Assessment of biomass ash applications in soil and cement mortars

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HIGHLIGHTS

- Assessing biomass ash use according to total and leaching based approaches.
- Consistent leaching pattern of elements despite variation in biomass ash content.
- Leaching approach provides a more realistic assessment of elements' availability.
- Soil and cement matrices control elements' release compared to biomass ash release.
- Current regulations would favour utilization of biomass ash in cement and not soil.

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ABSTRACT

The pH-dependent availability and leaching of major and trace elements was investigated for a wide range of biomass ash from different fuels and conversion technologies. A technical and environmental assessment of selected biomass ash for application in soil or cement mortars was performed, using both the total content and leaching of elements. A large variation in biomass ash composition, yet consistent pH dependent leaching patterns were observed for most elements and conversion technologies. Chromium showed a distinct behaviour which was hypothesized to reflect redox conditions during conversion of the biomass.

The leaching based approach was found to provide a more realistic assessment of the availability of desired (i.e. nutrients) and undesired elements (i.e. contaminants) in soil systems. When applied to a reference soil at a rate of 2% by weight, the selected biomass ash increased the concentration of particularly Cr, Mo and Zn in soil solution to a level of concern. For cement applications, the release of Ba, Cr and Mo can become of concern during the second life stage, but the release was not attributed to the included biomass ash.

Both soil and cement matrixes were found to control the release of elements such as Cu, V and Ni (soil) and As, Cr and Mo (cement) when compared to the released from pure biomass ash, underlining the importance of evaluating the availability and leaching of desired and undesired elements in the application scenario.

Given current regulatory criteria, beneficial utilization of biomass ash in cement may be more feasible than in soil, but regulatory criteria based on leaching rather than total content of elements may widen the application potential of biomass ash.

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1. Introduction

Thermal conversion of biomass is an established option to generate power and/or chemicals from renewable sources and to reduce fossil CO_2 emissions. Four thermochemical biomass conversion technologies have been developed: pyrolysis, gasification, direct combustion and liquefaction. The thermal conversion of

Acronym	
BA	Bottom Ash
FA	Fly Ash
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
BA_GAS	Bottom Ash from Gasification
FA_GAS	Fly Ash from Gasification
FA_COMB	Fly Ash from Combustion
OPC	Ordinary Portland Cement
SQD	Soil Quality Decree
MTR	Maximum Tolerable Risk
L/S	Liquid to Solid ratio

biomass results also in various residues that are commonly grouped into bottom ash (i.e. BA) and fly ash (i.e. FA). The basic difference between these two ash types is that BA is the fraction that is discharged from the combustion chamber whereas FA is entrained with the flue gas and recovered afterwards by flue gas cleaning techniques. Worldwide production of BA and FA from biomass combustion is currently estimated over 480 Mtons/year (Modolo et al., 2014; Vassilev et al., 2013). In the Netherlands, a scenario study has predicted a volume of ash from co-combustion and biomass stand-alone plants between 2 and 3 Mton/year in 2030 (Boersma, 2011). Although the technologies for biomass conversion are well developed and largely commercially available, limited research and development has been directed at the management and potential for beneficial utilization of the BA and FA residues (van Eijk et al., 2012). Feasible and acceptable waste management strategies for biomass ash need to be developed to contribute to the sustainability of energy production from biomass. The European Commission has initiated several actions towards a transition from a linear to a circular economy in which wastes are considered as potential resources, and reuse and recycling activities are favoured over disposal. Examples of these actions are the development of the End of Waste strategy (European Commission, 2011) and the revision of the European fertilizer regulation (European Commission, 2016). In the past years, studies have reported overviews on biomass ash properties as influenced by the type of thermal conversion and biomass composition (Obernberger et al., 2006, 1997; van Lith et al., 2006; Vassilev et al., 2014), and have also provided indications of potential bulk applications and reuse options for biomass ash residues. Two general categories have been identified as having the highest application potential for pure biomass ash: i) use in forestry and agricultural soils for fertilizing and liming purposes and ii) use in construction products, i.e. as secondary cementitious material, raw material for cement clinker production (Pels and Sarabèr, 2011; Siddique, 2012; van Eijk et al., 2012).

The practice of returning biomass ash to soil can preserve or restore the original level of nutrients and acid buffering capacity of soil, which are altered by intense harvesting of the biomass (Emilsson, 2006).

The category of building products includes direct utilization, e.g., in road construction, and utilization as raw material in the manufacturing of building products, e.g., as secondary cementitious material or filler in concrete and cement, or in lightweight aggregates. BA from grate combustion has been reported to be a suitable road building material and BA from fluidized bed an adequate sand substitute in construction and as a low quality filler material in concrete (Ribbing and Bjurström, 2011). Biomass FA has been shown to have binding properties or pozzolanic activity and can replace part of the clinker content in cement, and can thus contribute to reducing CO_2 emissions associated with traditional clinker production (Demis et al., 2014; Salvo et al., 2015; Siddique, 2012; Tosti et al., 2018).

Although biomass ash has a potential beneficial use in soil or construction products, this residue is still largely landfilled. This unsustainable practice is due to regulatory barriers as well as concerns about the potential leaching of contaminants to soil ecosystems. In order to facilitate the reuse of biomass ash, and thus the sustainability of biomass conversion, it is very important to assess the benefits and risks associated with its reuse.

The regulations and criteria for the utilization of biomass ash in forestry and agriculture or in construction vary between European countries. In Denmark, Finland and Austria national legislations are in force, whereas Sweden provides recommendations for utilization of biomass ash in forestry and agriculture (Emilsson, 2006). Both criteria and recommendations for utilization of biomass ash in soil are based on total content of elements in the biomass ash (Table 1).

The re-use of biomass ash as partial cement replacement material is not allowed by ASTM C 618 and CEN EN 450-1 that are the standards governing the use of FA as mineral admixtures in concrete. These two standards preclude the use of any material not derived from coal combustion, although biomass co-firing up to 20 wt% is allowed. The application in construction works (BMUB, 2015; Bodemkwaliteit, 2007) or final disposal in landfills (European Commission, 1999) is generally judged based on the emissions of contaminants from products by leaching processes. The Netherlands has a set of emission limit values for shaped and granular building materials which is included in the Soil Quality Decree (SQD) (Bodemkwaliteit, 2007). In short, this regulation specifies criteria for the (re-)use of mineral materials in construction applications. The SQD includes separate criteria for the use of shaped materials (e.g. bricks or concrete) and granular materials (e.g. steel slag or aggregates from construction and demolition waste). The latter category can be divided in so-called open applications (for relatively clean materials) or closed applications in which isolation measures need to be in place to limit contact with water (e.g. use of a liner system and monitoring requirements for the groundwater). The development of such limit values is based on the impact to soil and groundwater by leaching processes using human- and eco-toxicological limit values as reference. On the contrary, the application of biomass ash for forestry and agriculture purposes is judged based on the total content of elements.

In summary, an important concern regarding the application of biomass ashes in soil or in concrete is the potential enhanced leaching of contaminants. Research has shown that the total content of contaminants does not necessarily have a direct relation with the emission potential (leaching) in an application scenario (Kosson et al., 2002; van der Sloot, 2000). Nevertheless, there is very little information available in the current literature on biomass ash leaching properties and on the potential environmental risks associated with the most promising reuse options for biomass ash (Cruz et al., 2017; Freire et al., 2015; Maresca et al., 2017; van Eijk et al., 2012).

The overall aim of this study is to perform a technical and environmental assessment of biomass ash for application in soil and cement, on the basis of both the total content and the leaching of elements. The main differences and limitations of the two approaches will be discussed with the intent to increase the knowledge on biomass ash re-use options and identify ash properties that need consideration with regard to functional and environmentally safe recycling of this material.

