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EVALUATION OF METALS BIOAVAILABILITY IN AGRICULTURAL SOIL TREATED WITH WOOD ASH

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Abstract. In the present work, we aimed to study the effect of quantitative changes of micronutrients (Cu, Zn, Mn) in soil and plants caused by wood ash applied into the soil in increasing doses. A pot experiment with medium textured soil, white mustard as a test plant and six amendment treatments (doses of wood ash: 0, 1, 5, 10, 20, 30 $Mg \cdot ha^{-1}$) was performed. Total contents of Cu, Zn and Mn were determined in soil and plant samples. Single (DTPA and HCl) and sequential (BCR) extractions were used to evaluate the available amounts of metals and their distribution in fractions. A plant's ability to accumulate metals from soils was estimated using the bioconcentration factor (BCF), which is defined as the ratio of metal concentration in the plants to that in soil. The increasing doses of wood ash increased total and available contents of trace elements, especially Cu and Mn. The distribution of metals among particular fractions depended mainly on their geochemical character. The highest content of Cu was found in the reducible and oxidisable fractions, whereas, the greatest amounts of Zn and Mn were in the exchangeable and reducible fractions, and the lowest in the oxidisable fraction. Despite small wood ash influence on metal distribution in the individual soil fractions, increasing doses of wood ash increased the amounts of Cu, Zn, Mn in easily soluble fractions, which are potentially available to plants. As a result of wood ash increasing doses application, the higher amounts of Cu, Zn and Mn in plant tissues were found. However, only in the case of Zn, the value of BCF indicated on such accumulation in the plants.

Keywords: wood ash, micronutrients, available amounts, single extraction, sequential analysis

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INTRODUCTION

Forest biomass has become a substantial source of bioenergy. It is widely accepted because biomass energy is a renewable power source that does not release net CO_2 during the combustion process and complies with EU's (2009) directive on renewable energy to mitigate climate change (Shi *et al*. 2016). In European countries, the majority of wood and wood wastes are used for energy production in large plants for district heat and power production (Bartoszewicz-Burczy 2012; Olsson *et al*. 2017). Wood ash is a by-product of burning wood and its waste. It is chiefly produced by the power industry, but households also increase the amount of this waste. According to the waste catalogue (Official Journal 2014, Pos. 1923), ash generated in a household is categorised as municipal waste, under the code of 20 01 99 (other selectively collected municipal waste fractions not otherwise specified). Until recently ash disposal was based on storage. At present, following the waste management hierarchy in the Waste Act of 2012 (Official Journal 2015, Pos. 87), other, more rational methods of this waste management are applied. According to Kajda-Szcześniak (2014), ash can be used for land restoration, for sealing the bottom of a landfill or for construction (building roads, car park surfaces, embankments for transportation, production of cement, concrete, blocks and bricks). Many studies indicate that wood ash is characterised by high concentration of macroelements (Ca, Mg, K, P) and microelements (Cu, Zn, Mn, Fe, Ni) (Górecka *et al*. 2006; Jones and Quilliam 2014; Kajda-Szcześniak 2014; Lucchini *et al*. 2014; Mollon *et al*. 2016; Shi *et al*. 2016). Due to the composition and alkaline properties of wood ash, it can be used as an alternative to mineral fertilisers containing calcium, potassium and phosphorus. Taking into account the wood ash application is similar to lime application, but wood ash has an additional advantage of supplying additional nutrients. The aforementioned authors also indicate that ash may contain toxic elements, so it is necessary to analyse it in detail before it is applied into soil. Although these objections mostly apply to ash produced by the power industry, ash produced by households may also contain toxic elements, but in considerably smaller amounts. Wood and wood briquettes used as fireplace fuels cause seasonal production of small amounts of wood ash. It is disposed of as municipal waste or it is used in gardening. Possibility of applying wood ash for agriculture, horticulture and forestry has been intensively investigated (Jones and Quilliam 2014, Lucchini *et al.* 2014, Mollon *et al.* 2016, Nabeela *et al*. 2015, Park *et al.* 2012). There are several problems that need to be resolved in order to utilize this by-product in practice. First of all, bioavailability of the nutrients to plant should be assessed.

In the following study we examined the fate of Cu, Zn and Mn metals in agricultural soil amended with increasing doses of wood ash. The aim was to:

1. determine the bioavailability of metals (Cu, Zn, Mn) in soil treated with wood ash using single and sequential extractions;

2. ascertain whether the wood ash application could change the metal concentration (Cu, Zn, Mn) in test plants.

MATERIAL AND METHODS

Wood ash and soil

Wood ash was obtained through the combustion of beech wood in a detached house in a fireplace. After the combustion, the ash was collected, grinded and mixed. Some basic properties of wood ash are listed in Table 1. The soil (sandy loam) used in the study was collected from the 0–30 cm depth of an agricultural field. The soil was classified as Eutric Cambisols according to IUSS Working Group WRB (2007). The soil was air-dried and passed through a 2 mm mesh screen. Some basic properties of soil used are listed in Table 1.

