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Effect of Ash from Biomass Combustion on the Selected Elements Accumulation in Plants and Soil

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ABSTRACT

Ashes from biomass combustion (BAs) are waste materials that contain valuable nutrients, making them suitable for reuse in plant fertilization. The application of ash positively impacts soil properties, including the reduction of excessive acidification, which enhances nutrient absorption. However, the use of ash can also introduce potentially toxic elements into the soil in excessive amounts. This study analyzed the effect of different doses of BAs on the accumulation of zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr), lead (Pb), and cadmium (Cd) in the surface layer of Haplic Luvisol soil and in various parts of spring barley plants. The research was conducted over three years under field experiment conditions. Throughout the three-year study period, no significant changes were observed in the content of individual elements in the soil or in various parts of the spring barley plants. The analyzed elements tended to accumulate more in the roots of the plants than in their above-ground parts. When considering the average content of individual elements for the entire study period, no significant increase was noted in their levels within the analyzed soil. However, when examining each year of the experiment separately, significant dynamics in the content of individual elements in both plants and soil were identified. These fluctuations were likely influenced by variations in weather conditions, as the highest concentrations of the analyzed elements were typically recorded in the second year of the study, which coincided with the highest total rainfall of 792.4 mm. The findings indicate that analyzing changes in the content of elements introduced via biomass combustion ashes necessitates comprehensive studies conducted under both controlled and real-world conditions. Without such thorough investigations, conclusions regarding the release of components contained in BAs, particularly concerning their potential toxicity, may be misleading.

Keywords: ash from biomass combustion, microelements, trace element, spring barley, soil.

INTRODUCTION

Biomass combustion ash (BAs), derived from burning organic materials such as wood and agricultural residues, represents a significant waste stream that can be repurposed for agricultural use. The application of BAs in agriculture has garnered increasing attention due to their potential benefits for soil health and crop production, as well as their role in sustainable waste management. Numerous studies highlight the nutrient-rich profile of biomass ash, which typically contains essential macronutrients such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), and magnesium

(Mg). The presence of these nutrients contributes to improved soil fertility, enhanced plant growth, and consequently, increased agricultural yields (Demeyer et al., 2001; Wang et al., 2024).

In addition to the primary nutrients, BAs can also supply trace elements such as iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) (Szostek et al., 2023; Wierzbowska et al., 2020). Furthermore, BAs can mitigate soil acidity, improve soil structure, and increase moisture retention (Cruz-Paredes et al., 2017; Panda R.B. & Biswal T., 2018). The repurposing of biomass ash in agriculture aligns with the principles of a circular economy and sustainable development. By recycling waste materials, the use of BAs can reduce landfill utilization and decrease greenhouse gas emissions associated with the decomposition of organic waste. Additionally, incorporating BAs into soil can lessen the need for synthetic fertilizers, thereby minimizing the environmental impact of agricultural practices (Da Costa et al., 2020; Mendes et al., 2021; Wierzbowska et al., 2020).

Despite the potential benefits, the application of biomass ash in agriculture is not without challenges. A primary concern is the presence of potentially toxic elements, such as heavy metals (e.g., lead, cadmium, chromium), which can accumulate in the soil and potentially transfer to crops, posing health risks for consumers (Morrison et al., 2019; Qu et al., 2022). Moreover, if trace elements (Fe, Mn, Zn, Cu) occur in elevated concentrations, they can become toxic. This aspect must be carefully considered in terms of soil environmental protection. The variability in the chemical composition of BAs is another challenge in developing uniform guidelines for their application, as it can depend on factors such as the type of biomass burned and the combustion conditions. As such, the chemical composition of ashes should be comprehensively analyzed before agricultural use (Schiemenz & Eichler-Löbermann, 2010; Shi et al., 2017a).

The bioavailability of potentially toxic elements in BAs is influenced by their solubility in soil solutions. Previous studies suggest that the application of small doses of BAs carries minimal risk, associated with their low concentration of mobile and bioavailable metals. However, changing environmental conditions may trigger the release of these elements, necessitating careful environmental impact assessments of these wastes (Jukić et al., 2017; Szostek et al., 2023). Additionally, the potential redistribution of toxic elements from ash to the natural environment requires thorough exploration based on extensive field studies under real conditions. Currently, such studies constitute a small fraction of existing research, which often relies on short-term laboratory experiments (Yu et al., 2019).

Another critical consideration is that BAs may contain significant concentrations of readily soluble salts, particularly K, Mg, and Ca. When added to soil, these salts can contribute to salinization and excessive alkalinity, leading to various adverse effects. Furthermore, high levels of elements such as K, Mg, or Ca from ash may interfere with the uptake of other nutrients by plants, affecting their growth and development (Huotari et al., 2011; Kramar, 2020; Trivedi et al., 2016; Vassilev et al., 2013). These factors need to be comprehensively evaluated when assessing the long-term potential impact of BAs on soil environments (Zając et al., 2018).

Given the above, the aim of our research was to evaluate the effects of BAs on the concentrations of Zn, Cu, Cr, Ni, Pb, and Cd in both the aboveground and underground biomass of spring barley, as well as changes in the concentrations of these elements in the surface layer of Haplic Podzol soil over a three-year field experiment.

MATERIALS AND METHODS

Field experiment design

The effect of biomass combustion ash (BAs) on the accumulation of Zn, Mn, Cu, Cr, Ni, Pb and Cd in different parts of spring barley plants and in the surface soil layer (0-30 cm), was analysed based on a 3-year field experiment (2019-2021). The experiment was setup using the randomised block method with three repetitions. Each block corresponded to a given experimental variant (in total, 21 blocks were separated with a total area of 1 ha). During the study period, potatoes, winter rapeseed, and spring barley were cultivated simultaneously in the experimental area. In each year of the experiment, the plants were moved to the next field strip. The presented manuscript describes only the results for spring barley (*Hordeum vulgare* L.) of the RGT Planet variety 9FR, breeder RAGT 2n; brewery type) (Pycia et al., 2023). The detailed scheme of conducted experiment was previously described in earlier peppers (Szostek et al., 2023; Szpunar-Krok et al., 2022).

The experiment was carried out on Haplic luvisol soil, with a silt granulometric composition (Si). The detailed characteristics of the soil before the experiment and the properties of the BAs used in the experiment are presented in Table 1.

In the layer of 0–30 cm, the Haplic luvisol soil used in the experiment was characterized by a slightly acidic reaction (pH=6.64), low salinity (EC=121.5 µS cm^{-1}) and natural concentration of Zn, Cu, Cr, Ni, Pb and Cd (Table 1). The BAs used in the experiment were characterized by an alkaline reaction (pH=12.83), high salinity (EC=8810 µS cm^{-1}). In BAs used in experiment, the concentration of analyzed elements was arranged according to the following series of decreasing values: Cu>Zn>Pb>Cr>Ni>Cd.

