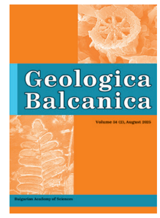
GEOLOGICA BALCANICA 54 (2), Sofia, August 2025, pp. 67–81



Occurrence of nutrient and contaminant elements in biomass ashes and their significance for potential soil fertilization

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(Received: May 15, 2025; accepted in revised form August 25, 2025)

Abstract. Eight biomass ashes (BAs) generated from agricultural, herbaceous, woody and aquatic biomass types were studied for the occurrence of 14 nutrient elements (NEs) and 6 contaminant elements (CEs) to evaluate their significance for potential soil fertilization. For that purpose, a combination of different mineralogical and chemical analyses, and leaching procedures was used. The data show that the contents of NEs in BAs are highly variable; however, the concentrations of B, Ca, Cl, Cu, K, P, S, and Zn, and, to a lesser extent, Mg, Mn, Mo, Na, and Ni in BAs are perspective for potential soil fertilization or soil conditioners. The inorganic matter of BAs comprises amorphous matter and different minerals among carbonates, silicates, chlorides, sulphates, oxyhydroxides, and phosphates. BAs have high yields of water-soluble solutions with alkaline character, which are favourable for BA use. NEs such as Ca, Cl, K, Mg, Na, P, and S occur significantly in water-soluble and bioavailable salts. Various NEs and CEs in BAs fulfilled the available regulation limits for fertilizing products, excluding some problematic concentrations of Cd, Co, Cr, Fe, Mo, Ni, and P for specific BAs. Therefore, each BA needs to be studied on a case-by-case basis for that purpose. The establishment of advanced regulatory framework for BA utilization as fertilizing products is required to generate strict limit values of NEs and CEs in BA leachates. The water-extractable proportions of elements from BA and their release in time are very important to predict the supply of bioavailable NEs or CEs for crops.

Vassilev, S., Vassileva, C., Velyanova, G., Georgieva, M., Petkova, V. 2025. Occurrence of nutrient and contaminant elements in biomass ashes and their significance for potential soil fertilization. *Geologica Balcanica* 54 (2), 67–81.

Keywords: Biomass ash, nutrient elements, contaminant elements, soil fertilization.

INTRODUCTION

It is currently accepted that the plant growth requires 18 essential elements (nutrients) as each of them has special functions to complete the plant life cycle. The fertilizing products normally include macronutrient elements such as C, Ca, H, K, Mg, N, O, P, S, whereas the micronutrient elements are commonly B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn (Kumar *et al*., 2021; Brown *et al*., 2022; Kirkby, 2023), and occasionally Na (EU, 2019; Yahaya *et al*., 2023; Mohanty *et al*., 2025). Six of the nutrient elements (B, Cu, Mg, Mn, Ni, and P) are also critical economically and strategically important elements for other industries. The critical elements with a high supply risk for EU provide greater security and sustainability for the community and they are crucial for a wide set of strategic industrial sectors including energy, electronics, metallurgy, aerospace, defence, food and feed pro-

https://doi.org/10.52321/GeolBalc.54.2.67

duction, sustainable organic agriculture, and other industries.

The global demand and depletion of conventional nutrient resources, as well as future restricted supply of such resources require actions to solve the problem. Therefore, the prospects of new alternative resources of nutrient elements (NEs) is important worldwide. This is particularly valid for EU countries which are heavily depended on imports and they need to ensure the highest level of diversification and supply chains of NEs to produce fertilizing products in a sustainable manner. Some waste products such as fuel ashes can be alternative and perspective resources for that purpose because they are in large quantities in Europe and worldwide, and occasionally enriched in certain nutrients. These ashes remain partially utilized and still provoke environmental concerns. The waste utilization approach is not only connected with the environmental protection, but also with the currently accepted "circular economy models" promoted by many governments for using secondary raw material and energy resources.

In contrast to fuel ashes produced from the combustion of solid, liquid and gaseous fossil fuels, biomass ash (BA) is generated from renewable and C-neutral biomass and has a huge energy potential. For instance, only about 3–6% of the global growth of biomass are used for bioenergy, but this biofuel generates approximately 476 Mt/yr. of BA worldwide because of biomass combustion (Vassilev *et al.*, 2013a). This amount could potentially rise to about 1000 Mt/yr. in near future (Zhai *et al.*, 2021) due to the replacement of coal by biomass. However, the application of these combustion products in industry is still restricted currently caused by the limited knowledge on their composition, properties, processing, and fate, and as a result most BA is landfilled. Despite that, it was found that BA can be enriched in nutrient elements such as B, Ca, Cl, Cu, K, Mg, Mn, Ni, P, S, and Zn (Cohen and Dunn, 2004; Vassilev *et al.*, 2014b) in comparison with Clarke values (worldwide average element concentrations) of lithosphere (Beus and Grigorian, 1975), sedimentary rocks (Grigoriev, 2009) or coal ash (Finkelman, 1994; Ketris and Yudovich, 2009). For example, the contents of many NEs in BA can rise up to: 60% for Ca in elm bark ash (Bryers, 1996); 50% for K in coffee husks ash (Werther *et al.*, 2000); 28% for Cl in tobacco stalks ash (Du *et al.*, 2014); 24% for Mg in marine algae ash (Ross *et al.*, 2008); 18% for P in meat-bone meal ash (Tortosa Masiá *et al.*, 2007); 17% for S in athel logs ash (Thy *et al.*, 2013a); 16% for Fe in beech wood ash (Heinzel *et al.*, 1998); 12% for Mn in spruce wood ash (Reimann *et al.*, 2008); 4.4% for Zn in birch wood ash (Reimann *et al.*, 2008); 1.0% for Cu in forest residue ash (Richaud *et al.*, 2004); 2160 ppm for B in Jose tall wheat grass ash (Thy *et al.*, 2013b); 1068 ppm for Ni in birch wood ash (Richaud *et al.*, 2004); and 121 ppm for Mo in wood sawdust ash (Cohen and Dunn, 2004). One of the most important reasons for the enrichment of certain NEs in this combustion product is the biophile character of these elements and the low ash yield of biomass. Hence, BA is highly perspective for producing of fertilizers and soil amendments from industrial and environmental points of view to reduce the use of traditional synthetic fertilizers. Finally, the soil application of BA as fertilizing products can result in the restoration of macro- and micro-nutrients that were initially taken by plants and thus leading to beneficial incorporation, circulation and balance of these NEs back to the biomass and soil systems.

