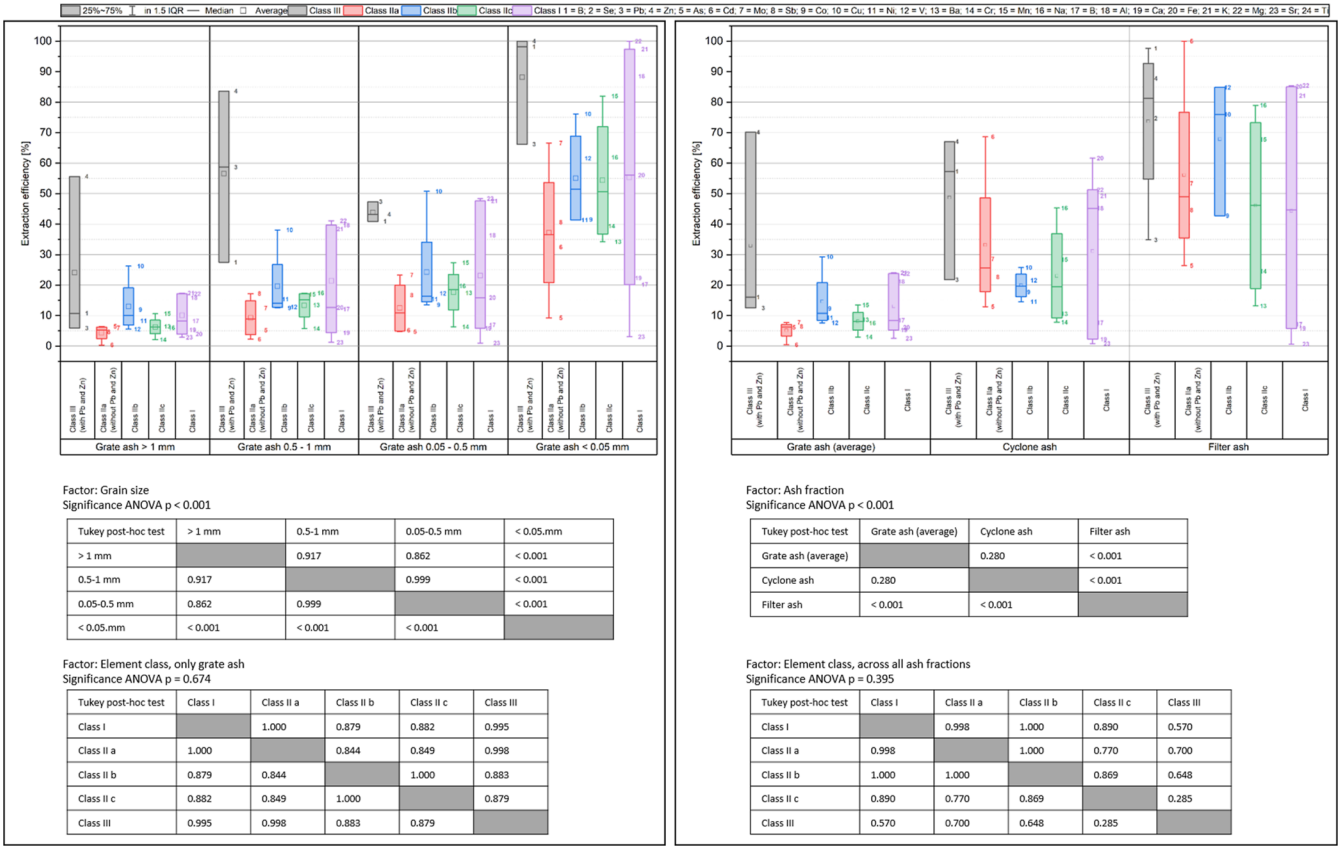

Factor: Grain size
Significance ANOVA p < 0.001

Tukey post-hoc test	> 1 mm	0.5-1 mm	0.05-0.5 mm	< 0.05 mm
> 1 mm		0.917	0.862	< 0.001
0.5-1 mm	0.917		0.999	< 0.001
0.05-0.5 mm	0.862	0.999		< 0.001
< 0.05 mm	< 0.001	< 0.001	< 0.001	