Table 1
Nutrient and minor element limits based on total content according to Northern European countries, Austria and Canada, distinguishing applications in agriculture and forestry. Further information can be found in Emilsson (2006), Hannam et al. (2017, 2016), Stupak et al. (2008), Swedish Forest Agency (2002).

	Austria		Canada	Denmark	Finland		Sweden
	Forestry	Agriculture	Soil amendment	Agriculture& Forestry	Agriculture	Forestry	Forestry
Nutrients (minimum) (g/kg)							
Ca					80	60	125
Mg							15
K					20 (K + P)	10 (K + P)	30
P					20 (K + P)	10 (K + P)	7
Zn							0.5
Minor elements (maximum) (mg/kg)							
As			75		25	30	30
B							800
Cd	8	5	20	15	1.5	17.5	30
Cr	250	250	1060	100	300	300	100
Co			150				
Cu	250	250	2200		600	700	400
Pb	100	250	500	120	100	150	300
Hg			5	0.8	1	1	3
Mo			20				
Ni	100	100	180	30	100	150	70
Se			14				
V							70
Zn	1500	1000	1850		1500	4500	7000

2. Material and methods

2.1. Samples

A wide range of 21 different biomass ash samples were collected from different laboratory and pilot scale experiments, as well as from full scale installations. The samples included BA and FA originating from various biomass sources that were either converted using combustion or gasification technologies, operating at a range of conversion temperatures (400−1400 °C). A general description of the samples is given in Table S1 of the Supplementary Material. Four biomass FA samples (i.e. FA1, FA2, FA3 and FA4) were selected for further investigation of the re-use potential. Sample FA1 originated from a circulating fluidized bed installation that combusts a mixture of clean wood and various clean biomass feedstock like cacao husks or molasses. Sample FA1 was collected from the electrostatic precipitator. Sample FA2 originated from the combustion of wood pellets in a pulverized fuel installation and was collected from the electrostatic precipitator. Sample FA3 was sampled from a bubbling fluidized bed incinerator. The fuel consisted of a mixture with an equal share of recovered paper sludge from the de-inking step of the paper recycling process and recovered waste wood. The sample was collected from the electrostatic filter (90% by mass) and the textile bag filter (10% by mass) flue gas cleaning system. Sample FA4 was collected from a full-scale combined heat and power plant operating with a grate furnace. The fuel for this installation consisted of forest wood from thinning and clipping activities.

2.2. Total composition of biomass ash

Total composition of biomass ash samples (i.e. BA (n = 3) and FA (n = 19)) was performed by digestion in a Berghof bomb with concentrated HNO_3 (65%): HF (40%): $HClO_4$ (65%) in the proportion 5: 4.5: 0.5 by weight. About 0.1 g of sample was weighed and mixed with the acid mixture (10 g) and brought to a final volume of 50 mL by adding HNO_3 (0.1 M). The samples were digested in closed containers in an oven at 190 °C for 10 h, filtered and subsequently analysed with an Inductively Coupled Plasma - Atomic Emission Spectrometer ICP-AES (Varian Vista AX PRO CCD) for major and minor elements.

Total content of chloride was measured in selected samples by fusion with lithium metaborate. About 0.1−0.2 g of sample was mixed with 1 g of $LiBO_3$ and heated in the oven for 30 min at 1150 °C. The fused sample was subsequently dissolved in 1 M HNO_3 and analysed for chloride by ion-chromatography (Dionex IC25 ion-chromatograph with a Dionex AS18 column and a Dionex DS3 conductivity detector).

2.3. Batch pH-static leaching experiments

The biomass ash samples were equilibrated with water for 48 h at a specific pH value between pH 2 and 12 (including the natural pH of the sample that was not adjusted) according to the EN 14997 (2015). A quantity of 15 g of dry ash was suspended in 150 mL nanopure demineralised water (i.e. at a liquid to solid (L/S) ratio of 10 L/kg) in acid-cleaned 300 mL Polytetrafluoroethylene (PTFE) vessels, under continuous stirring at 20 °C. The suspensions were in contact with the atmosphere. The pH of the different suspensions was controlled using solutions of 1 M HNO_3 and NaOH (analytical grade) and a computerised pH-stat system. After the equilibration period, the suspensions were filtered through 0.45 μm membrane filters. Subsamples of the filtrates were acidified with concentrated HNO_3 (suprapure) and analysed by ICP-AES to obtain solution concentrations of a wide range of elements. It was assumed that total S and P as measured by ICP-AES (Varian Vista AX PRO CCD) represented SO_4^{2-} and PO_4^{3-}, respectively. A carbon analyser (Shimadzu TOC 5000a) was used to determine dissolved inorganic and organic carbon in non-acidified subsamples. Chloride was determined by ion chromatography (see above).

2.4. Soil amendment leaching experiment

The influence of biomass FA on the leaching properties of the ash/soil system was tested by mixing FA1 and FA4 at 0.2 and/or 2% by weight with the reference Euro-Soil 4 (Kuhnt and Muntau, 1994). This soil was sampled (0−30 cm depth after removal of vegetation) in Normandy (France) and classified as an Orthic Luvizol (Organic carbon: 1.36%; Clay: 20.3%; pH: 6.8). The Euro-Soil 4 composition is reported in Table S3. Samples FA1 and FA4 were

selected as representatives for biomass ashes complying (i.e. FA1) or not complying (i.e. FA4) with the Swedish guideline. Next, the amended soils were equilibrated at different pH values using the pH dependence leaching test, carried out in the same way as described in Section 2.3.

In this work, the biomass ash is supposed to be applied into soil all at once in order to reach the 0.2 or 2% percentages (i.e. 15 and 150 ton/ha, respectively). In reality, this is not the case and biomass ash is applied at different time intervals, rather than in a single application. In order to put the ash/soil mixture in perspective we considered a typical soil bulk density of 1500 kg/m^3 as an indicative value, a depth of 50 cm (with homogeneous mixing) and an ash dosage of maximum 3 ton/ha in 10 years (Haglund, 2008; Swedish Forest Agency, 2002). This can be a plausible scenario for agricultural use. When this scenario is considered, a 0.2% ash/soil mixture would be reached in 50 years, whereas the 2% mixture would represent an application period of 500 years. In forestry, the biomass ash is spread on top of soil and no ploughing is performed thus we considered that mixing of ash and soil would happen only in the very first layer of soil (i.e. 1 cm). If we assume the same soil density (i.e. 1500 kg/m^3) and ash dosage (3 ton/ha in 10 years), 1 cm depth would require 1 year to reach 0,2% ash/soil and 10 years to reach 2% ash/soil.