The variable factor analyzed in the experiment was the dose of BAa. The doses of BAs were determined on the content of K, which was present in the highest amount (Table 1). Due to rational K fertilization, the experiment assumed the use of 5 doses of BAs, in the amount of 0.5 (D1), 1.0 (D2), 1.5 (D3), 2.0 (D4) and 2.5 (D5) Mg ha^{-1}, which corresponded to the application of K fertilization (in K_2O form) in the amount of 100, 200, 300, 400 and 500 kg ha^{-1}, respectively. The effect of BAs on the accumulation of microelements and toxic trace elements in soil and plants was compared with two control objects. The first included only mineral fertilization of N and P, which was the same for all experimental treatments (Control). In the second control variant, in addition to the mineral fertilization with N and P, mineral fertilization with K was also applied, and this element was supplied with potassium salt (NPK object).

Meteorological condition during the study period (2019–2021)

The course of weather conditions in 2019–2021 was characterised based on monthly precipitation totals and average air temperatures (Table 2). Total precipitation in 2019, 2020 and 2021 was 661.3, 792.4 and 610.3 mm, respectively, with mean annual air temperatures of 10.6, 8.4 and 7.0°C. In the spring barley growing season (April

Table 1. Physicochemical properties of the soil and ash from biomass combustion used in the experiment (Mean±SE)

Parameter	Unit	Soil	BAs
Sand	%	17±2	-
Silt		75±4	-
Clay		8±2	-
pH	H_2O	6.64±0.07	12.83±0.37
EC	µS cm^{-1}	121.5±1.95	8810±240
Zn	mg kg^{-1}	26.03±1.45	423±11
Cu		6.38±0.08	536±28
Cr		21.68±1.07	48.4±2.9
Ni		11.76±1.77	20.3±1.1
Pb		11.35±1.83	130±3.7
Cd		0.16±0.02	2.68±0.81

Table 2. Meteorological conditions during the study period (2019–2021)

Parameter	Year	Jan	Feb	Mar	Apr	May	Jun	Jul.	Aug	Sep	Oct	Nov.	Dec.
Mean air temperature (˚C)	2019	-2.5	3.2	5.7	10.4	13.4	20.8	19.0	20.3	16.1	11.9	6.1	2.7
	2020	0.2	2.3	2.3	6.9	9.7	17.4	18.1	17.9	13.1	9.1	3.5	0.2
	2021	-1.2	-3.6	1.1	4.9	11.6	17.8	20.2	16.4	10.9	5.7	2.6	-2.3
	1980-2015	-2.3	-1.4	2.6	8.8	13.0	15.2	17.5	17.2	13.0	8.7	3.2	-0.5
Sum of precipitation (mm)	2019	42.9	12.9	26.3	46.7	158.6	25.4	60.2	101.9	33.7	37.9	57.4	57.4
	2020	14.2	54.3	27.3	17.5	122.6	125.0	85.7	89.2	109.2	78.9	16.2	52.3
	2021	72.0	53.1	8.5	46.5	49.8	57.4	65.7	93.1	84.1	0.3	38.6	41.2
	1980-2015	31.5	29.7	37.8	42.1	42.1	75.1	90.4	58.8	62.1	43.7	34.2	34.1

- July) in 2019, 2020 and 2021, 290.9, 350.8 and 219.4 mm of precipitation occurred, respectively. However, the distribution of precipitation in individual months was uneven. The highest rainfall occurred in May and August 2019 and in May and June 2020. The average air temperature during the spring barley growing season in 2019 was 2.3°C higher, in 2020 it was 0.6°C lower, and in 2021 it was the long-term average (13.6°C).

Laboratory analysis

In each year of the experiment, plant and soil samples were collected after the end of the spring barley growing season.

From each plot, 30 spring barley plants were collected, immediately before harvesting in the phase of full maturity. After transport to the laboratory, the analyzed parts of the plants were separated: grain, straw and roots. The separated parts of the plants were dried in a laboratory dryer at 45˚C with forced air circulation and then homogenized. About 1 g of the obtained plants sample was mineralized in 60% HNO_3. The contents of Zn, Cu, Ni, Cr, Pb and Cd in the obtained solutions were determined by atomic absorption spectrometry using a HITACHI Z-2000 apparatus (Tokyo, Japan).

Soil samples for laboratory analysis were collected in accordance with the methodology adopted in soil science research (Page, 1982). Samples were collected from a layer to a depth of 30 cm. After being brought to the laboratory, the soil samples were air-dried for about 2 weeks, then crushed using a PULVERISERRE 8 soil deagglomeratore from Fritsch GmbH and sieved through laboratory sieves with a mesh diameter of 2 mm. The contents of total forms of Zn, Cu, Ni, Cr, Pb and Cd in the samples prepared in this way were determined by atomic absorption spectrometry using a HITACHI Z-2000 apparatus (Tokyo, Japan), after mineralization of about 2 g of the prepared sample in 70% $HClO_4$.

Statistical analysis

The obtained results were statistically processed using the Statistica 13.3 program (StatSoft, Tulsa, OK, USA). The comparison of the contents of total forms of microelements and toxic trace elements in the soil and in plants as a result of the application of different doses of BAs was were assessed using one-way analysis of variance (ANOVA) at the significance level ($p< 0.05$) and with the Tuckey post-hoc test (HDS).

RESULTS

Changes in selected elements concentration in different parts of spring barley plants

Zinc (Zn)

Regardless of the experimental object, Zn was accumulated in the largest amounts in roots and in the smallest amounts in straw. BAs fertilization increased the Zn content in individual parts of spring barley plants. The lowest Zn contents were found in grain, straw, and spring barley roots in Control and NPK, while the highest were found in the D1 object (Fig. 1 A-C).

The Zn content in individual parts of spring barley during the study period was characterized by varied dynamics, fluctuating in the ranges of: 21.25–28.00, 7.35–16.76 and 36.85–45.97 mg kg^{-1}, for grain, straw and roots, respectively (Fig. 1 D-F). In the Control and NPK objects, the lowest Zn concentrations in grain were observed in 2019 (Fig. 1 D). Similarly in objects D1, D4, and D5. In objects D2 and D3, the Zn concentrations in the grain were the highest in 2019 and decreased in the following years. In all experimental objects, the Zn concentration in straw and roots was the highest in 2020 (Fig. 1 E, F). In turn, the lowest concentration of Zn in straw was observed in plants in 2021 and in roots in 2019 (Fig. 1 E, F). In 2019 and 2021, the concentrations of Zn in the roots were similar. However, in 2021, in all analyzed experimental objects, a significant increase in the concentration of this element was observed (Fig. 1F).

Copper (Cu)

Regardless of the experimental object, the lowest Cu content was found in straw, while the highest was found in the roots. In general, the Cu content in grain and roots was higher after the application of Bas, compared to the Control and the NPK object, and similar in the case of straw. In most cases, the differences observed between the individual experimental objects were statistically insignificant (Fig. 2. A-C).