Factor: Ash fraction
Significance ANOVA p < 0.001

Tukey post-hoc test	Grate ash (average)	Cyclone ash	Filter ash
Grate ash (average)		0.280	< 0.001
Cyclone ash	0.280		< 0.001
Filter ash	< 0.001	< 0.001	

Factor: Element class, only grate ash
Significance ANOVA p = 0.674

Tukey post-hoc test	Class I	Class II a	Class II b	Class II c	Class III
Class I		1.000	0.879	0.882	0.995
Class II a	1.000		0.844	0.849	0.998
Class II b	0.879	0.844		1.000	0.883
Class II c	0.882	0.849	1.000		0.879
Class III	0.995	0.998	0.883	0.879	

Factor: Element class, across all ash fractions
Significance ANOVA p = 0.395

Tukey post-hoc test	Class I	Class II a	Class II b	Class II c	Class III
Class I		0.998	1.000	0.890	0.570
Class II a	0.998		1.000	0.770	0.700
Class II b	1.000	1.000		0.869	0.648
Class II c	0.890	0.770	0.869		0.285
Class III	0.570	0.700	0.648	0.285	

Figure 6. EE [%] per element volatility class across grate ash grain size fractions <0.5 mm to >1 mm (left) and ash fractions from grate, cyclone, and filter (right). Boxplots with 25% and 75% quantiles (box). Outliers were determined by ref 74 interquartile range (IQR), with outliers at 1.5 IQR (whisker). Test results from ANOVA and Tukey-honestly significant difference [honestly significant difference (HSD)] posthoc test for the factors considered.

Ti, V, Cr, Mn, Fe and Mo were extracted with the HCl solvent. Crushing of the material seems to be a promising method to easily increase the extractability of elements from the grate ash. In the standard procedure carried out with fine (milled) material, the element mobility increased by a factor of 2.9 compared to unprocessed (coarse) material.

The additional increase in reaction time (variant long-term) resulted only in a slight increase in EE by a factor of 3.2 compared to the unprocessed material. However, this varied between different elements. Higher shares were mobilized with the increase in extraction time compared to the standard procedure with fine material for Na (37.6% vs 19.3%), Co (48.7% vs 29.0%), Ni (45.1% vs 30.1%), and Cu (100% vs 60.0%). The leachability of these elements in the long term variant was comparable to or even higher than that in the HCl variant.

The highest increase in EE through parameter variations was found for P. In the standard procedure with coarse material, P leachability was relatively low. From fine material, more P could be extracted under oxidizing conditions (47.2% vs 11.9%). With HCl as an acidic solvent, the acid-soluble fraction could be mobilized in addition to the oxidizable fraction. This achieved an overall EE of 99.5%.

3.3. EE per Element Volatility Class. Figure 6 shows on the right the range of element EE for three ash fractions (bottom ash, cyclone ash, and filter ash) and on the left side various particle sizes within the bottom ash, differentiated according to element volatility class. First, the already described trend is evident that the leachability of elements increases for finer ash fractions.

The comparison of the grain size fractions from grate ash shows an increase in EE from coarser to finer particle sizes across all element volatility classes. The differences in EE mean values between grain size fractions are statistically highly significant ($p < 0.001$). However, the Tukey posthoc test shows that only the finest particle size fraction (<0.05 mm) shows this highly significant difference ($p < 0.001$) compared to the other three particle size fractions. A comparison of the values for grain size fractions >1 mm, 0.5−1 mm and 0.05−0.5 mm shows no significant difference according to Tukey HSD.

The comparison of the three ash fractions downstream the plant shows an increase in EE from grate ash < cyclone ash < filter ash across all element volatility classes. The differences in EE mean values between ash fractions are statistically highly significant ($p < 0.001$). However, also here the Tukey posthoc test shows the highest significant difference ($p < 0.001$) in EE only for filter ash against the other two fractions. Comparing the EE values for ashes from the cyclone and the grate (average) shows no significant difference according to Tukey HSD.