There are some advanced investigations and comprehensive reviews about the potential soil application of BA enriched in NEs (Steenari and Lindqvist, 1997; Demeyer *et al.*, 2001; Zhang *et al.*, 2002a, b; Park *et al.*, 2005; Reimann *et al.*, 2008; Sarenbo, 2009; Viana *et al.*, 2012; Jones and Quilliam, 2014; Freire *et al.*, 2015; Maresca *et al.*, 2017, 2018; Cruz *et al.*, 2019, 2023; Silva *et al.*, 2019; Tosti *et al.*, 2019; da Costa *et al.*, 2020; Munawar *et al.*, 2021; Ondrasek *et al.*, 2021; Albuquerque *et al.*, 2022; Rouhani *et al.*, 2024; Mohanty *et al.*, 2025; Pędziwiatr, 2025, among others). An extensive review about the recent advances in the chemistry of N, P, and K as fertilizers in soil application has been also published (Yahaya *et al.*, 2023). This review shows that all essential elements in plants are present in soil; however, mostly N, P, and K are needed to be supplied additionally as fertilizers to soil to promote optimum plant growth and development. Most BA is unutilized and landfilled, but this combustion product enriched in many NEs (excluding N) has the potential to be used as inorganic macronutrient and micronutrient fertilizers, as well as liming materials, soil improvers or plant biostimulants. For example, several studies suggested that BA could be recycled as fertilizers and liming agents rather than being discarded (Steenari and Lindqvist, 1997; Demeyer *et al.*, 2001; Park *et al.*, 2005; Maresca *et al.*, 2017, 2018; Tosti *et al.*, 2019; Ondrasek *et al.*, 2021; Albuquerque *et al.*, 2022; Cruz *et al.*, 2023; Vassilev *et al.*, 2023; Rouhani *et al.*, 2024). It was found in these studies that BA can significantly: improve fertility, properties, structure, water holding capacity, cation exchange capacity, and microbial activity of soil; reduce soil acidity; promote plant growth; and increase crop yield. However, the composition and properties of BAs vary significantly depending on biomass fuel type, combustion technology, and BA storage conditions, which hinder their potential for recycling (Vassilev *et al.*, 2013b; Vassilev *et al.*, 2015). For example, some limitations such as extra abundance of water-soluble salts and high concentrations of heavy metals in specific BAs can lead to an increase in soil salinity and potential toxicity to plants, respectively (Vassilev *et al.*, 2013b; Cruz *et al.*, 2023). Additionally, it was emphasized that BA produced from agricultural and herbaceous biomass appears to be a more practicable option for recycling purposes due to its lower contents of potentially toxic elements compared to woody biomass ash (Rouhani *et al.*, 2024). Therefore, a critical review of the existing regulatory framework about the use of BA for soil application as fertilizing products has been also conducted (Silva *et al.*, 2019). Overall, many remaining gaps concerning the BA soil utilization still occur due to the relatively limited knowledge about: the composition and properties of various BAs (particularly herbaceous, agricultural, algae and contaminated biomass); the effective and sustainable approaches for BA processing (granulation, stabilization, others); the behavior and fate of nutrient and potentially toxic elements; and the establishment of an advanced regulatory framework for BA utilization as fertilizing products.

The purpose of the present study is to summarize and systematize the data for NEs including their: (1) contents; (2) association with specific phases and minerals; (3) modes of occurrence; and (4) perspectives for potential utilization as fertilizing products or soil conditioners; based on our previous and present results for different BAs, as well as reference data. For that purpose, 20 major, minor and trace elements such as 14 NEs (B, Ca, Cl, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, and Zn) and 6 contaminant elements (As, Cd, Co, Cr, Hg, and Pb) in 8 BAs are considered in this study to evaluate their significance for potential soil fertilization. A critical overview on the content, modes of occurrence, and significance of nutrient P in biomass and BA has been conducted recently by some of the present authors (Vassilev *et al.*, 2023). Such data are an initial step for conducting some future detail investigations in this field.

MATERIALS, METHODS AND DATA USED

The selected 8 BA varieties generated from agricultural, herbaceous, woody and aquatic biomass types (Table 1) include: rice husks ash (RHA), corn cobs ash (CCA), switchgrass ash (SGA), sunflower shells ash (SSA), marine macroalgae ash (MMA), weathered plum pits ash (PPA), walnut shells ash (WSA), and beech wood chips ash (BCA). They were produced in an electric oven under static air at 500 ± 10 °C for 2 h with a heating and cooling rate of 5 °C min^{-1}. The above temperature and holding time were selected as the lowest ones for gentle and successful incineration of biomass (Vassilev *et al.*, 2013a). These BA samples were previously characterized for bulk chemical and phase-mineral composition, as well as contents of trace elements (Vassilev *et al.*, 2014a; Vassilev *et al.*, 2014b; Vassilev *et al.*, 2024) and the specific data for the present study are given in Tables 1 and 2. The selection of the above listed BA samples is based on their highly variable composition, which is a benefit for comparative studies.

The composition and properties of BA samples were studied using light microscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyser (EDX), inductively coupled plasma – mass spectrometry (ICP-MS), laser ablation (LA) ICP-MS, dual-cell double beam direct Hg analysis, and through additional ashing, leaching and precipitation procedures that were described in detail earlier (Vassilev *et al.*, 2014a, b; Vassilev *et al.*, 2024). Shortly, an ordinary stereomicroscope under transmitted and reflected light was used for optical observations. The investigation by SEM was carried out on a JEOL JSM 6390 microscope equipped with an Oxford INCA EDX. XRD patterns of finely ground samples were recorded by D2 Phaser Bruker AXS diffractometer, and collected at 10–70° 2θ using Cu Ka radiation. Dry, water-soluble residues (DWRs) were isolated from the BA samples by water leaching and subsequent evaporation and precipitation of the solutions. The leachates from this extraction procedure were generated from 10 g of BA samples placed in glass containers with 500 ml of distilled water and soaked for 24 h at ambient temperature. The suspensions were periodically stirred and consequently decanted and filtered. Then, the pH values of the generated water solutions were measured by a bench pH meter. Finally, the leachates were placed in a drying oven at 80 °C for evaporation and crystallization, yielding the DWRs given in Table 1.

The contents of 20 NEs and contaminant elements (CEs) in BAs were studied and given in Table 1. They were determined by: (1) ICP-MS following acid digestion of the samples by HCl, HNO_3 and HF and subsequent measurement of the solu-

Table 1
Contents of 20 nutrient and contaminant elements and values of some characteristics for 8 biomass ashes, ppm (indicated otherwise)

Element	Rice husks ash	Corn cobs ash	Switchgrass ash	Sunflower shells ash	Marine macroalgae ash	Plum pits ash	Walnut shells ash	Beech wood chips ash
Source	Kovachevo, Bulgaria	Debnevo, Bulgaria	Mead, USA	Billa, Bulgaria	Tsarevo, Bulgaria	Debnevo, Bulgaria	Debnevo, Bulgaria	Rosenberg, Germany
Sample code	RHA	CCA	SGA	SSA	MMA	PPA	WSA	BCA
As	9.4	6.4	9.4	5.2	5.6	2.6	7.5	4.5
B	4101	6619	7106	5900	8653	11311	8908	10257
Ca (%)	0.88	1.07	4.30	8.18	13.61	13.82	17.82	28.96
Cd	8.2	5.1	9.8	4.4	5.0	3.5	5.9	4.9
Cl (%)	0.15	0.40	0.15	0.96	8.32	0.10	0.20	0.05
Co	2.1	2.6	1.3	4.2	3.5	3.4	1.4	4.2
Cr	348	750	49	1504	66	160	167	24
Cu	76	139	66	331	36	636	477	98
Fe (%)	0.25	0.74	0.23	0.68	0.42	0.54	0.18	0.16
Hg	0.003	0.031	0.013	0.026	0.025	0.045	0.020	0.017
K (%)	3.02	27.79	12.15	30.29	5.40	5.93	26.69	9.64
Mg (%)	0.26	0.84	1.98	5.26	4.00	1.11	1.50	2.92
Mn	1825	404	872	365	167	466	202	10595
Mo	4.35	5.71	5.43	8.95	1.60	2.69	5.55	2.06
Na (%)	0.15	0.15	0.07	0.12	9.00	0.26	0.06	0.05
Ni	107	286	37	574	42	64	60	36
P	2299	14880	8320	21001	3668	19571	6758	7012
Pb	7.4	68.3	3.0	1.5	2.7	32.4	11.7	38.7
S (%)	0.46	0.97	0.68	3.35	9.84	1.36	0.53	0.20
Zn	103	1232	103	338	52	779	110	213
pH	8.1	11.3	9.8	12.9	8.4	8.9	10.5	12.1
DWR[a] (%)	3.9	45.1	23.3	29.8	42.8	9.4	41.1	20.2