Depending on the year of the experiment, the average Cu concentration in different parts of spring barley plants varied (Fig. 2 D-F). In

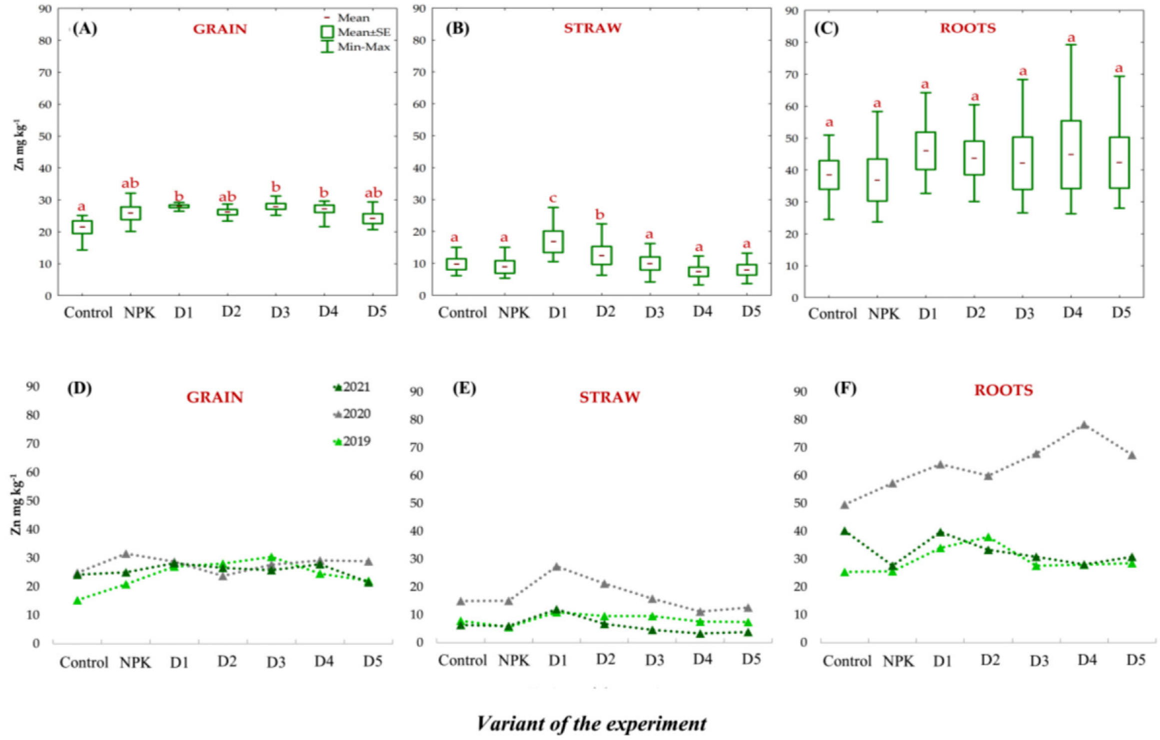

Figure 1. The mean concentration of Zn in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Zn concentration in grain (D), straw (E), and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE); Mean values ± standard error. (a-c) Identical superscripts denote no significant ($p<0.05$) differences ($p <0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 - doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

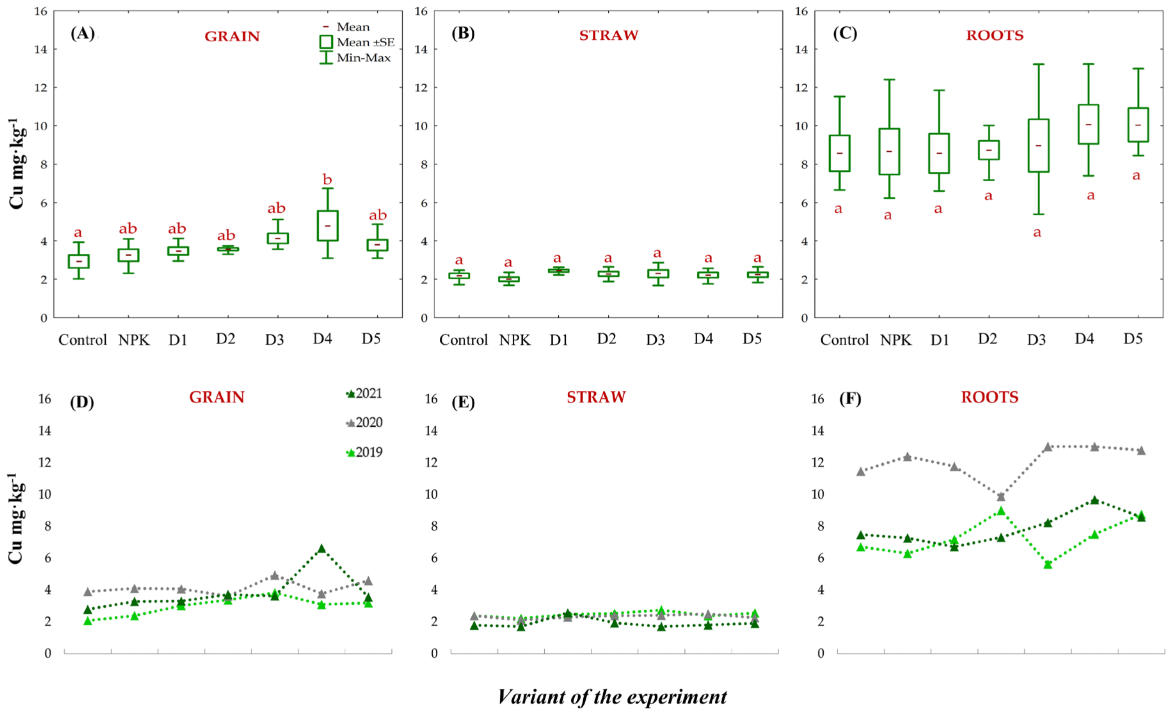

Figure 2. The mean concentration of Cu in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Cu concentration in grain (D), straw €, and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE), Mean values ± standard error. (a-c) Identical superscripts denote no significant ($p<0.05$) differences ($p <0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 – doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

general, the highest Cu content in grain was found in 2020 and the lowest in 2019. The exception was plants fertilized with the D4 dose, in which the Cu content in the grain increased successively over the years of the study, reaching the highest values in 2021 (Fig. 2 D). Although in 2021 a decrease in the Cu content in grain was observed in most of the experimental objects, the Cu content was significantly higher compared to 2019 (Fig. 2 D). Similar relationships were also observed in roots, where the Cu content was the highest in 2020 and the lowest in 2019, which was found for all experimental objects (Fig. 2 F). Contrary to grain and roots, in straw in all treatments, the highest Cu content was observed in 2019. In the following years, the Cu content decreased, reaching lower values in 2021 compared to 2019 (Fig. 2 E).

Chrome (Cr)

Cr concentration was the lowest in spring barley grain, the highest in roots (Fig. 3 A-C). The Cr content in the grain ranged from 0.94 to 1.15 mg kg^{-1}, with the lowest values found for object D5 and the highest for object D2. Despite these differences, there was no statistically significant effect of Bas on changes in Cr content in spring barley grain (Fig. 3 A). In straw, the average Cr content ranged from 2.31 to 4.41 mg kg^{-1}. After Bas application, lower Cr contents were found in all analyzed doses, compared to both Control and NPK object (Fig. 3 B). In roots, Cr content was significantly higher compared to grain and straw. Furthermore, the Cr content in roots generally increased after the application of Bas, starting from the D2 dose, and the values obtained for these treatments were higher compared to the Control and NPK treatments (Fig. 3 C).