2.5. Cement applications

Cement mortar samples were prepared by dry mixing of Portland Cement CEM I 42.5N with biomass FA (i.e. FA1, FA2 and FA3) in accordance with the EN 196-1 (2005). The FA4 sample was excluded due to its very high K content that would lead to a poor cement quality. Ordinary Portland cement (OPC) was partly replaced with biomass FA at 20% and 40% by total binder weight. All specimens were prepared with a water-binder weight ratio (w/b) of 1:2 and a sand-binder ratio of 3:1. Rectangular blocks (160 × 40 × 40 mm) were casted and removed from the mould after 24 h of curing. Next, the casted blocks were cured for 28 days in a controlled temperature and humidity room (20 °C and 95% humidity). After 28 days of curing, the specimens were subjected to compressive strength (EN-196-1, 2005) and batch pH-static leaching tests (EN 14429, 2015) after grinding the material to < 1 mm size. These experiments with partial replacement of cement with biomass ash were performed, despite the fact that none of the ashes comply with the current EN 450-1 standard for the utilization of FA from co-combustion of coal with biomass as mineral admixtures in concrete. Currently, the use of biomass fuel in co-combustion of coal is limited to 20 wt%, while we are using 100% biomass ash. The biomass ashes FA1, FA2 and FA3 do also not comply with the technical requirements of EN 450-1 as described in more detail in Tosti et al. (2018). However, this previous study has shown that replacing 20 and 40% of traditional Portland cement with FA1 and FA3, as we have done here, produced cement mortars that comply with strength requirements of class 42.5 (20% replacement) and class 32.5 (40% replacement) after 28 days of curing (EN-196-1, 2005). In addition, the resulting mortars showed an acceptable environmental performance.

2.6. Comparison of total content and leaching of biomass ash with current quality criteria

The average total content of major and minor elements in BA and FA was compared with an average global soil composition (Mielke, 1979), in order to identify potentially beneficial or unfavourable effects of high or low element contents in biomass ash when used in applications that interact with soil. Next, the total content of individual elements in the ashes was compared with their maximum leachability in order to identify if any relation exists between the two different quantification approaches, and evaluate potential consequences when a regulatory approach based on total content is substituted by a leaching-based approach. The minimum requirements for nutrients and the limit values for contaminants in biomass ash according to the current legislations and recommendations are reported in Table 1. Values in Table 1 vary from country to country, as well as other properties (not listed in Table 1) such as fuel type, content of unburned matter, pH, conductivity, dosage etc. For further detail the reader is referred to Emilsson (2006), Haglund (2008), Ribbing and Bjurström (2011) and Stupak et al. (2008).

It is well known that the pH of materials has a major influence on the leaching of elements (Dijkstra et al., 2006; Kosson et al., 2014). Therefore, the pH dependency of the release from biomass ash was also investigated to evaluate the behaviour of these materials when exposed to different pH, and to identify general trends among ash types.

Finally, the technical and environmental performance of the two application scenarios (i.e. soil and cement) were assessed relative to the existing regulations and criteria. Particular attention was dedicated to the potential use of biomass ash in agriculture or forestry, since the lack of consistent regulations (i.e. contrary to construction products) has been identified among the main reasons that are currently preventing large-scale recycling of biomass ash as potentially functional soil amendments (Cruz et al., 2017; Riding et al., 2015).

3. Results and discussion

3.1. Composition of the biomass ash samples

Total composition of FA1, FA2, FA3 and FA4 samples together with MIN and MAX values for the three categories bottom ash from gasification (BA_GAS), Fly ash from gasification (FA_GAS) and fly ash from combustion (FA_COMB) is reported in Table 2. The biomass ashes showed a large variety in composition due to the different sources of the fuel, ash type and conversion technology.

The most abundant element was Ca with a content of 10^5–10^6 mg/kg dry ash. The content of plant nutrient K was between 10^4 – 10^6 mg/kg dry ash with no observed distinction among biomass ash categories. The Phosphorous content showed the highest value in the FA_COMB category. The content of Cl showed a large variation (10^2–10^6 mg/kg dry ash) with a high content in the FA_COMB category as already observed for P. Concerning the content of trace elements, no clear distinction was observed between biomass ash categories, with the exception of Cd that was generally enriched in biomass FA samples. These findings were consistent with other wood ash studies (Freire et al., 2015; Maresca et al., 2017; Vassilev et al., 2010). Mineralogical analysis of the crystalline phases showed that FA samples consists mainly of lime (CaO), Quartz (SiO$_2$), Portlandite (Ca(OH)$_2$) and Arcanite (K$_2$SO$_4$). Calcium silicate and Gehlenite were also present in FA3 samples (Carr, 2019) (see Supplementary Material Fig. S1).

3.2. Comparison of total composition of biomass ash and soil

Fig. 1 shows a double log plot of the average weight percentages for elements in natural soil (data taken from Kirby and Rimstidt (1993) based on a globally averaged dataset for soil composition as reported in Mielke (1979)) versus the average weight percentage in biomass BA (n = 3) and FA (n = 18) samples. Fig. 1 gives a preliminary indication of the content of elements that is generally higher in biomass ash than in average soil. This assessment is important because the applications of biomass ash could result in a

Table 2
Total composition of FA1, FA2, FA3 and FA4 samples together with MIN and MAX values for the three categories Bottom ash from gasification (BA_GAS), Fly ash from gasification (FA_GAS) and Fly ash from combustion (FA_COMB). All values are expressed in mg/kg of dry ash. Between brackets the number of samples in each category. Full dataset is reported in the Supplementary Material Table S2.

	FA1	FA2	FA3	FA4	BA_GAS (n = 3)		FA_GAS (n = 9)		FA_COMB (n = 9)	
					MIN	MAX	MIN	MAX	MIN	MAX
pH[a]	12.8	12.9	12.7	10.3	10.3	12.2	10.3	12.7	10.7	12.8
As	12.0	<6.80	88.0	113	0.843	55.3	0.062	93.0	6.80	113
Ba	669	1771	831	38.9	97.3	1426	91.6	3647	38.9	1771
Ca	190,361	197,209	402,533	24,602	16,644	31,945	10,941	87,932	24,602	402,533
Cd	22.9	7.97	3.02	40.1	0.183	0.208	0.071	7.51	0.100	40.1
Cl	6563	8217	2995	124,898	950	15,925	645	18,684	2995	124,898
Co	7.9	13.5	10.9	1.60	2.36	11.0	1.96	20.1	1.60	15.4
Cr	69.8	109	160	151	72.4	232	12.9	444	69.8	1913
Cu	121	141	559	280	23.3	313	15.5	506	30.7	559
K	64,779	77,638	7761	373,686	7357	149,226	5643	143,453	7761	373,686
Mo	15.1	21.9	<1.90	40.0	5.36	12.9	1.50	37.7	1.90	547
Na	5472	9317	5705	26,757	1371	6231	1171	13,795	194	26,757
Ni	36.8	47.6	55.7	8.60	51.0	114	5.71	68.4	8.60	316
P	15,783	9864	1375	5991	474	37,748	308	46,567	1375	27,413
Pb	163	50.2	279	1277	10.5	873	0.762	4698	6.33	1277
S	15,441	12,837	5856	116,416	985	9202	105	8025	372	116,416
Sb	4.7	<17.0	<7.50	21.3	0.00	24.8	0.00	42.0	3.60	21.3
Se	0.600	9.25	<3.10	5.60	0.095	0.856	0.150	1.89	0.150	9.30
Sn	3.20	31.6	5.48	36.7	1.19	2.78	0.150	58.4	0.600	36.7
V	27.8	33.8	18.7	3.50	6.03	73.0	2.45	27.5	3.50	77.0
Zn	1400	884	2564	10,820	58.8	1411	52.0	3913	8.83	10,820

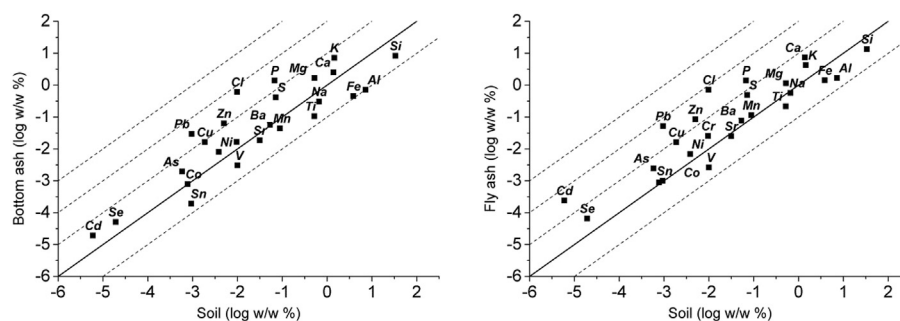[a] Natural pH measured at L/S 10.