[a] *Dry, water-soluble residue.*

Table 2
Major (M), minor (Mi) and accessory (A) inorganic phases and minerals in 8 biomass ashes based on XRD data

Phase, mineral	Formula	RHA	CCA	SGA	SSA	MMA	PPA	WSA	BCA
1. Inorganic amorphous matter		M	M	M	M	M	M	M	M
2. Inorganic crystalline matter		M	M	M	M	M	M	M	M
2.1. Carbonates									
Butschliite	$K_2Ca(CO_3)_2$							M	
Calcite	$CaCO_3$			M	Mi	M	M	M	M
Fairchildite	$K_2Ca(CO_3)_2$				Mi		A	M	
Kalicinite	$KHCO_3$		M		Mi			Mi	
2.2. Silicates									
Kalsilite	$KAlSiO_4$		Mi						
Leucite	$KAlSi_2O_6$		Mi	Mi					
Quartz	SiO_2	Mi	A	Mi		A	Mi		A
2.3. Chlorides									
Halite	NaCl					M			
Sylvite	KCl	Mi	Mi			A			
2.4. Sulphates									
Anhydrite	$CaSO_4$		A	A	A	M	A	A	
Arcanite	K_2SO_4	Mi			M				
2.5. Oxides and hydroxides									
Periclase	MgO				Mi				
Portlandite	$Ca(OH)_2$					Mi			
2.6. Phosphates									
Apatite	$Ca(PO_4)_3(Cl,F,OH,CO_3)$						Mi		
Whitlockite	$Ca_3(PO_4)_2$								Mi

tions (for B and Mn) by Perkin Elmer ELAN DRC-e mass spectrometer; (2) LA-ICP-MS following preparation of discs after fusion of the samples with $Li_2B_4O_7$ at 1000 °C and subsequent measurement of the glass discs (for As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, P, Pb, and Zn) by the above apparatus combined with New Wave UP193FX excimer LA system using NIST SRM glasses 610 and 612 as external calibration standards; (3) SEM-EDX for contents of S and Cl in the carbon coated BA material using internal standards (Vassilev *et al.*, 2014b); and (4) dual-cell double beam DMA-80 Evo direct analyzer (Milestone Inc.) of Hg using certified reference material NIST 2702 (Vassilev *et al.*, 2024). Nitrogen is also a very important nutrient element in biomass; however, this element is almost completely volatilized during biomass combustion and it is not characteristic of BA (Ozgen *et al.*, 2021).

RESULTS AND DISCUSSION

Contents of nutrient elements in biomass ashes

Table 1 shows the contents of 14 NEs in the studied 8 BAs. The concentrations of 6 CEs in these combustion products are also listed in Table 1 for some discussion from an ecological point of view (see below). It can be seen that most NEs reveal high variations in their contents, especially for Ca (0.9–29.0%), Na (0.2–9.0%), Cl (0.1–8.3%), Cu (36–636 ppm), K (3.0–30.3%), Mg (0.3–5.3%), Mn (167–10595 ppm), Ni (36–574 ppm), P (2299–21001 ppm), S (0.2–9.8%), and Zn (52–1232 ppm). Table 3 shows: (1) the Clarke contents of 14 NEs in lithosphere (Beus and Grigorian, 1975), sedimentary rocks (Grigoriev, 2009), soils (Bowen, 1966),

Table 3
Clarke contents of 14 nutrient elements in lithosphere, sedimentary rocks, soils, coal ash, and world reference plant ash. Mean concentrations of these elements in 8 biomass ashes (BAs) and their enricment/depletion factor (EDF) are also given, ppm (indicated otherwise)

Element	Lithosphere[a]	Sedimentary rocks[b]	Soils[c]	Coal ash[d,e]	World reference plant ash[f]	8 BAs (mean)	EDF[g]	EDF[h]	EDF[i]	EDF[j]	EDF[k]
B	7.0	72	10	335[d]	816	7857	1122	109	786	24	9.6
Ca (%)	4.30	7.28	1.37	3.51[e]	20.41	11.08	2.6	1.5	8.1	3.2	0.5
Cl (%)	0.01	0.65	0.01	0.14[d]	4.08	1.29	129	2.0	129	9.2	0.3
Cu	65	31	20	92[d]	204	232	3.6	7.5	12	2.5	1.1
Fe (%)	5.70	3.54	3.80	9.92[e]	0.31	0.40	0.1	0.1	0.1	<0.1	1.3
K (%)	1.80	1.98	1.40	1.37[e]	38.78	15.11	8.4	7.6	11	11	0.4
Mg (%)	2.40	1.83	0.50	0.84[e]	4.08	2.23	0.9	1.2	4.5	2.7	0.5
Mn	900	730	850	490[d]	4082	1862	2.1	2.6	2.2	3.8	0.5
Mo	1.3	1.5	2	14[d]	10	4.54	3.5	3.0	2.3	0.3	0.5
Na (%)	2.30	1.31	0.63	0.61[e]	0.31	1.23	0.5	0.9	2.0	2.0	4.0
Ni	95	38	40	76[d]	31	151	1.6	4.0	3.8	2.0	4.9
P	1000	670	650	1350[d]	40816	10439	10	16	16	7.7	0.3
S (%)	0.03	0.36	0.07	13.74[e]	6.12	2.17	72	6.0	31	0.2	0.4
Zn	87	69	50	140[d]	1020	366	4.2	5.3	7.3	2.6	0.4

[a] Clarke for lithosphere (Beus and Grigorian, 1975).
[b] Clarke values for sedimentary rocks (Grigoriev, 2009).
[c] Clarke values for soils (Bowen, 1966)
[d] Clarke for coal ash worldwide (Ketris and Yudovich, 2009).
[e] Clarke for US coal ash (Finkelman, 1994).
[f] World reference plant ash (Cohen and Dunn, 2004) recalculated from plant data for 4.9% ash yield (Vassilev et al., 2010).
[g] EDF is defined as a ratio of the mean element content in 8 biomass ashes to the respective Clarke value in lithosphere.
[h] EDF is defined as a ratio of the mean element content in 8 biomass ashes to the respective Clarke value in sedimentary rocks.
[i] EDF is defined as a ratio of the mean element content in 8 biomass ashes to the respective Clarke value in soils.
[j] EDF is defined as a ratio of the mean element content in 8 biomass ashes to the respective Clarke value in coal ash.
[k] EDF is defined as a ratio of the mean element content in 8 biomass ashes to the respective Clarke value in world reference plant ash.