During the study years, the content of Cr in individual parts of spring barley varied (Fig. 3 D-F). The Cr content in spring barley grain, in Control, NPK and D1, was the highest in 2020 and the lowest in 2019rst. In the D4 and D5 objects, the lowest Cr content in the grain was in 2020 and the highest in 2019. For the object D2, the lowest Cr content was characteristic of the grain collected in 2019 and the highest in 2021. In the D3 object, the highest Cr content was found in grain collected in 2020, and the lowest in 2021

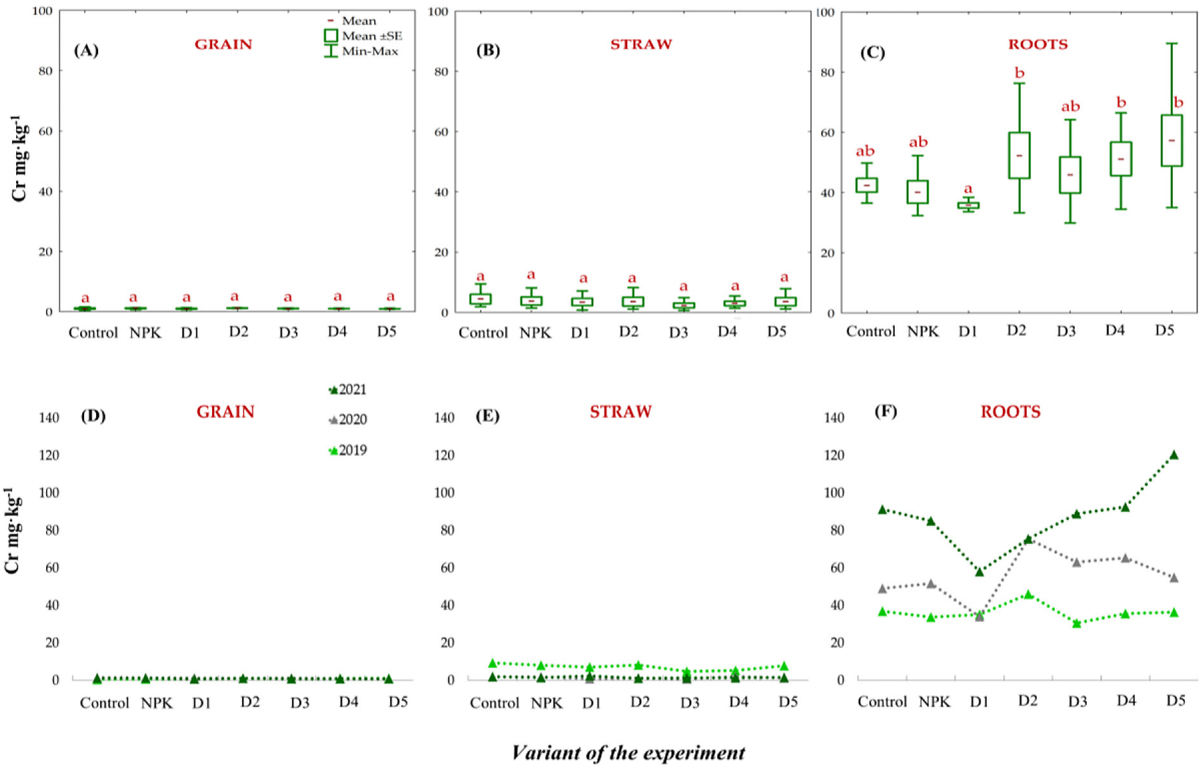

Figure 3. The mean concentration of Cr in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Ni concentration in grain (D), straw €, and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE); Mean values ± standard error. (a-c) Identical superscripts denote no significant ($p<0.05$) differences ($p <0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 – doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

(Fig. 3 D). In straw, regardless of experimental objects, significantly higher Cr content was observed in 2019, the lowest in 2020 or 2021 (Fig. 3 E). The Cr content in the roots also varied significantly during the experimental period, depending on the variant. In the case of the Control, NPK and D3 and D4, the lowest Cr content in roots was observed in the first year of the 2019, and the highest in the 2020. In D1, the highest Cr content was observed in 2021, while the lowest was observed in 2020. In D2, the highest Cr content was observed in 2020, while the lowest in 2021. In the roots of plants of object D5, the Cr content increased over the years of the study, reaching the highest values in the last year of the experiment (Fig. 3 F).

Nickel (Ni)

Regardless of the experimental object, Ni was accumulated in the smallest amounts in spring barley grain, and in the largest amounts in roots (Fig. 4 A-C). There was no clear effect of the Bas used in the experiment on changes in Ni content in grain and straw, for which the ranges of mean values determined for the entire study period were: 0.61–0.81 and 1.68–2.33 mg kg^{-1}, respectively. In grain, the lowest Ni content was found in the Control, while the highest in plants from the D5 object. In straw, the lowest Ni content was found in plants fertilized with the D4 dose, while the highest occurred in plants fertilized with traditional NPK fertilizers. In spring barley roots, the average Ni content during the study period ranged from 18.91 to 27.98 mg kg^{-1} and was the lowest in the Control, and the highest in plants from D2 object. The mean Ni content in the roots of plants fertilized with the D2 dose was significantly higher compared to the remaining experimental objects. In the remaining ones, the differences noted were statistically insignificant, although after the application of ash, the average content of this element increased compared to the Control (Fig. 4 C). The Ni concentration in grain was the lowest in the first year of the study and increased successively in the following years. The highest concentration of this elements was found in the third year of the study, which concerned all analyzed objects (Fig. 4 D). An opposite trend was observed in the case of straw. The highest Ni