For all ash fractions and grain sizes, Class III elements showed the greatest solubility. Mean values for the total SF of elements ranged from 24% (>1 mm), 57% (0.5−1 mm), 44% (0.05−0.5 mm), to 88% (<0.05 mm) in grate ash, and from 33% (grate ash average), 49% (cyclone ash), to 74% (filter ash). The lowest solubility was found for class II a elements in grate ash, II b elements in cyclone ash and class I elements in

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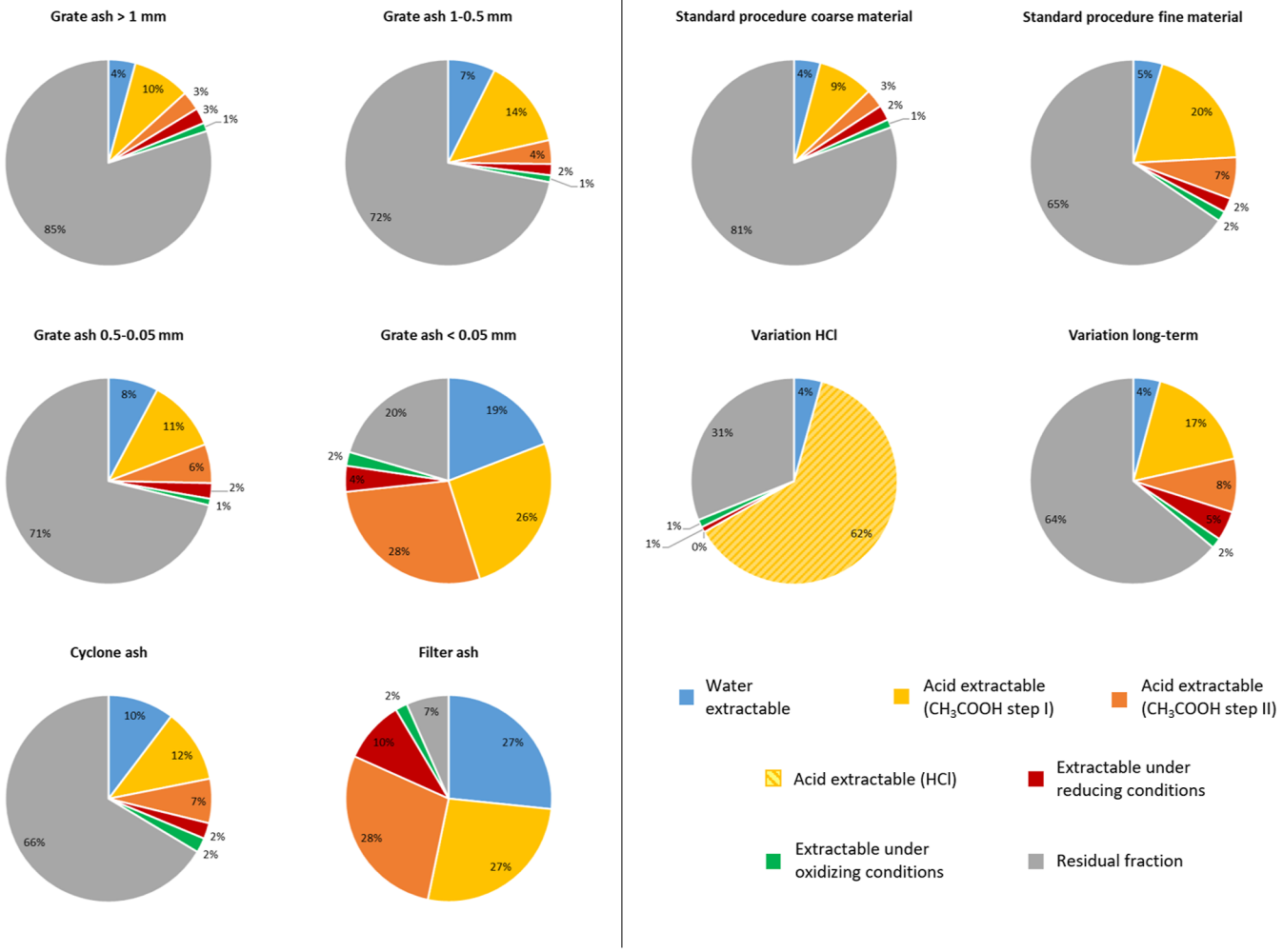