Fig. 1. Double log plot of average element contents (weight%) in biomass BA (n = 3) and FA (n = 19) samples versus natural soil (Kirby and Rimstidt, 1993). The thick solid line represents equal contents in both materials. Each of the thin dotted lines represent one order of magnitude depletion or enrichment relative to the average content in soils.

net accumulation of heavy metals or other harmful substances in soil and their subsequent transfer to crops and/or surface or groundwater. At the same time, for specific soil amendment purposes such as nutrient (re)supply and/or pH control, elements such as Ca, K and P should be present at elevated levels in the ash. For any application of specific biomass ash in a specific soil, a more detailed assessment is appropriate, for which we provide considerations and suggestions below.

The thick solid line in Fig. 1 represents equal contents in biomass ash and soil matrices. The thin solid lines indicate tenfold higher or lower element content in biomass ash relative to soil. These graphs show averaged contents of major and minor elements in ash over the whole range of biomass sources and conversion technologies. Fig. 1 clearly shows a lower content of the major elements Al, Fe and Si in the biomass ash and an approximately one order of magnitude higher content of phosphorus, some heavy metals (Cd, Cu, Pb and Zn) and chloride Calcium, Magnesium and Potassium contents are also generally higher in biomass ash, indicating potentially functional properties as soil amendment.

3.3. Total content versus potential leachability of elements in biomass ash

In this Section, we explore relationships between the total content and the leachability of major and minor elements in biomass ash. Fig. 2 shows the total content of As, Ca, Cr, K, Mo, Ni, P and Pb in the biomass ash (x-axis) versus the potential leachability of elements estimated at the pH value at which their mobility is generally highest (Dijkstra et al., 2008; Freire et al., 2015), (i.e. for metals, measured at pH around 2, for oxyanions Mo and Sb measured in the range 8 < pH < 12) at L/S of 10 L/kg. The selected elements were representative of a linear or non-linear correlation as explained later in the text. Data for other measured elements is presented in the Supplementary Material (Fig. S2).

The potentially leachable amount of elements can be interpreted as the maximum amount of elements that is expected to be released from the biomass ash in the long term. In some cases, (i.e. Ca, K, Mo, Na, Zn, Cl and P) the total content and potentially leachable concentrations can get very close and show dependency (i.e. elements with a high and largely pH-independent solubility).
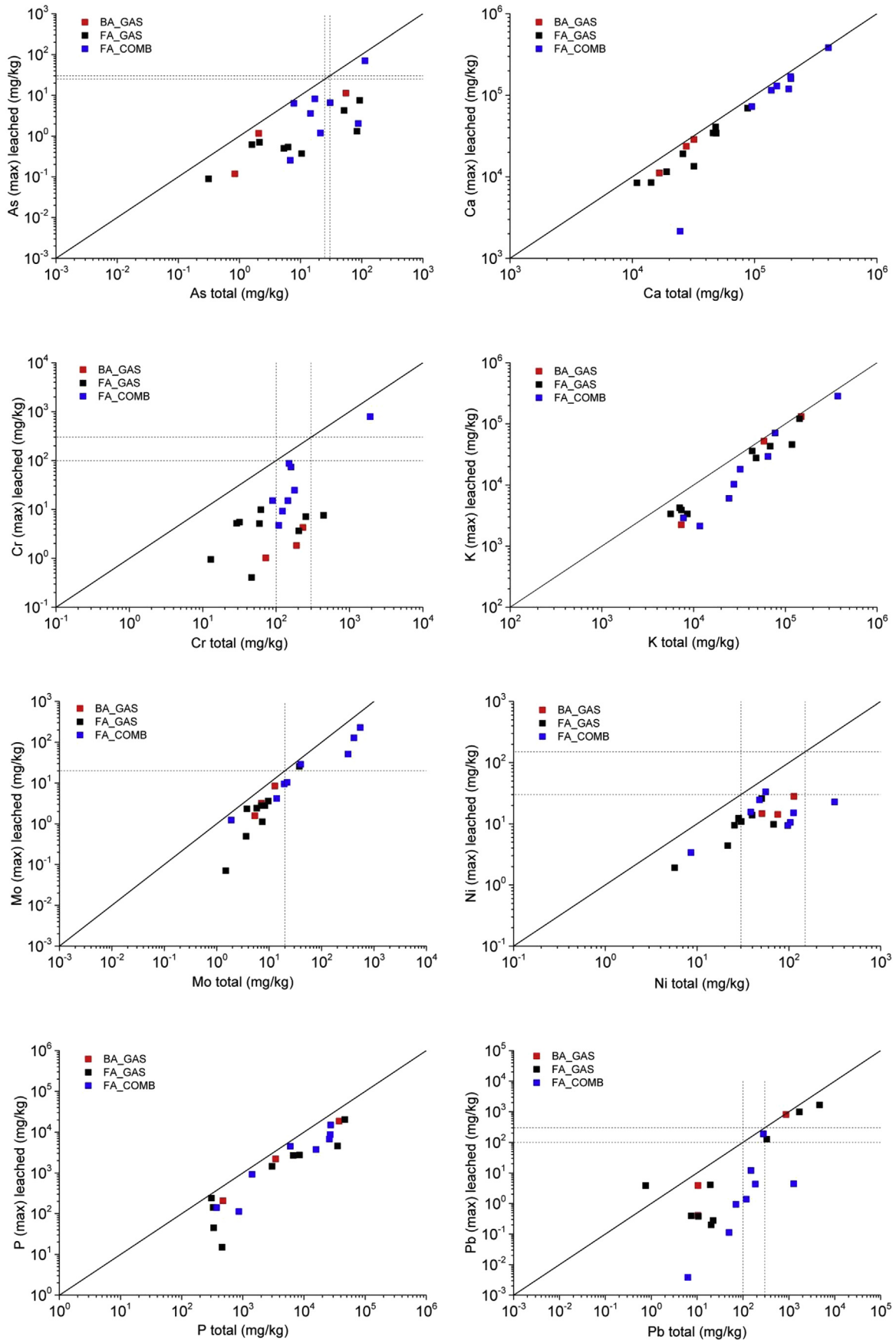
Fig. 2. Total content of As, Ca, Cr, K, Mo, Ni, P and Pb versus the potential leachability expressed in mg/kg (48 h, L/S = 10 L/kg) at pH 2 or 8 < pH < 12 (only for oxyanion-forming Mo and Sb) of the biomass ash samples. Continuous black line indicates a ratio 1:1 where total content equals the maximum leached amount from the biomass ash. When available, the limit values (MIN-MAX) from Table 1 were plotted on both X and Y-axis in order to identify any discrepancies between judgement based on total content vs. potential leachability. Canadian regulation (Hannam et al., 2016) is used only for Co and Mo limits.

In these cases, the total content provides a good indication of the potential release from the biomass ash. Other elements (i.e. As, Ba, Cr, Co, Ni, Pb, Sb, Se, Sn and V), however, show a potential leachability that is mostly 1-2 orders of magnitude lower than their total content, with little correlation between the two measurements (see Figs. 2 and S2). If we look at the recommendations and limits in Table 1, a judgment based on total content would preclude the use of 32% of the total ash samples due to exceeding the limit for As content, 54% due to Cr, 60% due to Ni and 41% due to Pb. When a hypothetical judgment based on potential leachability is used, this would result in exclusion of only 4% of total biomass ash due to As, 4% due to Cr, 4% due to Ni and 22% due to Pb.