coal ash (Finkelman, 1994; Ketris and Yudovich, 2009), and world reference plant ash (Cohen and Dunn, 2004; Vassilev *et al.*, 2010); (2) the mean contents of these elements in the studied 8 BAs; as well as (3) their enrichment/depletion factor (EDF). This factor is defined as a ratio of the mean element content in 8 BAs to the respective Clarke value. Overall, the number of over Clarke NEs in the studied BAs decreases in the order: soils > sedimentary rocks > lithosphere = coal ash > world reference plant ash (Table 4). The highest mean EDF (>5) of 8 BAs show: B > Cl > S > P > Cu > K > Ca > Zn in contrast to soils; B > P > K > Cu > S > Zn in comparison with sedimentary rocks; B > Cl > S > P > K in contrast to lithosphere; B > K > Cl > P compared to coal ash; and B in contrast to world reference plant ash (Table 4). Hence, the concentrations of NEs such as B, Cl, S, P, Cu, K, Ca, and Zn, and, to a lesser extent, Mg, Na, Ni, Mo, and Mn in BAs are particularly perspective for the application of these combustion products for producing of macronutrient, micronutrient and combined fertilizers, as well as liming materials, soil improvers or plant biostimulants. The reasons for the enrichment of NEs in BA is the biophile character of NEs and low ash yield of biomass during combustion. For example, the content of inorganic elements in BA normally increase by one to two orders of magnitude compared to biomass (Vassilev *et al.*, 2014b). Certainly, specific BAs have different concentrations of NEs (Table 1) and each BA needs to be studied on a case-by-case basis due to the diverse contents, modes of occurrence, and behavior of NEs in these combustion products. For instance, definite NEs show a strong affinity to some BAs based on their maximum concentrations, namely: K, Mg, Mo, Ni, and P for SSA; Cl, Na, and S for MMA; Ca and Mn for BCA; Fe and Zn for CCA; and B and Cu for PPA (Table 1). Finally, six of the 14 NEs in BAs (B, Cu, Mg, Mn, Ni, and P) are also critical elements for industry of EU and some of them could also be perspective for recycling and subsequent utilization.

The summarized data show that the contents of NEs in the studied BAs are highly variable and depend mostly on the type of combusted biomass.

Association and modes of occurrence of nutrient elements in biomass ashes

Biomass ash is a complex heterogeneous mixture of inorganic matter and, to a lesser extent, organic matter containing numerous solid and fluid intimately associated phases or minerals formed mostly during biomass combustion. The inorganic matter of BAs produced at 500 ºC (Table 2) comprises both amorphous matter and crystalline constituents represented by carbonates (calcite, kalicinite, butschliite, and fairchildite), silicates (quartz, kalsilite, and leucite), chlorides (sylvite and halite), sulphates (anhydrite and arcanite), oxides and hydroxides (portlandite and periclase), and phosphates (apatite and whitlockite). The organic matter consists of char which occurs only at trace contents in these BAs. It can be seen that NEs such as Ca, Cl, K, Mg, Na, P, and S occur in specific and discrete minerals in BA. On the other hand, the reference data show that other NEs may also occur in various discrete minerals and phases in BA, namely Fe (oxyhydroxides, silicates, and phosphates), Mn (oxides), Mo (selenides), Zn (oxides and chlorides) (Vassilev *et al.*, 2013a). It should be stated that the mineral constituents of soils are rather different than those of BAs and include mostly stable silicates such as quartz, muscovite, chlorite, sepiolite, plagioclases, K-feldspar, amphibole, pyroxene, and kaolinite (Albuquerque *et al.*, 2022).

Table 4
Enrichment of 14 nutrient elements in 8 biomass ashes in comparison with the Clarke values in lithosphere, sedimentary rocks, soils, coal ash, and world reference plant ash (based on Table 3). The bold and italic fonts show elements with enrichment/depletion factor (EDF) ≥5.0 and 2.0–4.9, respectively

Clarke	Over Clarke nutrient elements in decreasing order of EDF
Soils	**B (786) > Cl (129) > S (31) > P (16) > Cu (12) > K (11) > Ca (8.1) > Zn (7.3)** > *Mg (4.5)* > *Ni (3.8)* > *Mo (2.3)* > *Mn (2.2)* > *Na (2.0)*
Sedimentary rocks	**B (109) > P (16) > K (7.6) > Cu (7.5) >S (6.0) > Zn (5.3)** > *Ni (4.0)* > *Mo (3.0)* > *Mn (2.6)* > *Cl (2.0)* > Ca (1.5) > Mg (1.2)
Lithosphere	**B (1122) > Cl (129) > S (72) > P (10) > K (8.4)** > *Zn (4.2)* > *Cu (3.6)* >*Mo (3.5)* > *Ca (2.6)* > *Mn (2.1)* > Ni (1.6)
Coal ash	**B (24) > K (11) > Cl (9.2) > P (7.7)** > *Mn (3.8)* > *Ca (3.2)* > *Mg (2.7)* > *Zn (2.6)* > *Cu (2.5)* > *Na (2.0)* > *Ni (2.0)*
World reference plant ash	**B (9.6)** > *Ni (4.9)* > Na (4.0) > Fe (1.3) > Cu (1.1)

The correlation analysis among the contents of elements and other characteristics in BA provides an initial information for understanding some basic trends and associations of these elements in the BA system. The statistically significant positive correlations of major elements with trace and minor elements confirm association of elements with common minerals or phases identified in BAs. These correlations are the result both of indirect (coexistence of mineral assemblages) or direct (mineral parageneses and generations) genetic associations of elements in BA. However, the statistically significant positive correlation between an element and phase does not specify that this phase is the main host of that element, whereas some statistically insignificant correlations could be important in the BA system. Therefore, additional studies and literature data connected with the modes of element occurrence in BA should always be considered in conjunction with the correlation tests. The results from this test (Table 5) show that there are: significant positive correlations among NEs such as: (1) Ca with Mn and

Table 5
Correlation coefficient values (R^2)[a] among contents of 14 nutrient elements and some characteristics for 8 biomass ashes