Figure 7. Total proportion of all 24 analyzed elements under each extraction condition and in the residual fractions relative to the initial element content in each ash fraction in the standard SE procedure (left) and in parameter studies (right).

filter ash. However, a comparison of the EE values of elements grouped in individual volatility classes showed no statistically significant difference with regard to element leachability depending on element volatility class. This applies both to the extraction efficiencies within grate, cyclone, and filter ash fractions ($p = 0.395$) and within grate ash particle size fractions ($p = 0.674$). Therefore, the null hypothesis (H_0) that there are no statistically significant differences in EE depending on the element volatility class cannot be rejected. The Tukey HSD test shows varying values between different volatility classes but none of them significant.

However, it should be critically noted that the sample size in the ANOVA is very small at $n = 5$. The data set for the comparison of EE depending on element volatility contains 92 values (4 grain size fractions × 23 elements) and 69 values (3 ash fractions × 23 elements). This may also be a reason so few significant differences were found.

3.4. Material Flows in the Extraction Procedure. To summarize the results, Figure 7 shows the proportions of elements dissolved in the extractants and remaining in the RF relative to the initial element content in the untreated ash. In the standard SE process (Figure 7 on the left), the proportion of insoluble elements (RF) decreases with decreasing grain sizes within the grate ash. The solubility of elements from cyclone ash is comparable to grate ash grain size fractions 1–0.05 mm. The highest element solubilities and therefore the lowest element proportions in the RF are found in grate ash grain size fraction <0.05 mm and filter ash. Most of the soluble elements could be extracted from all ash and grain size fractions with acid (CH_3COOH). In the parameter studies, the element solubility was increased by crushing the material (variant fine material) and by increasing the extraction time (variant long-term). However, the effect was only moderate, resulting in 65% and 64% of all elements in the RF compared to 81% in the reference variant (standard procedure coarse material). The variation of the acidic extraction agent (HCl instead of CH_3COOH) had the greatest effect, resulting in the lowest element content in the RF (31%) with only one acidic washing cycle.

Figure 8 shows the material flows during the standard SE procedure for grate ash, cyclone ash, and filter ash in Sankey diagrams. Elements are categorized as environmentally relevant metals (As, Pb, Cd, Cr, Ni, Cu, Zn) and plant nutrients (P, Ca, K, Fe, Mg, Na). On the input side, 100% ash enters the process. Its composition varies between the three ash fractions. The metal content increases from 2.7% in grate, 3.8% in cyclone to 42.9% in filter ash.