The results discussed in this Section show that the total content of As, Ba, Cr, Co, Ni (for Ni only when the total content is of about 10^2 mg/kg dry ash), Pb, Sb, Se, Sn and V is not representative of the maximum amount that can be potentially leached from the biomass ash. Moreover, the actual release is also a function of the pH (both natural pH of biomass ash or imposed by the application scenario) as shown in Fig. 3. The actual release is very important for a more realistic assessment of biomass ash quality (e.g. nutrients content) and potential risk associated with contaminants in reuse applications.

3.4. pH dependent leaching behaviour of biomass ash

In this Section we evaluate the leaching of the different biomass ash samples in response to a pH change. The aim was to measure the actual release, in addition to the potentially leachable concentrations, and to identify common and specific pH-dependent release trends among the different types of biomass ash, fuel and/ or combustion technology. Fig. 4 shows the pH-dependent leaching behaviour of K, Cr, Mo and Zn in the tested biomass ash samples. These elements were selected as representatives of typical pH dependent leaching behaviour (i.e. cations, oxyanions and elements forming soluble compounds).

Generally, the trends in the pH dependent leaching behaviour were similar for most ash samples indicating that the chemical processes that control the release of individual elements are consistent for this wide range of different biomass ash samples. However, distinct differences in the absolute levels of leached concentrations at comparable pH were observed among the different samples. This observation can be explained by differences in the potential leachable amounts of elements in individual ash samples. The natural pH of biomass ash samples varies between 10 and 13 (at an L/S ratio of 10 L/kg, after 48 h equilibration, see Table 2). At this pH range the actual release from biomass ash is lower than the potential leachability as described in Section 3.3. Figs. 4 and S3 (Supplementary Material) show a difference between the release measured at natural pH and the potential release of up to 3 orders of magnitude for Cd, Co, Cu, Ni and Zn. Accordingly, the release at natural pH results in an extremely lower concentration when compared with the total content.

An exception is represented by Mo and, to a lesser extent, V. For these two elements the natural pH of ash coincides with the pH of potential leachability. Another exception is represented by Cl and K. The leached concentrations of Cl and K, elements that are normally present in highly soluble phases (i.e. NaCl, KCl), are essentially independent of solution pH, but rather controlled by their total content in the ash. The described leaching trends are very similar to those observed in previous studies on FA from coal combustion (Kosson et al., 2009) and biomass ash (Freire et al., 2015; Maresca et al., 2017).

Despite the wide variation in the absolute leached amounts of contaminants, the leaching behaviour as a function of the pH was generally very consistent among the different ashes, with a few
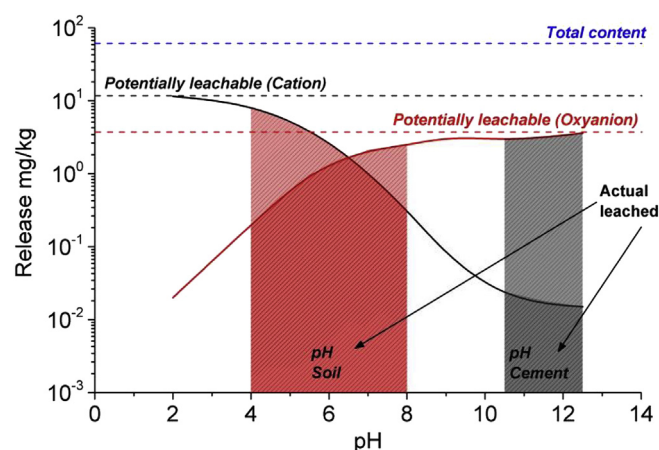

Fig. 3. Graphical representation of the concept of total content, maximum leachability and actual leaching from materials or materials exposed to different conditions. Black curve represents typical cation behaviour whereas the red curve indicates the behaviour of oxyanionic species. The red area highlights the pH range of soil and the grey area the pH of cement. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

exceptions, notably one observed for Cr release. The release pattern and level of Cr showed a distinct relation with the applied conversion technology (Fig. 4). These differences were probably related to the oxidation state of Cr in the biomass ash, i.e. Cr (III) (immobile) and Cr (VI) (mobile) as has previously been observed in studies of leaching mechanisms in cement (van der Sloot et al., 2008; van der Sloot, 2000). Based on our observations, we hypothesize that the conditions during biomass gasification and combustion lead to a different oxidation state of Cr in the ash.

One of the FA sample (i.e. sample ID #1, see Supplementary Material, Table S1) in Fig. 4 showed an exceptionally high Cr leaching over the whole pH domain. This sample was collected from a lab-scale experiment. The total content of Cr in this sample is unusually high and it is thought that the source of Cr is contamination as a result of corrosion of the stainless steel reactor that was used in the laboratory experiment.

Overall, we conclude that the consistent pH-dependent leaching patterns for individual elements shown in Figs. 4 and S3 in the Supplementary Material point at similar geochemical processes that determine their release from this wide range of biomass ash samples.

The pH-dependent leaching test provides essential information on the effect of pH changes that occur in different ash re-use or disposal scenarios on the leaching of contaminants. However, interactions with the surrounding environment (e.g. soil or cement matrices) are also very important in determining the net release from the complete system composed of biomass ash plus soil or cement, as will be further investigated in Sections 3.5 and 3.6.

3.5. Recycling of biomass ash to soil

An assessment based on the total content of elements would exclude utilization of FA1, FA2, FA3 and FA4 in agriculture according to the limit values reported in Table 1. Common exceeding elements are Cd, Cr, Pb and Zn depending on the specific country. According to the Swedish guidelines FA1 is suitable for forestry and FA2 is almost compliant with a Cr content of 109 mg/kg (i.e. limit for Cr is 100 mg/kg) utilization, whereas FA3 and FA4 have a content of 160 and 151 mg/kg and are hence not suitable.