Element	Correlation coefficient among elements and characteristics:
B	(+) **Ca (0.78)**; Cu (0.49); Mn (0.31); P (0.17); Na (0.14); Zn (0.10); Cl (0.09); S (0.07); Mg (0.06); DWR (0.05); pH (0.02) (-) Mo (–0.59); Ni (–0.48); K (–0.20); Fe (–0.15)
Ca	(+) **B (0.78)**; **Mn (0.68);** Mg (0.31); pH (0.28); Cu (0.22); Na (0.10); Cl (0.07); DWR (0.04); S (0.03) (-) Mo (–0.49); Fe (–0.45); Ni (–0.36); Zn (–0.29); K (–0.13); P (–0.12)
Cl	(+) Na **(0.99); S (0.98)**; Mg (0.48); DWR (0.45); Fe (0.10); B (0.09); Ca (0.07) (-) Mo (–0.41); pH (–0.36); Cu (–0.35); P (–0.32); K (–0.28); Zn (–0.28); Mn (–0.23); Ni (–0.13)
Cu	(+) P (0.61); B (0.49); Zn (0.28); K (0.25); Ca (0.22); Fe (0.22); Mo (0.16); Ni (0.12); pH (0.07) (-) Cl (–0.35); Na (–0.34); Mn (–0.30); S (–0.24); DWR (–0.12); Mg (–0.11)
Fe	(+) **P (0.77)**; **Zn (0.76)**; **Ni (0.73)**; K (0.45); Mo (0.40); DWR (0.30); pH (0.27); S (0.25); Cu (0.22); Mg (0.21); Cl (0.10); Na (0.05) (-) Mn (–0.47); Ca (–0.45); B (–0.15)
K	(+) **Mo (0.80)**; **pH (0.75)**; **Ni (0.70)**; **DWR (0.63)**; P (0.50); Fe (0.45); Zn (0.35); Cu (0.25); Mg (0.25) (-) Na (-0.35); Cl (-0.28); Mn (-0.27); B (-0.20); S (-0.19); Ca (-0.13)
Mg	(+) S (0.60); pH (0.49); Cl (0.48); Ni (0.48); Na (0.41); DWR (0.34); Ca (0.31); K (0.25); P (0.24); Mo (0.22); Fe (0.21); Mn (0.08); B (0.06) (-) Zn (–0.33); Cu (–0.11)
Mn	(+) **Ca (0.68)**; pH (0.36); B (0.31); Mg (0.08) (-) Fe (–0.47); Mo (–0.41); S (–0.31); Cu (–0.30); DWR (–0.29); K (–0.27); Ni (–0.27); P (–0.25); Cl (–0.23); Na (–0.20); Zn (–0.18)
Mo	(+) **Ni (0.81); K (0.80)**; pH (0.56); P (0.49); Fe (0.40); Mg (0.22); DWR (0.20); Cu (0.16); Zn (0.14) (-) B (–0.59); Na (–0.50); Ca (–0.49); Cl (–0.41); Mn (–0.41); S (–0.27)
Na	(+) **Cl (0.99); S (0.95);** Mg (0.41); DWR (0.40); B (0.14); Ca (0.10); Fe (0.05) (-) Mo (–0.50); pH (–0.43); P (–0.37); K (–0.35); Cu (–0.34); Zn (–0.29); Ni (–0.23); Mn (–0.20)
Ni	(+) **Mo (0.81)**; **Fe (0.73)**; **K (0.70)**; **P (0.67)**; **pH (0.64)**; Mg (0.48); Zn (0.33); DWR (0.21); Cu (0.12); S (0.04) (-) B (–0.48); Ca (–0.36); Mn (–0.27); Na (–0.23); Cl (–0.13)
P	(+) **Fe (0.77)**; **Ni (0.67)**; **Zn (0.65)**; Cu (0.61); K (0.50); pH (0.50); Mo (0.49); Mg (0.24); B (0.17); DWR (0.01) (-) Na (-0.37); Cl (-0.32); Mn (-0.25); S (-0.14); Ca (-0.12)
S	(+) **Cl (0.98)**; Na (0.95); Mg (0.60); DWR (0.43); Fe (0.25); B (0.07); Ni (0.04); Ca (0.03) (-) Mn (–0.31); Mo (–0.27); pH (–0.27); Cu (–0.24); Zn (–0.23); K (–0.19); P (–0.14)
Zn	(+) **Fe (0.76)**; **P (0.65)**; K (0.35); Ni (0.33); Cu (0.28); pH (0.23); DWR (0.17); Mo (0.14); B (0.10) (-) Mg (–0.33); Ca (–0.29); Na (–0.29); Cl (–0.28); S (–0.23); Mn (–0.18)
pH	(+) **K (0.75)**; **Ni (0.64)**; Mo (0.56); P (0.50); Mg (0.49); Mn (0.36); DWR (0.33); Ca (0.28); Fe (0.27); Zn (0.23); Cu (0.07); B (0.02) (-) Na (–0.43); Cl (–0.36); S (–0.27)
DWR	(+) **K (0.63)**; Cl (0.45); S (0.43); Na (0.40); Mg (0.34); pH (0.33); Fe (0.30); Ni (0.21); Mo (0.20); Zn (0.17); B (0.05); Ca (0.04); P (0.01) (-) Mn (–0.29); Cu (–0.12)

[a] *The significant R^2 values at 95% confidence level are: ≥0.63 and ≤–0.63 for 8 variables (in bold font).*
Abbreviation: DWR, dry, water-soluble residue.

B; (2) K with Ni and Mo; (3) P with Fe, Zn, and Ni; and (4) Na with Cl and S (Fig. 1). Such associations indicate favourable BAs for producing of different fertilizing products, especially multi-nutrients.

The yield of DWR fraction from the 8 BAs studied (Table 1) is 4–45% (mean 27%), which specifies sea saline and brine mineralization character according to the classification for natural waters (Perelman, 1989). The decreasing order of DWR yields from BAs is as follows: CCA > MMA > WSA > SSA > SGA > BCA > PPA > RHA. The water-soluble fraction of BA contains various nutrient components which are bioavailable for plants. For example, the reference data for a set of different woody and straw BAs (Vassilev and Vassileva, 2019 and references therein) show that significant proportions of NEs such as Cl, S, K, Na, Mn, Ni, Zn, Mo, Mg, Ca, Cu, and P may occur in water-soluble forms (Table 6). However, CEs such as Cd, Co, Cr, Hg, and Pb may also occur in such mobile forms (Table 6). Another set of woody BAs revealed similar releases of elements, namely K, S,