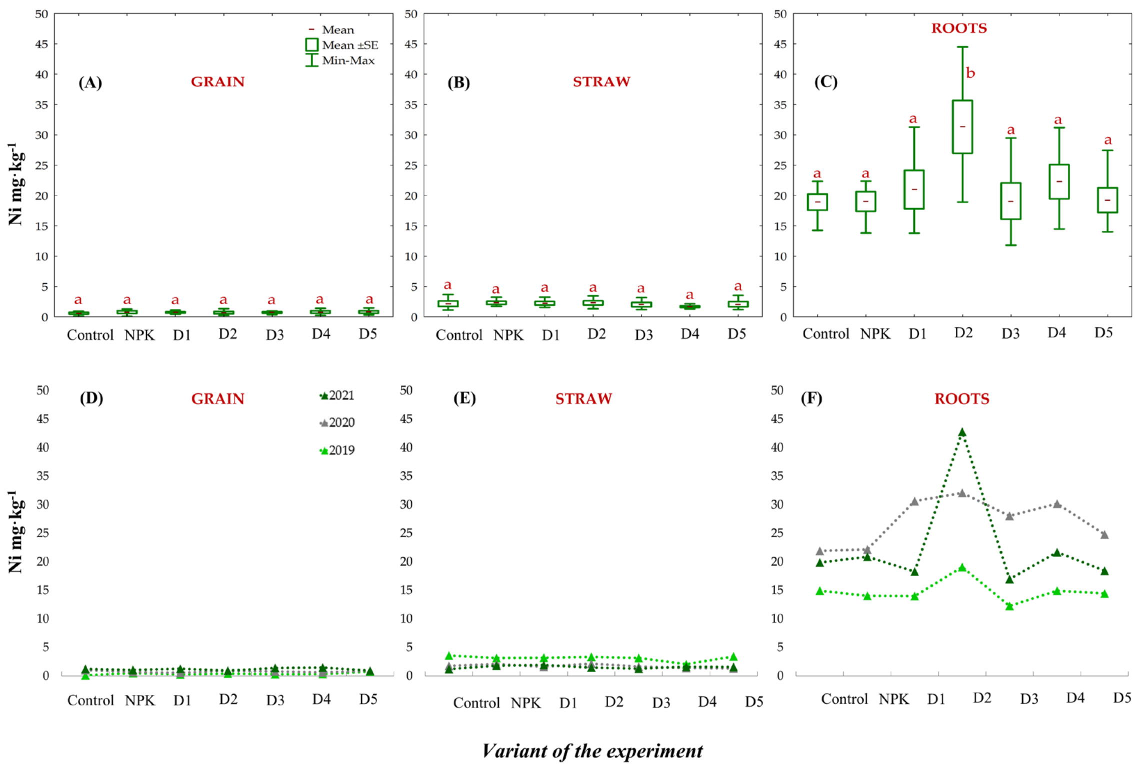

Figure 4. The mean concentration of Ni in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Ni concentration in grain (D), straw (E), and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE); Mean values ± standard error. (a-c) Identical superscripts denote no significant ($p<0.05$) differences ($p <0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 – doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

content in straw was noted in the 2019 and the lowest in the 2021. This trend did not apply to objects D1, D4, D5, in which the average Ni content was slightly higher in the 2020 (Fig. 4 E). The lowest Ni content in spring barley roots was noted in the 2019. In the 2020, the average Ni values in roots were the highest. In the 2021, except for object D2, the average Ni contents in roots were lower compared to the 2020, but remained at a higher level compared to the 2019 (Fig. 4 F).

Lead (Pb)

Similarly to the other elements, the highest Pb content was found in the roots, while the lowest in the straw (Fig. 5 A-C). No clear effect of the BAs applied on the Pb content was observed in the spring barley grain was observed (Fig. 5 A). A similar relationship was also observed in roots, although after applying the lowest doses of BAs, the average content of Pb content was higher compared to the other experimental objects (Fig. 5 C). The average Pb content in barley straw after BAs application was significantly higher in the objects on which the highest doses were applied – D4 and D5 (Fig. 5 B). In the individual years of the experiment, the concentration of Pb in the parts of the spring barley plants analyzed was varied. In grain, straw and roots, the Pb content ranged from 0.03 to 0.99, 0.04 to 0.45 and 0.28 to 6.29 mg kg^{-1}, respectively (Fig. 5 D-F). In grain after BAs application, a tendency to decrease the Pb content with increasing dose of BAs was observed, and this tendency was observed in each year of the experiment. Regardless of the experimental object, the highest content of this element was observed in 2019, while the lowest in 2021 (Fig. 5D). In straw, the highest Pb concentration was found in 2020, the lowest, similar to grain, also in 2021 (Fig. 5E). In 2021, the lowest Pb content was also found in roots. In turn, the highest Pb content in roots, similar to grain, was found in 2019 (Fig. 5F).

Cadmium (Cd)

The Cd content in spring barley grain ranged from 0.002 to 0.003 mg kg^{-1}. Compared to Control and NPK, the Cd content in the grain increased

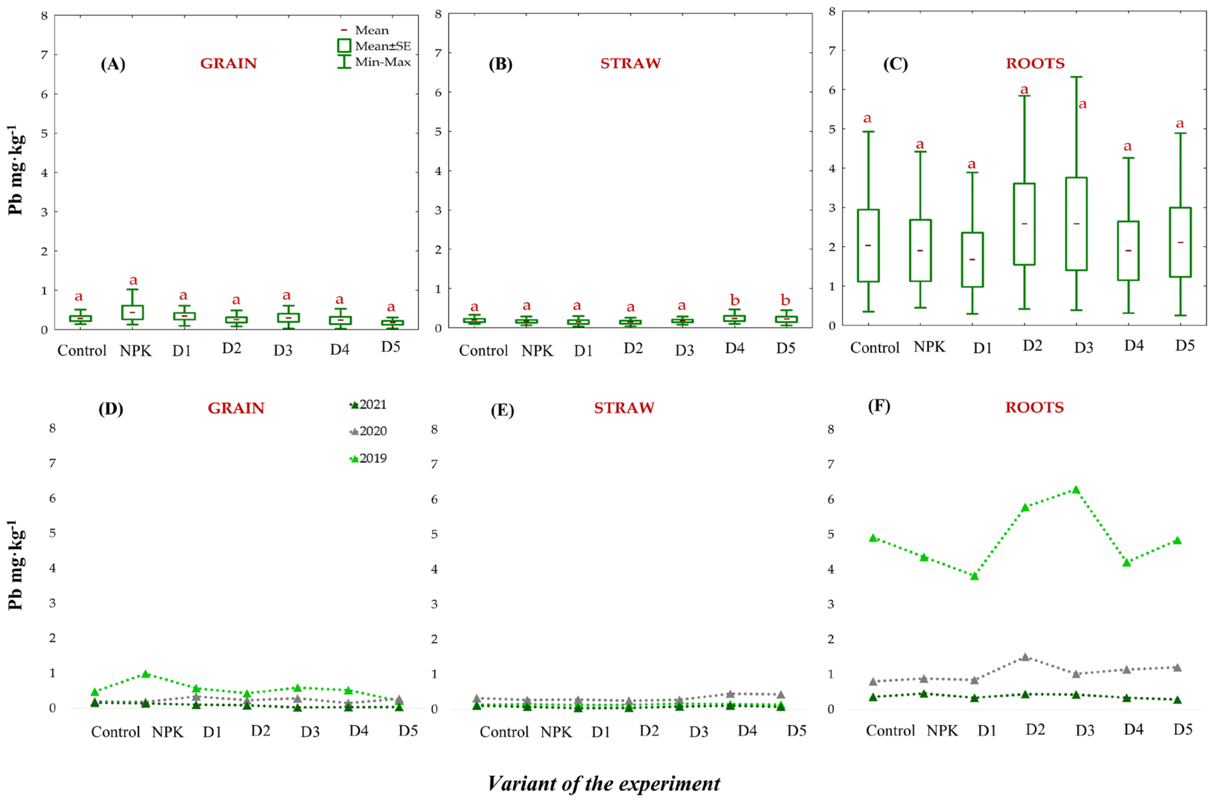

Figure 5. The mean concentration of Pb in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Pb concentration in grain (D), straw (E), and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE); Mean values ± standard error. (a,b…) Identical superscripts denote no significant ($p<0.05$) differences ($p<0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 – doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