Calculated contents of elements in theoretical mixtures of 2% FA1, FA2, FA3 and FA4 in soil were compared to the Dutch SQD
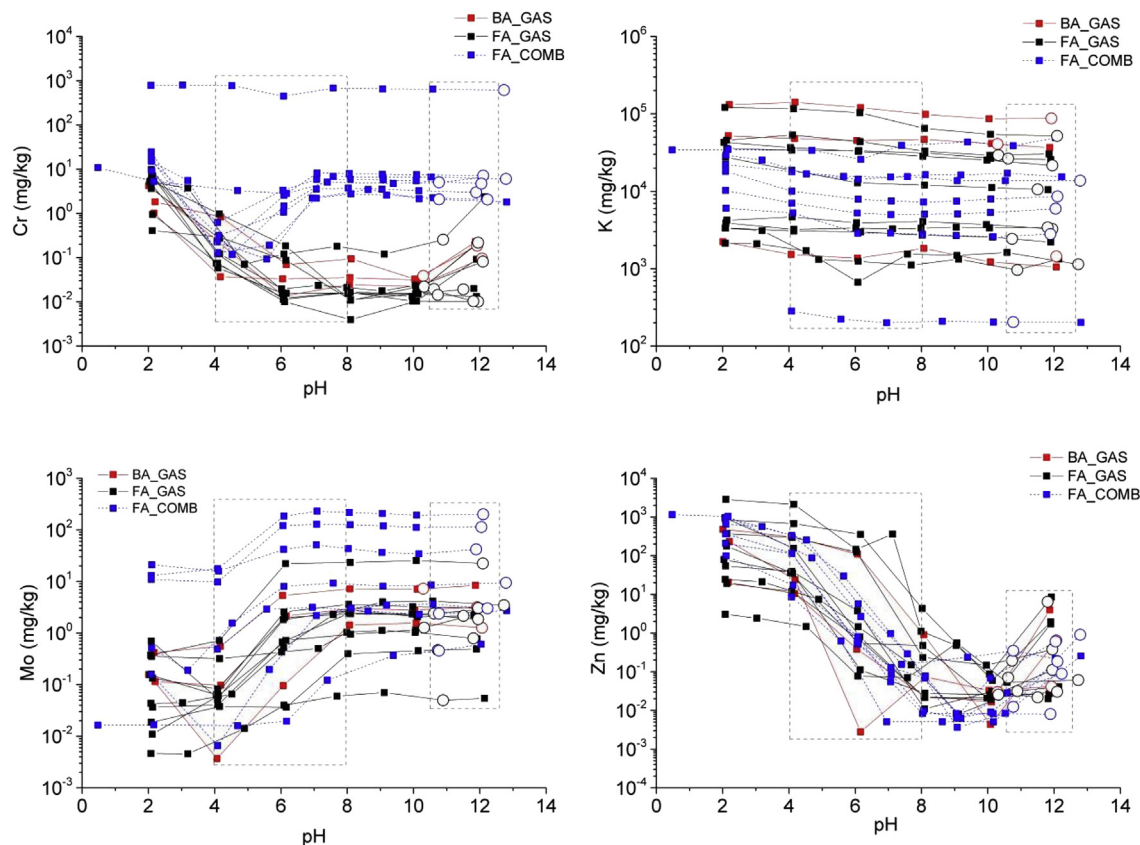
Fig. 4. Leaching of K, Cr, Mo and Zn as a function of pH in all biomass ash samples. Red square indicates bottom ash samples from gasification processes, black square indicates fly ash from gasification and blue squares represent fly ash samples from combustion processes. Open circles indicate the natural pH of each ash without pH adjustment. The dotted grey areas indicate a typical pH range for soil (4–8) and cement (10.5–12.5). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

criteria for utilization of contaminated soil (Dirven-Van Breemen et al., 2007). Complete information on criteria and element contents in amended soils can be found in Table S3. This comparison resulted for all four ash-soil mixtures in an amended soil quality that complies with most of the limits for residential use. Two exceptions were observed. The Ni content was higher in all of the amended soils, since the high content of Ni contained in Euro-Soil 4 (48 mg/kg) already exceeded the limit for residential application (39 mg/kg). The second exception was observed for the Zn and Cd content of the soil amended with 2% FA4. This addition of FA4 resulted in an increase of the Zn and Cd content to above the limit for residential application. When we disregard the Ni data that are determined by the selected soil, rather than by the biomass ashes, it can be concluded that FA1, FA2 and FA3, when mixed at 2%, comply with the criteria for residential soil application, but that FA4 does not comply.

Soil amendment experiments were performed using FA1 and FA4 for the assessment of the availability of nutrients and contaminants in the soil/ash system. In this Section, we investigate the pH dependent release (Fig. 5) of macronutrients Ca, K and P and trace elements (including potential contaminants) from the Euro-Soil 4 reference soil sample, pure FA1 and FA4 from clean wood combustion, and the soil mixed with 0.2 and 2 wt% of these FA samples. The applied dosage represents an equivalent of 15 and 150 ton/ha if biomass ash was to be spread in the soil (i.e. bulk density of 1500 kg/m^3) all at once (see Section 2.4 for more details). Leached concentrations of trace elements were compared with the Dutch Maximum Tolerable Risk (MTR) values in groundwater

(Verschoor et al., 2007), as a first indication of possible risks of these biomass ash types and application levels in soil. When leached concentrations are lower than the MTR values, it is considered that these levels do not pose an unacceptable risk for the groundwater.

The original pH of the soil was 6.8 and increased slightly after addition of 2% FA to a value of 7.0 (2 wt% FA1) and 7.2 (2 wt% FA4), due to the presence of alkali and alkaline earth metal oxides and carbonates in these FA samples (Fig. 5). When Ca-rich FA is used as liming agent in acidic soils, a larger than 2 wt% amendment rate may be required to reach an appropriate soil pH between 6 and 7 (Cruz et al., 2017). Amending FA1 and FA4 to soil had a general positive effect on the availability of most nutrients (i.e. Ca, K, Mg) and Na and Cl (see Fig. S4 of the Supplementary Material). The release of K, Na and Cl reflected the amendment rates of the FA, indicating that these elements are present mainly as soluble compounds that are readily released when mixed with soil. Conversely, phosphorus is in a poorly soluble form at relevant soil pH values, and only a very small fraction was released from the ash to the soil during the test time. The availability of P in the amended soil with 2 wt% FA1 and 2 wt% FA4 at the natural pH (i.e. pH 7 and 7.2 respectively) increased by about a factor of 2 compared to the availability of P in the reference soil at natural pH (i.e. pH 6.8) (see the release of P between pH 6 and 8 in Fig. 5). Since the pH variation is limited, the increased P availability was attributed to the FA addition.

With regard to the release of trace elements, the mixture of 0.2% FA1 essentially showed no significant difference when compared
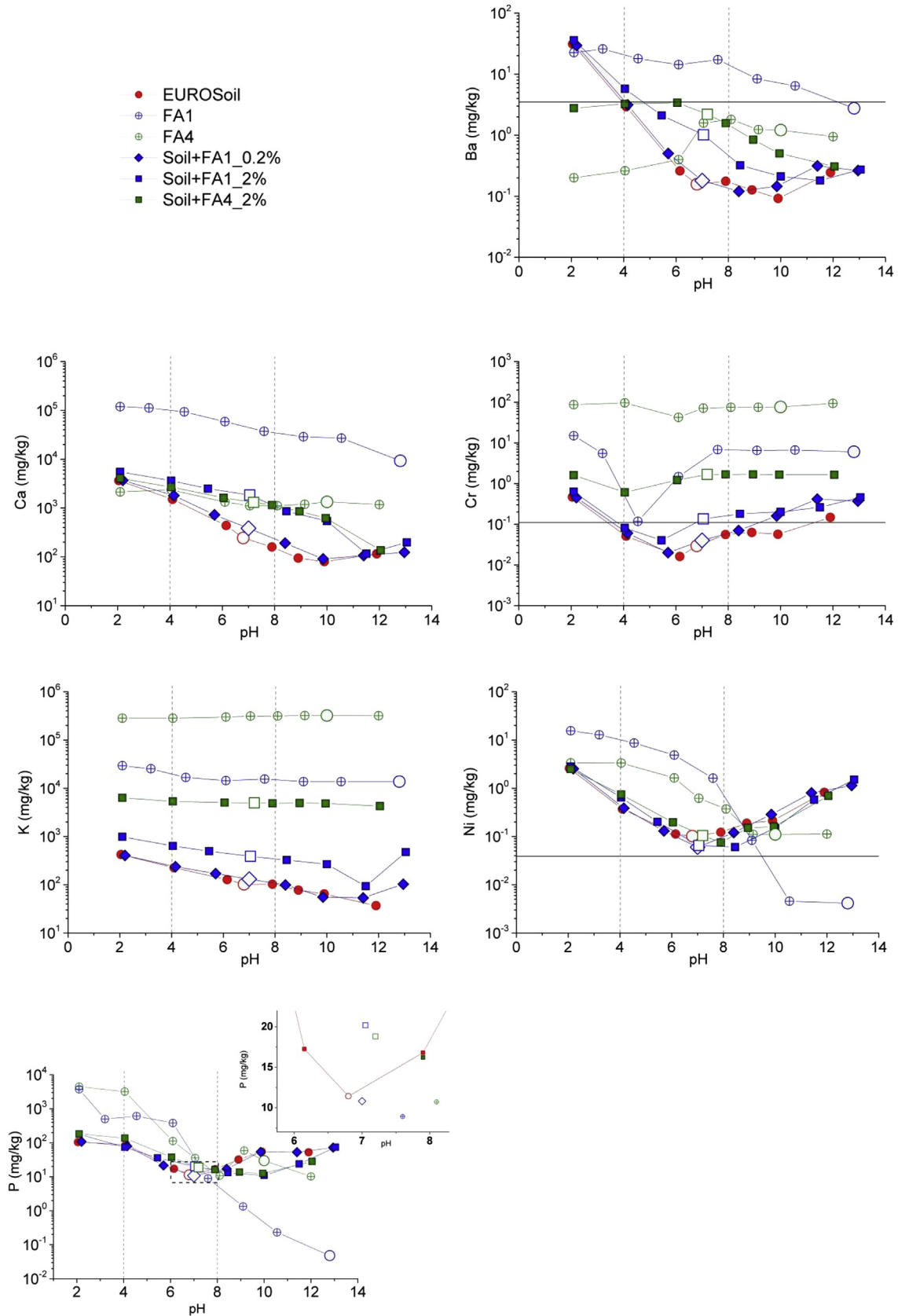
Fig. 5. Release of Ba, Ca, Cr, K, Ni and P as function of pH for two biomass FA samples from clean wood combustion (i.e. FA1 and FA4) and mixtures with soil (i.e. 0.2 and 2 wt% of FA_1 and 2 wt% of FA_4, respectively). The release from the pure FA and from the reference soil is also shown. The natural pH values are indicated by open circles for the pure FA i.e. pH 12.8 (FA1) and pH 10.3 (FA4) and reference soil (i.e. pH 6.8), open diamond for the addition of 0.2 wt% of FA1 (i.e. pH 7) and open squares for the addition of 2 wt% of FA1 (i.e. pH 7) and FA4 (i.e. pH 7.2) to soil. Solid black line specifies the Maximum Tolerable Risk (MTR) limits for groundwater quality which are expressed as mg/kg.