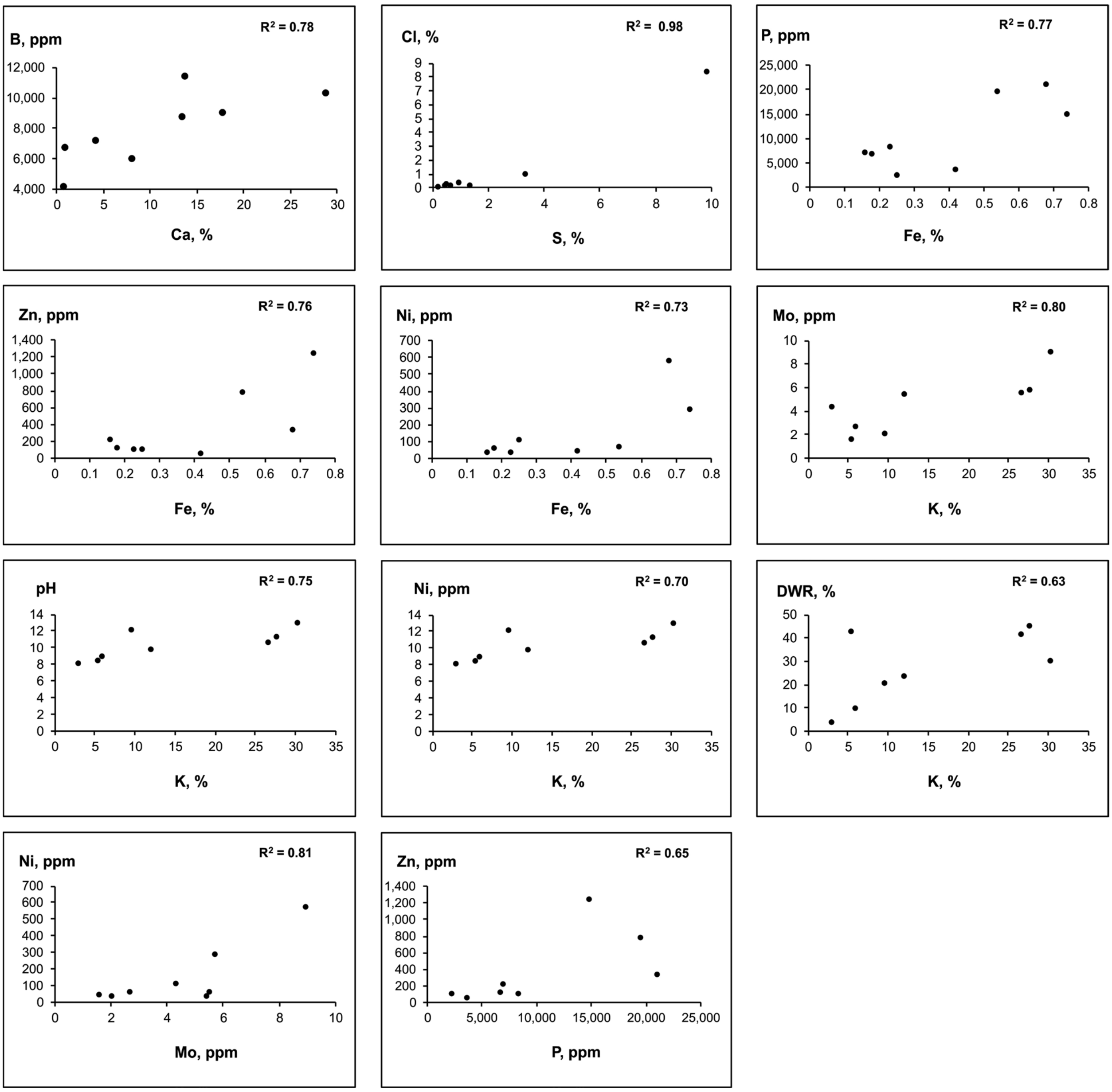

Fig. 1. Correlation trends among contents of nutrient elements and values of some characteristics for 8 biomass ashes.
Abbreviations: DWR, dry, water-soluble residue.

Table 6
Proportions of 20 water-soluble nutrient and contaminant elements leached from various biomass ashes, %

Element	Biomass ash		
	Minimum	Maximum	Mean
Cl	8	99	68
S	16	97	58
K	2	98	44
Na	0	100	36
Mn	0	46	10
Ni	0	18	10
Cd	0	49	8
Co	0	15	8
Cr	0	30	8
Zn	0	44	8
Mo	Trace	12	6
Mg	0	39	4
Pb	Trace	15	4
Ca	0	20	3
Cu	0	10	3
P	0	15	2
Fe	0	1	<1
Hg			Trace
As			0
B			0

Na, and Ca at 40–100%, followed by Cr, Mg, Zn, Cd, Co, Fe, Pb, Mn, and P at <5–18% (Maresca *et al.*, 2018). DWR has significant positive correlation with K, and relatively strong positive correlations with pH and other mobile elements such as Cl, S, Na, and Mg (Table 5). The reason for the high DWR contents in BAs is the intensive formation of water-soluble inorganic matter generated from both organic and inorganic matter during biomass combustion at 500 °C. The diverse phase-mineral transformations among the inorganic matter during biomass combustion are the reason for such differences as discussed elsewhere (Vassilev *et al.*, 2013c; Vassilev *et al.*, 2014a). For example, BAs enriched in salts such as carbonates, oxyhydroxides, phosphates, sulphates, and chlorides increase DWR yields (Table 2).

The pH values of the 8 BA leachates are 8.1–12.9 (mean 10.3), confirming their moderately to highly alkaline character (Table 1). The decreasing order of pH values for these BA solutions is: SSA > BCA > CCA > WSA > SGA > PPA > MMA > RHA. The pH characteristic has significant positive correlation with K and Ni, and relatively strong positive correlations with DWR, Mo, P, Mg, and Mn. The increased pH value reflects the intensive formation mostly of water-soluble alkaline-earth and alkaline oxyhydroxides and carbonates in BAs (Vassilev and Vassileva, 2019). It is well known that the water solubility for most elements in BAs is pH sensitive. For example, the more alkaline character of BAs causes greater release of oxyanionic-forming species of nutrient B and Mo, and lower mobility of a large number of species containing nutrient Cu, Fe, Mn, Ni, and Zn (Izquierdo and Querol, 2012). The reference data (Vassilev and Vassileva, 2019) also show that electrical conductivity of water leachates from different BAs varies between 3.0 and 49.5 mS cm^{-1} (mean 20.2 mS cm^{-1}).

The summarized data show that the phase-mineral composition and properties of the studied BAs are highly variable and depend mostly on the type of combusted biomass. Different modes of NEs occurrence are involved in this BA system; however, these elements associate significantly with unstable, water-soluble and bioavailable Ca, Mg, K and Na chlorides, sulphates, oxyhydroxides, carbonates, and phosphates.

Technological and ecological significance of nutrient and contaminant elements in biomass ashes

The present data (Table 1) show that the 8 BAs studied are normally enriched in many NEs, the pH values of BA leachates have alkaline character, whereas the yield of DWR fractions from these combustion products is normally high. These results are favourable for BA use as fertilizing products such as inorganic macronutrient and micronutrient fertilizers, liming material, soil improver or plant biostimulant.

The elemental data (Tables 1, 3 and 4) reveal that the concentrations of NEs such as B, Ca, Cl, Cu, K, P, S, and Zn, and, to a lesser extent, Mg, Mn, Mo, Na, and Ni in BAs, are more enriched in BA than in soil. Hence, this combustion product is perspective for producing of inorganic macronutrient, micronutrient and especially combined fertilizers because these essential elements occur significantly in unstable, water-soluble and bioavailable Ca, Mg, K and Na salts in BAs (Table 2). Strong associations among NEs were also found such as Ca-Mn-B, K-Ni-Mo, P-Fe-Zn-Ni, and Na-Cl-S, which are important for combined fertilizing products with a possible prolonging nutrient effect. Additionally, six of NEs in BA (B, Cu, Mg, Mn, Ni, and P) are also critical elements for industry of EU and some of them could also be perspective for recycling and subsequent non-agricultural utilization because they are crucial for a wide set of other strategic industrial sectors. The recovery of these elements can include numerous procedures such as: (1) thermal treatment; (2) dry or wet separation processes using grinding, sieving, flotation, and leaching (by water and acidic or alkaline solutions); and (3) concentration and purification (precipitation and extraction) by ion exchange, selective adsorption, membranes, additives, and other procedures (Vassilev *et al.*, 2023).