after the application of BAs in doses D3, D4 and D5 (Fig. 6 A). In straw, an opposite trend was observed, where the Cd content was lower in the D3, D4 and D5 treatments compared to the Control and the NPK and also D1 and D2 (Fig. 6B). In roots, the Cd content was the highest compared to grain and straw, ranging from 0.008 to 0.015 mg kg^{-1}. Similarly to straw, plants fertilized with BAs at the D1 dose had the highest Cd content in the roots, while the plants fertilized with the D5 dose the lowest (Fig. 6C). The Cd concentration in the parts analyzed from spring barley plants during the experiment varied (Fig. 6 D-F). The Cd content in grain was the lowest in 2020 and the highest in 2021. In the first and second years of the study, no clear trend of increasing Cd content in the grain was observed, depending on the increase in BAs dose. This dependency was observed in 2021 (Fig. 6D). In turn, in straw, the lowest Cd content, regardless of the experimental object, was observed in 2021. On the other hand, the lowest Cd content was observed in straw collected in 2020 (Fig. 6E). In roots, the lowest concentration of Cd in all experimental objects, was observed in 2020, while the highest in 2021 (with exception for D4 and D5) (Fig. 6F).

Changes in selected elements concentration in soil

The average contents of Zn, Cu, Cr, Ni, Pb and Cd and the ranges for the years of study are summarized in Table 3.

The mean concentration of zinc (Zn) in the 0-30 cm layer of the analyzed soil was similar across all experimental objects. It is noteworthy that, regardless of the experimental object analyzed, the Zn concentration in the soil fluctuated over the study years. In general, the highest Zn concentration was observed in the soil in 2020, while the lowest occurred in 2021. A significant increase in Zn content was noted in 2019 after the application of BAs in doses D2, D3, and D5 compared to the Control and NPK treatments. In 2020, the Zn content increased compared to 2019, with the highest levels recorded for the Control

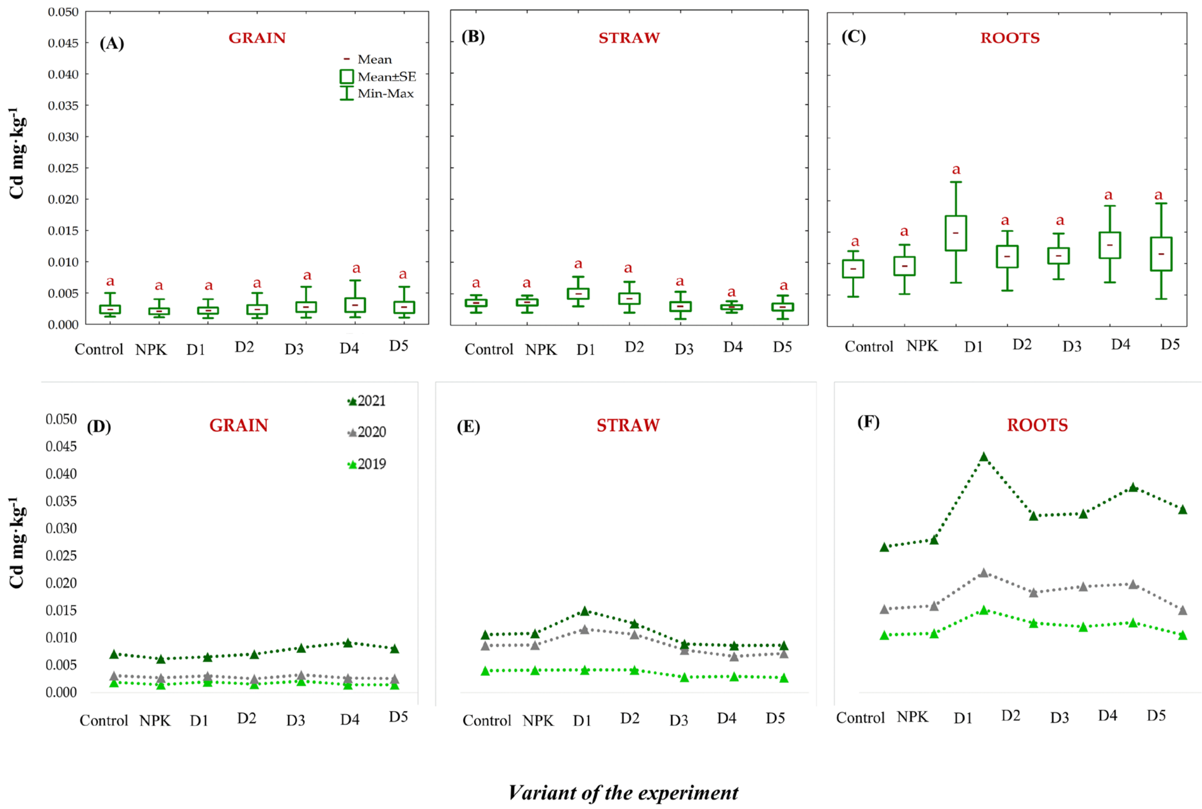

Figure 6. The mean concentration of Cd in grain (A), straw (B), and roots (C) of spring barley plants and changes in the Cd concentration in grain (D), straw (E), and roots (F) in the particularly study years, in depends on the applied fertilization (mean±SE); Mean values ± standard error. (a,b…) Identical superscripts denote no significant ($p<0.05$) differences ($p<0.05$) between experimental objects according to the post hoc Tukey HSD test. Explanation: D1-D5 – doses of biomass combustion ashes: 0.5, 1.0, 1.5, 2.0, and 2.5 Mg ha^{-1}

Table 3. Mean concentration [mg kg^{-1} DW] of elements in soil

Variant	Zn	Cu	Cr	Ni	Pb	Cd
	mg kg^{-1}					
Control	23.93^{a}±2.37 (9.24-37.25)	3.80^{a}±0.39 (1.42-5.72)	13.17^{a}±0.82 (8.22-17.14)	5.71^{a}±0.40 (3.49-8.76)	9.68^{a}±0.60 (4.87-12.27)	0.17^{ab}±0.00 (0.14-0.20
NPK	21.89^{a}±1.98 (9.72-31.47)	3.51^{a}±0.31 (1.68-5.17)	12.87^{a}±0.73 (8.50-17.14)	5.89^{a}±0.40 (3.61-8.09)	9.23^{a}±0.51 (5.53-11.40)	0.15^{a}±0.01 (0.12-0.20)
D1	21.83^{a}±1.97 (10.06-31.25)	3.42^{a}±0.21 (2.28-4.57)	13.65^{a}±0.76 (8.43-17.15)	6.39^{a}±0.32 (4.15-8.10)	9.40^{a}±0.65 (4.90-13.13)	0.18^{b} ±0.01 (0.12-0.20)
D2	21.42^{a}±1.89 (9.70-30.50)	3.39^{a}±0.26 (1.84-4.70)	13.51^{a}±0.82 (8.32-16.92)	6.24^{a}±0.37 (3.88-7.88)	9.37^{a}±0.52 (5.76-11.80)	0.19^{b}±0.01 (0.15-0.21)
D3	22.19^{a}±1.59 (12.64-28.95)	3.37^{a}±0.23 (1.77-4.20)	14.20^{a}±0.57 (11.22-17.39)	6.00^{a}±0.42 (3.58-8.01)	9.88^{a}±0.46 (6.22-12.63)	0.17^{b}±0.00 (0.15-0.20)
D4	21.36^{a}±1.62 (12.79-30.07)	3.19^{a}±0.22 (1.91-4.25)	13.48^{a}±0.57 (9.30-17.39)	5.86^{a}±0.37 (3.75-8.01)	10.29^{a}±0.73 (7.11-16.05)	0.17^{ab}±0.01 (0.12-0.20)
D5	23.35^{a}±2.07 (11.97-36.65)	3.99^{a}±0.40 (2.22-7.67)	14.79^{a}±0.68 (11.27-21.41)	6.56^{a}±0.30 (4.09-8.42)	9.30^{a}±0.64 (4.69-12.58)	0.16^{ab}±0.01 (0.12-0.29)