with the soil reference. This observation can be extended to all the other investigated elements reported in the Supplementary Material, Fig. S4.

At 2% amendment rate and natural pH values an increased released of trace elements was observed for both FA1 and FA4, the latter showing generally higher levels and for a broader range of elements (Figs. 5 and S4 in the Supplementary Material). Some of the elevated trace elements in biomass ash, such as Zn and Se (Fig. 1), but also Mo and B, may function as beneficial micronutrients in soil applications, provided that they do not leach at undesirably high (i.e. toxic) levels. When the release of elements from amended soil with 2% of FA1 and FA4 was compared with MTR

values, we could distinguish three situations. In the first, the addition of biomass ash caused an increase in the release but below MTR values at the natural pH of mixtures. This situation was observed for As, Ba and Pb (only for 2% FA4 since the solution concentration of the 2% FA1 mixture is below detection limit). A second situation was observed for Cu, Ni and V, for which the concentration at natural pH in the soil solution reference (red open circle in Fig. 5) were already above the MTR values. Addition of FA1 or FA4 resulted in no significant alteration of these values. The third situation referred to Cd, Co, Cr, Mo, Sb, Se and Zn, for which the FA addition caused the concentration in soil solution at natural pH to increase above the MTR values. In particular, Cr, Mo and Zn showed
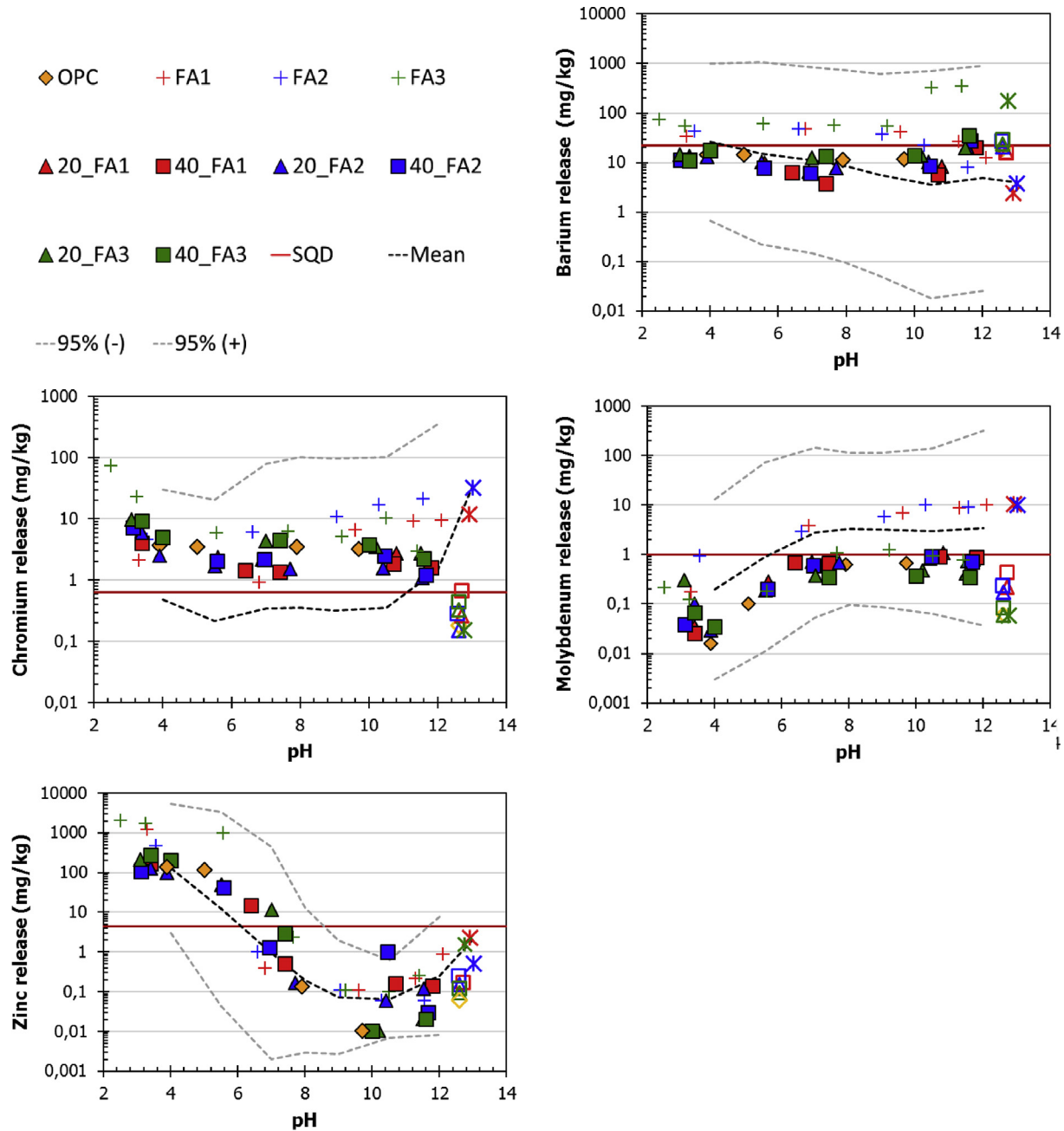

Fig. 6. Leaching of Ba, Cr, Mo and Zn as function of pH in pure biomass FA and cement products. Ordinary Portland Cement (OPC) is added as reference cement. The black dotted line represents the average leaching at different pH for all biomass ash samples investigated in this study (see Table 2). Grey dotted lines reports the 95% confidence level. The red line indicates the SQD limit value for open application of granular materials. The natural pH of pure biomass ash samples and blended cement is indicated by asterisks and open symbols respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

a substantial increase. The mixture containing 2% of FA4 resulted in a Cr release of about 55 times that of the reference soil, resulting in a concentration of about one order of magnitude higher that MTR limit.