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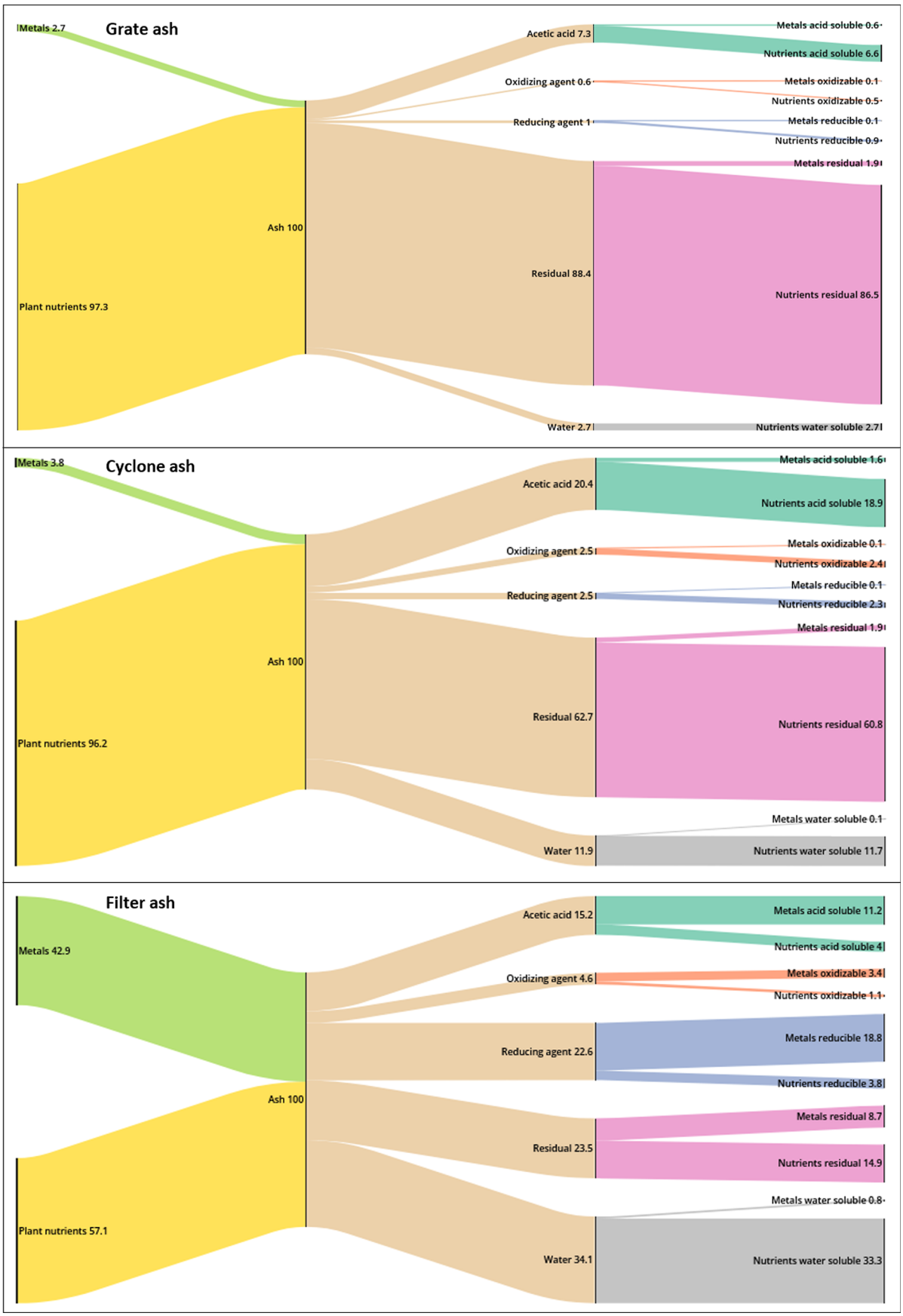

Figure 8. Sankey-diagram of the material flows in grate, cyclone, and filter ash during the SE. Elements are categorized as metals (As, Pb, Cd, Cr, Ni, Cu, Zn) and plant nutrients (P, Ca, K, Fe, Mg, Na). For the Filter ash, Ca was not considered since the content is distorted by the addition of the sorbent $Ca(OH)_2$.

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The RF of elements not soluble in the standard SE process decreased from 88.4% in grate, 62.7% in cyclone to 23.5% in filter ash. It can be concluded that element mobility is lowest in grate ash, medium in cyclone ash, and highest in filter ash. This can be explained by the formation of ash fractions during combustion and flue gas cleaning. Grate ash consists mainly of inorganic fuel components that remain after the organic fuel components have burned out. The elements contained therein, most of which are not very volatile, are still present in the mineral matrix, or have undergone mineral fragmentation processes. They are relatively difficult to remove from this matrix. Cyclone ash and filter ash consist of fine fly ash particles. After nucleation and coagulation, the predominantly volatile elements they contain are trapped in the particles or condense on the surface. Due to their formation history, they can be relatively easily dissolved or desorbed from these particles. In addition, the particle size, which decreases from the grate to filter ash fractions, provides a larger reaction surface and facilitates leaching.