The pH values of 8 BA leachates have alkaline character (8.1–12.9, mean 10.3), whereas the yield of DWR fractions from these combustion products is high (4–45%, mean 27%), which are favourable for BA application as fertilizing products. It is estimated that acidic soils cover >70% of potentially arable land globally as the surface layer in topsoil horizons in croplands, pastures and forests has pH of 4.2–5.8 (Ondrasek *et al.*, 2021). Such an acidity reduces the availability of nutrients, decreases the high yield and quality of food/feed production (Ondrasek *et al.*, 2021) and increases the mobility of some dangerous heavy metals (Izquierdo and Querol, 2012). In contrast, the alkaline character of soil provoked by liming effect of BA promotes: (1) nutrient cycling; (2) input of base cations; (3) acid neutralizing potential; (4) higher salinity (electrical conductivity); (5) mineral weathering (dissolution of aluminosilicates and their dispersion and illuviation); (6) lower acidic leaching of hazardous elements from soil and their less mobilisation and bioavailability; (7) reduced Al, Mn and Fe plant toxicity by decreasing the exchangeable contents of these ions in soil; (8) enhanced biological activities and better environment to some microorganisms; and (9) capture and storage of atmospheric CO_2 and improved texture, aeration and water holding capacity (Park *et al.*, 2005; Vassilev *et al.*, 2013b; Vassilev *et al.*, 2015; Ondrasek *et al.*, 2021; Albuquerque *et al.*, 2022; Cruz *et al.*, 2023; Rouhani *et al.*, 2024). The capability of a liming agent to neutralize soil acidity depends on the presence of water-soluble and hydrolysable oxyhydroxides, carbonates, sulphates, phosphates, and chlorides, which are characteristic of the BAs studied (Table 2). For instance, a conversion of hydroxides into carbonates occurs due to the CO_2 content in air when BA is spread on the soil. Following this, the pH value of the ash will decrease to a neutral value and the pH value of the soil will increase. However, each BA source must be carefully analysed before land applications.

Table 7 shows the limit values of minimum nutrient contents and maximum contaminant concentrations of elements in BA according to the EU Fertilizing Products Regulation (EU, 2019) for inorganic macronutrient and micronutrient fertilizers, liming material, soil improver or plant biostimulant. The mean contents of these elements in the 8 BAs

Table 7

Limit values of 19 nutrient and contaminant elements according to the Regulation of the European Parliament (EU, 2019) for inorganic fertilizing products. Mean contents in 8 biomass ashes (BAs) are also given, ppm (indicated otherwise)

Element	Macronutrient fertilizer	Micronutrient fertilizer	Liming material	Soil improver	Plant biostimulant	8 BAs (mean)
As	<40	<40	<40	<40	<40	6.3
B		>100				7857
Ca (%)	>1.1		>10.7			11.1
Cd	<3	<3	<2	<1.5	<1.5	5.9
Co		>20				2.8
Cr (VI)	<2	<2	<2	<2	<2	384 (total)
Cu	<600	>100	<300	<300	<600	232
Fe (%)		>0.5				0.4
Hg	<1	<1	<1	<1	<1	0.02
K (%)	>2.5					15.1
Mg (%)	>0.9					2.2
Mn		>1000				1862
Mo		>10				4.5
Na (%)	>0.7(<29.6)					1.2
Ni	<100	<100	<90	<100	<50	151
P (%)	>1.3					1.0
Pb	<120	<120	<120	<120	<120	20.7
S (%)	>0.6					2.2
Zn	<1500	>100	<800	<800	<1500	366

studied are also given in Table 7 based on Table 1 and (Vassilev *et al.*, 2014b; Vassilev *et al.*, 2024) just for an overall comparison. In general, most elements in the studied BAs fulfilled these limits, excluding some problematic concentrations of Cd, Co, Fe, Mo, Ni, P, and probably Cr for some specific fertilizing products (Table 7). There are also government legislations and regulations with similar, lower or higher limit values of NEs and CEs in BA for soil application in some European countries (Sarenbo, 2009; Viana *et al.*, 2012; Silva *et al.*, 2019; Tosti *et al.*, 2019; Ondrasek *et al.*, 2021; Rouhani *et al.*, 2024). For example, the summarized guideline values for soil application of BA in agriculture and forestry for 6 European countries (Austria, Denmark, Finland, Portugal, Spain, and Sweden) show the following limits for:

(1) Nutrient elements: >6–12.5% for Ca, >1.5% for Mg, >1–2% for K + P, >3% for K, >0.7% for P, and >0.05% for Zn.

(2) Contaminant elements: <20–30 ppm for As, <800 ppm for B, <1.5–40 ppm for Cd, <100 ppm for Co, <100–1500 ppm for Cr, <250–1750 ppm for Cu, <0.8–3 ppm for Hg, <30–400 ppm for Ni, <100–1200 ppm for Pb, and <1000–7000 ppm for Zn (Viana *et al.*, 2012; Tosti *et al.*, 2019).

Overall, most elements in the studied BAs also fulfilled these limits, excluding the dangerous contents of Cd, Cr, and Ni (Table 7); however, these limits vary in a wide range in these regulations. Certainly, specific BAs (Table 1) show variable nutrient and contaminant concentrations that fulfil or not the limit values for different fertilizing products (Table 7).

The future large-scale BA application as fertilizing products may create new environmental and technological concerns related to the fate of some water-soluble phases and elements in soil and biomass. These issues include potentially serious problems related to: (1) unavailable nutrients as water-insoluble glass, silicates, phosphates, and char; (2) hazardous heavy metals in/on mobile inorganic phases; (3) polluted char with polychlorinated dioxins and furans, and polycyclic aromatic hydrocarbons; (4) groundwater contamination; (5) pH shock and chemical burning damage to plants; (6) disturbing the microorganisms; (7) extra salinity problems; (8) dust emissions; (9) ash swelling and obstructing soil pores; and (10) extra accumulation of N, P, K, Na, and other plant nutrients causing eutrophication (Vassilev *et al.*, 2015; Cruz *et al.*, 2019; Albuquerque *et al.*, 2022). For instance, there are indications that significant proportions of the nutrients are present as water-insoluble phases (glass, silicates, phosphates, char), while other dangerous trace elements such as As, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn can be present in water-soluble phases in BA due to their surface enrichment in mobile salts on the inert (immobile) ash particles (Cohen and Dunn, 2004; Obernberger *et al.*, 2006; Koppejan and van Loo, 2008; Vassilev *et al.*, 2013b; Tosti *et al.*, 2019). This is a result of intensive volatilisation of such trace elements during biomass combustion and their subsequent homogeneous and heterogeneous condensation and precipitation on the surface of more stable ash particles during cooling of flue gas emissions (Vassilev *et al.*, 2013b). For example, the present data show that dangerous concentrations of Cd, Co, Cr, Mo, and Ni in specific BAs can be above the limits for fertilizing products (Tables 1 and 7, and see above). Therefore, in many cases BA cannot be directly applied to soils and certain preliminary physical and chemical processing is required to improve properties and reduce environmental risks. In this case the separation, granulation, pelletizing, stabilization, and/or hardening of BA were proven effective to improve the physico-chemical stability, neutralizing capacity, and leaching of elements, as well as to reduce pH and electrical conductivity in soil, particularly during long-term and slow-release fertilizer applications (Steenari and Lindqvist, 1997; Cruz *et al.*, 2019, 2023; Silva *et al.*, 2019). For instance, BA is granulated and considered stabilized for soil application when Ca and Mg oxyhydroxides such as lime, periclase, portlandite, and brucite become calcite and magnesite following the reaction with atmospheric moisture and CO_2 and subsequent self-hardening of the material.