The above analysis of actual leaching properties of biomass ash shows that the effects of ash application directly to soil may be substantially different from those assumed on the basis of the total content or potential leachability as shown in Section 3.3. For macronutrients such as Ca and P the different total contents in FA1 and FA4 have been shown to result in a very similar enhanced availability in the amended soil, while for the mobile macronutrient K the effect is in line with the difference in total content. These elements showed a maximum leachability close to total content. In addition, leached concentrations of contaminants allow for a more direct comparison with undesirable (e.g. MTR) concentration levels in groundwater.

Another important observation is that the soil matrix can mitigate the sometimes large differences in the concentrations of elements leached from individual FA samples (e.g. Cu, Ni and V) due to processes such as precipitation, sorption or complexation which affect their mobility.

3.6. Utilization as secondary cementitious material

The utilization of the ashes as secondary cementitious material was investigated on the basis of the crushed mortars made with samples FA1, FA2 and FA3.

The first reason for this approach was to follow a single consistent framework for comparison of the ash characteristics in the two investigated application routes. The cement product characteristics and leaching properties are described in Tosti et al. (2018). The second reason for this approach was that use of crushed mortars is regarded as the second life phase of the cement mortars where it is expected that most of the leaching takes place. Since in the first phase, e.g. in intact concrete structures, the exchange with the environment is minimal, the leaching of crushed mortar is particularly relevant for the assessment of the environmental risk associated with the reuse of biomass ash in concrete products over the entire life cycle. Fig. 6 shows the pH dependent release of Cr, Mo, Se and Zn from the pure FA samples that were used as secondary cementitious material (FA1, FA2 and FA3), as well as and from the resulting cement mixtures. In addition, the average release of all other FA samples considered in this study is reported, together with the 95% confidence interval. Measured concentrations below the detection limits were set equal to the detection limit. The pH dependent release of OPC was included as a reference. Complete information is reported in the Supplementary Material, Fig. S5.

Fig. 6 shows that the pH-dependent release patterns and magnitude for Ba, Cr, Mo, and Zn from OPC (reference) and from the blended cement samples are very similar. This observation can be extended to all other elements reported in Supplementary Material (Fig. S5) with the exception of Cd, Cl, Co and Sn at alkaline pH. For these elements the displayed difference between OPC and blended cements were related to different detection limits applied. Concerning pure biomass FA, an interesting observation is that leaching pattern of FA3 followed the pattern of OPC (reference) while FA1 and FA2 did not (e.g. Cr and S). What distinguishes FA3 is its very high Ca, and relatively low K, Cl and P content (Table 2). The natural pH of FA1, FA2 and FA3 is comparable. Apparently, with regard to leaching, the cement chemistry was dominant over the chemistry of the biomass ash in the blended cements, even at 40% replacement, as was also evidenced by the different pH-dependent release patterns and magnitude for the pure biomass ash samples.

The inclusion of biomass ash into the cement matrix has a considerably lower influence on the net release from the mixture compared to that of biomass ash amendment to the soil matrix, even though higher percentages of biomass ash were added to cement compared to soil (Figs. 5 and 6). The release of most of the regulated elements remained below the limits of the SQD at the natural pH of the materials (see Figs. 6 and S5 in the Supplementary Material). The release of Cr and Ba at the natural cement pH was very close to the SQD limit. The release of these elements from blended cement was somewhat increased by the inclusion of FA1 and to a certain extent FA3 at the natural pH, but they were all still below the SQD limits. The inclusion of biomass FA plays a minor role. As shown in Fig. 6 and described in Tosti et al. (2018), the carbonation of crushed cement can increase the leaching of particularly (oxy)anions up to a point which is above the SQD (i.e. Cr) or very close (i.e. Mo, V).

Similar to our findings for the soil application scenario (e.g. with regard to Cu, V and Ni; see Figs. 5 and S4), the cement matrix plays a major role in controlling the net leaching of many of the investigated elements, such as, Cr and Mo, when biomass ash is used in cement. These observations underline that it is essential to evaluate and interpret the (pH-dependent) availability and leaching of both desired (e.g. nutrients) and undesired (contaminants) elements in the environment in which biomass ash is applied.

4. Conclusions

In this study, we have characterized the pH-dependent availability and leaching of major and trace elements, including potential nutrients and contaminants, for a wide range of FA and BA samples that originate from different biomass fuel and energy conversion techniques. In addition, a technical and environmental assessment was performed of the suitability of selected biomass ash for application in soil or cement mortars. The biomass ashes showed a large variety in composition due to the different sources of the fuel, ash type and conversion technology. Despite this large variation, the actual leaching behaviour of biomass ashes as a function of pH showed quite consistent patterns for most elements and biomass conversion technologies. Chromium was a noticeable exception and showed distinct features that we hypothesize reflect oxidising/reducing conditions during conversion of the biomass.

When the total composition of elements in biomass ash was compared with their potential leachability at low pH, some elements (i.e. Ca, Cd, K, Mo, Na, Zn, Cl and P) show a good correlation, while others (i.e. As, Ba, Cr, Co, Ni, Pb, Sn and V) do not. A substantial part of the total content of the latter elements was found to be not accessible for leaching even at extreme pH conditions. We demonstrated that an assessment based on total element content leads to different conclusions on the applicability of biomass ash as soil amendment than when based on potential leachability. We conclude that an approach based on potential leachability instead of total content does provide a more realistic assessment of the availability of both desired (i.e. nutrients) and undesired (contaminants) in soil systems, and could help improving the usability of biomass ash as soil amendment. This approach could enhance opportunities towards the use of biomass ash as a potentially valuable resource, e.g. with regard to the recycling of nutrients to the soil, and reduce landfilling.

Three FA samples were used to replace cement by 20 and 40% of total binder weight, for which it was shown earlier that the technical performance of produced mortars complies with strength requirements for class 42.5 and 32.5 cement, respectively. Here, we have shown that these mortars also complied with environmental leaching criteria for construction products. In addition, the emissions during a second life phase of the cement mortars (e.g. as recycled and aged aggregates) should preferably be taken into

account to assess the environmental consequences of such applications over their entire life cycle. We have demonstrated how such an assessment, that would be appropriate for alkaline construction materials in general, can be made on the basis of the pH dependence leaching test.

Returning biomass ash to soil would be beneficial from the viewpoint of closing element cycles. However, our results suggest that individual ashes may have insufficient total amounts of nutrients (e.g. Ca and P) or too high amounts of trace elements (e.g. As, Cu, Cr, Ni, Pb and V) under the current guidelines for this application. Although not currently considered in prevailing regulations, we have shown that an approach based on leaching could lead to substantially different results and a potentially more realistic quantification of element availability in soil applications. Given current regulatory criteria, the beneficial utilization of biomass ash in cement may be more feasible than direct soil application. However, an assessment and regulatory criteria based on the leaching rather than total content of elements may widen the application of biomass ash.

Finally, we recommend that biomass ash applications should be assessed also from a lifecycle perspective, in order to account for all additional processes and associated environmental impacts.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2019.02.045.

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