Note: Mean ± SD (range); identical superscripts (a, b, c…) denote non-significant differences between means in columns (separately for determined elements) according to the post-hoc Tukey's HSD test.

treatment. In 2021, a decrease in Zn content was noted as the applied BAs dose increased, while all experimental objects exhibited values significantly lower than those seen in 2019 and 2020 (Table 3).

Overall, no effect of the applied BAs fertilization on the increase in copper (Cu) concentration in the soil was observed. The Cu concentration fluctuated significantly during the experiment. During the study period, Cu content ranged from 3.12 to 4.30 mg kg^{-1}, with the lowest levels found in object D4 and the highest in object D5. Except for object D5, the average Cu content was lower compared to the Control and NPK treatments. Generally, Cu content was highest in 2020 and lowest in 2021, although for object D5, the highest Cu content was recorded in 2019. In all variants analyzed, Cu content in soil in 2021 was at least two times lower compared to 2019 (Tab. 3).

Chromium (Cr) content in the soil varied depending on the experimental object, ranging from 12.64 to 14.41 mg kg^{-1}. An insignificant effect of the applied BAs fertilization on Cr content was found. However, significant changes in Cr content were observed during the study period. In general, the Cr content in the soil decreased across the experimental objects throughout the study years, reaching its lowest values in 2021. Notably, in 2021, a clear trend of increasing Cr content in soil was observed with higher applied BAs doses, although in the remaining years, these changes were ambiguous.

The mean nickel (Ni) content in the soil ranged from 5.65 to 6.65 mg kg^{-1}. The lowest Ni content was found in the Control and NPK treatments, while the highest was determined for soils fertilized with the lowest and highest doses of bioash – D1 and D5. However, the observed changes were statistically insignificant. In the Control and NPK treatments, mean Ni content was highest in the first year of the study and decreased in subsequent years. Conversely, in the objects fertilized with BAs, mean Ni content was generally highest in 2020, with the lowest values observed in 2021. Similar to the Control and NPK treatments, the average Ni contents in 2021 were the lowest for these objects.

The mean lead (Pb) content in the soil, determined over the entire study period, ranged from 9.25 to 10.08 mg kg^{-1}, with the lowest content found in the NPK treatment and the highest in object D4. Following the application of BAs in doses D3, D4, and D5, the average Pb content in the soil increased slightly compared to the Control; however, these changes were statistically insignificant. In the individual years of the experiment, Pb content in the 0-30 cm layer of soil varied. Regardless of treatment, the lowest Pb content was observed in 2021, whereas the highest was generally noted in 2020.

Cadmium (Cd) concentration in the soil varied depending on the experimental object. Significant differences were noted across the research years for objects fertilized with the highest doses of BAs, D4 and D5. The average Cd content in the soil ranged from 0.144 to 0.184 mg kg^{-1}, with the lowest concentration observed for the NPK treatment and the highest in D2 and D3. The dynamics of changes in Cd content in individual years varied depending on the object. In the Control, the highest Cd content was recorded in 2019, while the lowest was seen in 2021. A similar trend was noted for the NPK treatment. In the objects where BAs fertilization was applied, Cd content

DISCUSSION

The application of biomass ash can vary in effectiveness depending on crop type, soil characteristics, and environmental conditions. For example, research by Patterson et al. (2004) conducted under greenhouse conditions showed an increase in the dry mass yield of barley plants after the application of ash compared to the control, with improvements ranging from 17.5% to 49.6% (Patterson et al., 2004). Similarly, our studies indicated increased seed yields, improvements in physiological parameters, and enhanced nutritional quality of spring rape plants following the use of the same ash (Szostek et al., 2022). The timing of application and the integration of biomass ashes (BAs) with other soil management practices also influence these outcomes. Biomass ash fertilization can significantly modify soil properties, impacting pH, organic matter content, sorption capacity, Fe and Mn oxide levels, and granulometric composition. Changes in these properties directly affect the absorption of elements by plants (Demeyer et al., 2001; Kramar, 2020; Vassilev et al., 2013). Various studies have shown that using lower doses of ash yields more beneficial effects on plant growth and development. Low doses of fly ash appear to stimulate plant growth by increasing the availability of macroelements and microelements. In contrast, higher doses can reduce positive effects due to stress associated with elevated concentrations of toxic metals. Applying BAs at low rates of less than 25 tonnes per hectare can enhance net profits through improved agricultural production and can serve as a sustainable alternative to agricultural limestone, offering numerous economic and environmental advantages if managed correctly (e.g., based on soil fertility, plant needs, or calcareous requirements) (Patterson et al., 2004).