The majority of soluble elements in the grate and cyclone ash were acid-soluble (7.3 respectively 20.4%), followed by water-soluble (2.7 respectively 11.9%). Only a small proportion was mobile under reducing (1 respectively 2.5%) or oxidizing (0.6 respectively 2.5%) conditions. This distribution is different in the filter ash. The majority of elements was water-soluble (34.1%), which indicates a high share of exchangeable elements that can easily be mobilized through hydratation mechanisms. Relatively high shares were mobile under acidic (15.2%) or reducing (22.6%) conditions, indicating that the elements are bound as acid-soluble carbonates or reducible oxides (mainly Fe- and Mn-oxides). Like in the other ash fractions, the smallest proportion of elements was mobile under oxidizing conditions (4.6%). On the output side, a high share of both plant nutrient elements and metals remained in the RF, which is considered as not environmentally mobile. For all three ash fractions, the nutrient/metal ratio in the output remained comparable to the ratio in the input. Thus, none of the two element categories has been predominantly leached out.

4. CONCLUSIONS

This study describes the solubility of 24 elements in wood ash in aqueous, acidic, reducing, and oxidizing extractants. A SE procedure according to an adapted BCR protocol was carried out, and extraction parameters (particle size, extraction time, and strength of acidic solvent) were varied.

The influence of particle size on element solubility in raw, untreated ash fractions separated with decreasing particle size downstream the plant and flue gas cleaning facilities (particle sizes in grate ash > cyclone ash > filter ash), as well as in raw vs manually crushed grate ash was determined. The results showed that finer ash fractions had both higher initial element concentrations and a tendency toward higher element mobility. This was true both for the particle size fractions within the grate ash and for the ash fractions downstream the plant (grate, cyclone, and filter ash). In terms of quantity, however, coarser ash fractions are particularly relevant.

The results showed a strong influence of the process parameters on element solubility. For all elements, solubility was increased by pretreating the ash by crushing, reducing particle size, and increasing surface area for the reaction with solvents. For some elements (Na, Co, Ni, and Cu), the solubility was increased by longer extraction times. The use of HCl as an acid solvent had the greatest effect on increasing the element solubility, quadrupling the EE compared with the reference for all elements.

Statistical evaluation showed highly significant differences in EE only for the finest ash fractions. This applied both for grate ash grain size fractions (>1 mm, 0.5−1 mm and 0.05−0.5 mm, <0.05 mm) and the ash fractions downstream the plant (grate ash < cyclone ash < filter ash). The concept of element volatility classes was used to investigate the relationship between element leachability and the specific behavior of elements during mineral phase transformation in combustion. The hypothesis that low volatile elements show a rather low leachability, and high volatile elements are easier to leach could not be statistically proven. However, it should be critically noted that the sample size in the ANOVA is very small ($n = 5$). This may also be a reason why so few significant differences were found.

From the substance flow analysis performed, it can be concluded that element mobility is lowest in grate ash, medium in cyclone ash, and highest in filter ash. For the grate and cyclone ash, a high proportion of both plant nutrient elements and metals remained in the RF. Most of the soluble elements in the grate and cyclone ash were acid-soluble, and a smaller amount was water-soluble. Only a small proportion was mobile under reducing or oxidizing conditions. This was different for filter ash with high proportions of elements that are readily mobilized under aqueous, acidic, or reducing conditions. No reliable separation of plant nutrients and metals could be achieved through the extraction process. For each extraction step, the leachates contained both groups of elements. Therefore, an important task for further research is to find ways to recover valuable elements from leachates while minimizing environmental risks by separating potential pollutants from plant nutrient elements.

APPENDIX

Actual values of element concentrations in extractants including the end pH values after extraction are listed in the appendix.

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Notes

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■ ABBREVIATIONS

EE	extraction efficiency
HPP	heat and power plant
MSWI	municipal solid waste incineration
RE	relative enrichment factor
SE	sequential extraction

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