The above own and reference data show that the micronutrient and contaminant elements in BA require a special attention for soil applications. For example, some micronutrient elements (Cu, Mn, Ni, and Zn) can be hazardous depending on their concentration in BA. The present study also shows that the hazardous Cd and Cr in some BAs (Table 1) have contents much higher than their respective Clarke values for soils which are 0.06 ppm for Cd and 100 ppm for Cr (Bowen, 1966). Therefore, the concentration and leaching of pollutants is a serious concern during BA application as fertilizing products. For instance, it was found that BA applied to a soil increased the concentration of Cr, Mo, and Zn in soil solution to a level of concern (Tosti *et al.*, 2019). It was also identified that the concentrations of Cd, Pb, and Zn in some wood BAs exceed the upper limits for soil application (Reimann *et al.*, 2008) as the potential release of Cd from such BAs was found to be the most critical concern (Maresca *et al.*, 2017). Furthermore, it was identified the mobilisation of As, Cd, Cr, Mn, and Zn in soils treated by household and greenhouse ashes is significant and their contents are higher than those in soils (Pędziwiatr, 2025). Finally, some BAs generated from contaminated biomass such as municipal solid waste, refuse-derived fuel, sewage sludge, demolition wood and other industrial organic wastes should be avoided for soil application to a maximum extent, because they are commonly highly contaminated with potentially hazardous trace elements (Vassilev and Braekman-Danheux, 1999; Vassilev *et al.*, 2013b). In such cases the BA soil utilization requires preliminary ash processing to reduce the heavy metals toward safe levels. Hence, it is necessary to consider whether BAs should be treated as dangerous waste rather than as fertilizers (Reimann *et al.*, 2008). Nevertheless, there is no legislation for the strict limit values of nutrient and contaminant elements in BA leachates from a fertilization point of view to fulfilled any criteria. The water-extractable proportions of elements from BA and their release in time are very important to predict the supply of bioavailable NEs or heavy metals for crops during the growing season. Furthermore, the concentration and leaching behavior of: (1) additional potentially toxic elements such as Ag, Bi, F, Sb, Se, Sn, Tl, V, radioactive elements and others; and (2) nutritionally essential elements in high doses; should also be included in these regulations. Therefore, each BA application to soil should be supplemented by the establishment of new and suitable technical, health safety and risk assessment protocols and standards. Finally, the concentrations of nutrient and contaminant elements in BAs vary significantly and each BA needs to be studied on a case-by-case basis.

Despite above limitations and concerns, BA as a waste product is favourable resource for producing of different fertilizing products, especially as multi-nutrient (complex) sources with or without additional processing. There are examples about the successful soil application of BAs. For instance, the use of BAs from bagasse and rice husks considerably increased the wheat and rice grains yield by 24–25%, and 10–11%, respectively, whereas no substantial impact on the levels of potentially toxic elements in the grains and straw (Rouhani *et al.*, 2024). Another study shows that the application of BAs from palm seeds and tropical wood chips to soil promoted positive effects on biomass production (62%) and increased uptake of macronutrients such as P (306%), Ca (181%), Mg (131%), and K (38%), as well as micronutrients, namely B, Cu, Fe, and Mo (Albuquerque *et al.*, 2022). It was also found that the soil amended by different BAs had a positive effect on plants growth due to increase of pH and availability of Ca, K, Mg, Na, Cl, P, and B, and a decrease in Al and Mn toxicity (Demeyer *et al.*, 2001; Park *et al.*, 2005; Tosti *et al.*, 2019). Finally, the BA utilization as fertilizing products avoids the need of landfilling and can provide an efficient way to recycle waste products from renewable resources into valuable nutrient supplements using sustainable practices that reduce carbon emissions. The knowledge about the composition, properties and behavior of BA is the first stage toward a circular economic systems integrating waste management approaches and a future detailed research of multifunctional BA utilization in different industries is required.

CONCLUSIONS

Eight biomass ashes (BAs) generated from agricultural, herbaceous, woody and aquatic biomass types were studied for the occurrence of 14 nutrient elements (NEs) and 6 contaminant elements (CEs) to evaluate their significance for potential soil fertilization. The following conclusions can be made according to these data.

(1) The contents of NEs in BAs are highly variable and depend mostly on the type of combusted biomass. The inorganic matter of BAs comprises both amorphous matter and crystalline constituents represented by different minerals among carbonates, silicates, chlorides, sulphates, oxyhydroxides, phosphates, as well as trace of organic matter as char.

(2) The concentrations of NEs such as B, Ca, Cl, Cu, K, P, S, and Zn, and, to a lesser extent, Mg, Mn, Mo, Na, and Ni in BAs are particularly perspective for the application of these combustion products for producing of fertilizing products, namely macronutrient, micronutrient, and combined fertilizers, as well as liming materials, soil improvers or plant biostimulants. Six of these NEs in BAs (B, Cu, Mg, Mn, Ni, and P) are also critical elements for EU industry and some of them could also be perspective for recycling and subsequent utilization for other purposes.

(3) BAs have high yields of water-soluble solutions with alkaline character, which are favourable for BA use as fertilizing products. NEs such as Ca, Cl, K, Mg, Na, P, and S occur in specific and discrete minerals in BA and these elements associate significantly with unstable, water-soluble and bioavailable salts, namely chlorides, sulphates, oxyhydroxides,

carbonates, and phosphates. The strong associations found among NEs, namely: (1) Ca with Mn and B; (2) K with Ni and Mo; (3) P with Fe, Zn, and Ni; and (4) Na with Cl and S; are beneficial for producing of multi-nutrients.

(4) Various NEs and CEs in BAs fulfilled the available regulation limits, excluding some problematic concentrations of Cd, Co, Cr, Fe, Mo, Ni, and P for specific BAs and fertilizing products. Therefore, each BA needs to be studied on a case-by-case basis for that purpose.

(5) The establishment of advanced regulatory framework for BA utilization as fertilizing products is required to generate strict limit values of NEs and CEs in BA leachates. The water-extractable proportions of elements from BA and their release in time are very important to predict the supply of bioavailable NEs or heavy metals for crops and the establishment of new and suitable technical, health safety and risk assessment protocols and standards are crucial.

Acknowledgements

The authors gratefully acknowledge the financial support of the Project No BG-RRP-2.017-0032-C01 “Sustainable utilization of critical elements for environmental products based on phosphates, biomass and technogenic materials”. The project is financed by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria. The authors also thank to reviewers Assoc. Prof. P. Knutsson and Prof. I. Kostova for their useful comments.

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