The studies conducted demonstrate that the effect of BAs on the accumulation of elements in spring barley and their changes in the soil is ambiguous and should be evaluated separately for each year of the study, incorporating other factors that influence element bioaccumulation. The bioaccumulation of elements in plants is affected by various factors, including significant soil and climatic conditions (Sheoran et al., 2016). Generally, higher concentrations of the analyzed elements were found in the second year of the experiment, likely due to meteorological factors. This year experienced the highest total precipitation (794.4 mm) compared to other years (Table 2), which could have influenced the dissolution of components in the ash and their increased availability to plants (Liu et al., 2020). Changes may also result from soil property modifications influenced by ash fertilization. The effect of biomass ash fertilization on the content of microelements and toxic trace elements in the soil, and consequently in plants, depends on the concentration of specific elements in the ash and the amount used (Huotari et al., 2011). Potentially toxic elements in biomass combustion ash may include zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), and lead (Pb), with average concentrations typically ranging from 0.1 to 19.0, 0.011 to 1.1, 0.0013 to 0.11, 0.0002 to 0.14, 0.0059 to 1.005, 0.0018 to 0.26, and 0.002 to 5.318 g kg^{-1}, respectively (Cruz et al., 2019). High concentrations of Ni and Cd in ashes often significantly limit their agricultural use (Singh et al., 2016). Literature on the content of potentially toxic elements in biomass combustion ashes is diverse. Zając et al. (2018) determined the chemical composition of ash from biomass samples originating from agricultural and forest production, agro-food processing, and experimental plantations of energy plants. The results for microelement and toxic trace element contents obtained for these types of biomass fall within a wide range of values for Cu, Zn, Cr, Mn, Pb, and As, respectively: 18.8–765, 40.4–826, 10.7–95.6, 10.1–6920, 3.82–70.6, and 0.07–1.91 mg kg^{-1} (Zając et al., 2018). Száková et al. (2013) analyzed the composition of ashes from the combustion of commercial biomass (wood chips and wood waste), reporting determined contents of Cr, Mn, Cu, Zn, As, and Pb at 118, 6200–10700, 153, 300–1100, 9.8, and 313 mg kg⁻¹, respectively (Száková et al., 2013). Vassilev et al. (2013) also found a wide range of microelement and toxic trace element contents in ashes from biomass combustion (Vassilev et al., 2013). According to Zając et al. (2018), the content of toxic elements such as arsenic and lead in the ashes from the combustion of the most popular types of biomass is low. Trivedi et al. (2016) obtained similar results, finding trace amounts of chlorine (Cl), chromium (Cr), copper (Cu), nickel (Ni), strontium (Sr), rubidium (Rb), zinc (Zn), and zirconium (Zr) in all the ashes they tested (Trivedi et al., 2016). In turn, Smołka-Danielowska & Jabłońska, 2022 showed a significant content of arsenic (As), lead (Pb), nickel (Ni) and mercury (Hg) in the tested ashes of the forest industry, in particular wood briquettes. According to (Poluszyńska, 2013), increased levels of microelements and toxic trace elements in ashes from biomass combustion are found sporadically, most often concerning lead. When evaluating the impact of ashes from biomass combustion on the spread of toxic elements in the environment, the solubility of these elements should be taken into account. It is also noteworthy that ashes resulting from the combustion of straw or other plant parts from agricultural crops are generally characterized by a much lower content of heavy metals compared to wood biomass. This phenomenon is related to the longer vegetation period of trees, leading to increased accumulation of these elements in plant tissues (Müller-Stöver et al., 2012; Nunes et al., 2016). Many potentially toxic components found in ash are microelements, the deficiency of which in plants can adversely affect crop quality, susceptibility to diseases, and response to unfavorable environmental factors, ultimately reducing yields. Numerous laboratory and field studies confirm that the application of microelements enhances the effectiveness of macroelement fertilization while simultaneously improving the qualitative value of the yield.

Research on the mechanisms of nutrient uptake by plants and fertilization efficiency is crucial from an environmental protection standpoint, as microelements have a narrow safety margin between deficiency, adequate content, and toxicity. The ash used in the experiments concerning the analyzed elements generally fell within prescribed values (Table 1). The high variability of trace element content in biomass combustion ashes – including essential elements for plant fertilization and highly toxic ones—indicates that thorough analysis is required before using these ashes for any specific purpose (Alves et al., 2019).

Elements such as cadmium (Cd) and lead (Pb) in ash from biomass combustion are very slowly soluble, attributed to the high pH of the ash, which decreases the absorption and mobility of these elements. Consequently, a larger quantity may accumulate in the root zone and not be transferred to the above-ground parts of plants. Such relationships were confirmed in studies, which indicated that most of the detected elements were primarily accumulated in roots, with significantly lower levels found in the above-ground biomass of barley. Poluszyńska (2013) pointed out that heavy metals in ash are not absorbed by plants growing on alkaline soils because they exist in forms that are difficult to dissolve in water.

As indicated by the data presented in the study by Szostek et al. (2023), the use of biomass ashes (BAs) for fertilization purposes is associated with a relatively small environmental risk, characterized by a risk assessment code (RAC) coefficient of less than 1. This coefficient is determined based on the content of individual speciation of elements present in the ash, as quantified by the BCR method, in relation to their total content. Due to the small share of the exchangeable/extractable fraction of the F1 fraction in the BAs used in the experiment, which is the most mobile and bioavailable, their application to the soil appears to be relatively safe for the natural environment (Szostek et al., 2023). However, research by Jukić et al. (2017) indicates that the highest potential risk of contamination associated with the use of BAs pertains to nickel (Ni) and chromium (Cr), as determined by examining their mobile fractions. Despite the relatively low content of elements available in mobile and bioavailable forms in BAs, their use as fertilizers can lead to the increased accumulation of various elements, including toxic ones. For instance, research by Shi et al. (2017) shows that using ashes from biomass combustion increased the content of heavy metals in wheat grain. Although the values for copper (Cu), zinc (Zn), cadmium (Cd), and chromium (Cr) were below the limits specified by Food Safety Standards, there were exceedances concerning lead (Pb). Consequently, the use of ashes from biomass combustion may pose a risk of contamination and facilitate the entry of trace elements into the food chain (Shi et al., 2017). Additionally, research by Singh et al., (2016) clearly demonstrates that the application of biomass combustion ashes significantly influenced an increase in cadmium (Cd), chromium (Cr), lead (Pb), arsenic (As), and mercury (Hg) content in the grain of cultivated plants, with levels of these elements being 4 to 20 times higher compared to other experimental groups analyzed. In the conducted studies, elevated levels of the aforementioned elements were observed following the use of ashes, particularly concerning Zn, Ni, Cr, Pb, and Cd. Analysis of elemental content over the years of the study revealed significant fluctuations in both the surface layer of the soil and the plant parts analyzed. This suggests that the accumulation of individual elements in spring barley plants was influenced more by meteorological conditions than by the fertilization applied. Similar fluctuations were observed in the soil surface layer, where the dynamics of changes in the analyzed element content varied depending on the year of the experiment. Further research is needed to understand the aspects related to the use of ash from biomass burning, particularly regarding the release and accumulation of microelements and toxic trace elements. The dynamics of individual elements' release from ashes into the soil environment and their subsequent accumulation in various parts of plants are complex processes that are challenging to observe under real conditions. Capturing these changes requires extensive studies; otherwise, drawing conclusions about the effects of biomass ash combustion on soil properties and the spread of potentially toxic elements may be misleading (Jala & Goyal, 2006).

CONCLUSIONS

The studies conducted revealed an ambiguous effect of biomass combustion ashes (BAs) on the content of Zn, Cu, Ni, Cr, Pb, and Cd in different parts of spring barley plants, as well as in the soil throughout the study period. The application of biomass combustion ashes introduces significant amounts of microelements and toxic trace elements into the soil. Following the use of BAs, an increase in the concentrations of the analyzed elements was generally observed in various parts of the plants and in the soil. However, in most cases, the elements introduced with the ashes were primarily accumulated in the root zone of the plants, with only minimal accumulation in the aboveground parts.

The release of components contained in the ash and their accumulation within the plants appears to depend on meteorological conditions, particularly the amount of precipitation, which directly influences the solubility of the components present in the ashes. Therefore, the assessment of the impact of BAs should be conducted independently for each year. Otherwise, drawing conclusions about their environmental effects may lead to inaccurate interpretations.

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