TABLE 1. CHOSEN PROPERTIES OF USED WOOD ASH AND SOIL

Property	Wood ash	Soil
pH	12.8	6.8
	Total content (mg·kg^{-1})	
Zn	170	100
Mn	1088	156
Cu	69.2	13.3
	HCl – extractable (mg·kg^{-1})	
Zn	2.1	79.6
Mn	9.3	109
Cu	2.8	7.6
	DTPA – extractable (mg·kg^{-1})	
Zn	1.8	23.5
Mn	2.8	6.3
Cu	2.7	1.8

Experimental design

The experiment was conducted in black PVC pots (volume 1 L) in greenhouse conditions (20 ± 3°C, natural daylight) employed a randomized, factorial design with one soil, one test plant – white mustard (*Sinapis alba* L.) and six amendment treatments: T1 – soil control, T2 – soil with wood ash at the rate equivalent to 1 Mg·ha^{-1} (0.33 g of ash/pot), T3 – soil with wood ash at the rate equivalent to 5 Mg·ha^{-1} (1 g of ash/pot), T4 – soil with wood ash at the rate equivalent to 10 Mg·ha^{-1} (1.66 g of ash/pot), T5 – soil with wood ash at the rate equivalent to 20 Mg·ha^{-1} (3.33 g of ash/pot), T6 – soil with wood ash at the rate equivalent to 30 Mg·ha^{-1} (10 g of ash/pot). Samples of 900 g dried soil were weighed in triplicate and mixed with the doses of wood ash. As ash contains low N amount, all pots were supplemented with NH_4NO_3 at the rate equivalent to 100 kg·ha^{-1}. Soil and each soil-ash mixtures were wetted to 60% water field capacity. Plants were watered daily with tap water, or as needed to maintain moisture level. Twelve white mustard seeds were sown in each pot. The plant samples were collected in the 69th term (after 120 days after sowing) corresponding to the growth stage of white mustard, determined according to BBCH key (Adamczeski and Matysiak 2011). The plants were harvested by cutting the plants at the soil surface. At the same time, the soil samples were gathered. Collected plants after oven drying (60^{o}C, 48 h) were finely ground. Soil samples were air-dried. Thus the prepared plant and soil material was subjected to chemical analysis.

Methods

Wood ash pH was determined with standard electrode in distilled water (1:10 w/v) and soil pH in 1 mol·dm^{-3} KCl (1:2.5 w/v). Total content of metals (Cu, Zn, Mn) in wood ash was determined after digestion in concentrated HF+HNO_3+HCl (USDA 2014). Total content of metals (Cu, Zn, Mn) in soil was assessed according to the *aqua regia* procedure ISO (1995). Concentrations of metals (Cu, Zn, Mn) in plants were measured after ignition at 550^{o}C during 5 hours and followed by digestion with 6 mol·dm^{-3} HCl.

Plant available amounts of metals were assessed by the single extractions. Both soil and wood ash were undergone to the same procedures using 2 different extractants: DTPA and HCl. The details of the experimental protocols are available elsewhere (Jakubus 2009; Zorpas and Loizidou 2008). Briefly, they were presented in Table 2. The method of sequential extraction of soil used in this study was developed by the Community Bureau of References (present Standards, Measurement and Testing Programme). The details of the experimental protocol are shown in Table 3.

Concentrations of metals in extracts and digests were determined by flame atomic absorption spectrometry (FAAS) using Varian Spectra AA 220 FS.

On the basis of the metals total content in plants and soil with and without wood ash application the Bioaccumulation Factor (BCF) was calculated. The BCF is defined as the ratio of metal concentration in plant shoots to total metal concentration in soil (Pérez-Esteban *et al*. 2014) and may be an indicator of the white mustard accumulation behavior.

TABLE 2. ONE-STEP EXTRACTION PROTOCOLS

Extractor	Soil: solution ratio	Extraction procedures
1 mol·dm^{-3} HCl	1:20	Shake 1 h at room temperature. Separate the extract from the solid residue by centrifugation for 10 minutes.
0.005 mol·dm^{-3}DTPA+0.1 mol·dm^{-3} TEA+0.01 1 mol·dm^{-3} $CaCl_2$, pH = 7.3	1:2	Shake 3 h at room temperature. Separate the extract from the solid residue by centrifugation for 10 minutes.

TABLE 3. BCR SEQUENTIAL EXTRACTION PROCEDURE (MOSSOP AND DAVIDSON 2003)

Fraction	Extracting agent	Extraction conditions	
		Time	Temperature
Fr I – Exchangeable, water and acid soluble	0.11 mol·dm^{-3} CH_3COOH (pH= 7.0)	16 h	20–25°C
Fr II – Reducible, represents metals bound to iron and manganese oxides	0.5 mol·dm^{-3} NH_2OH-HCl (pH = 1.5)	16 h	20–25°C
Fr III – Oxidisable, represents metals bound to organic matter and sulphides	30% H_2O_2 (pH=2.0). And next 1.0 mol·dm^{-3} CH_3COONH_4 (pH=2.0)	1 h, 2 h, 16 h	20–25. 85. 20–25°C
Fr IV – Residual, represents nonextractable metals bound with the strongest association to the crystalline structures of the minerals	*Aqua regia*	2.5 h	60–70°C

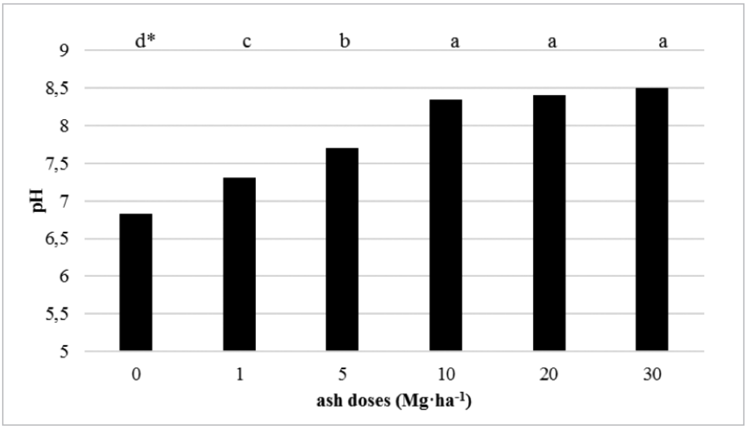
Statistical analysis

The effect of ash treatments on selected soil properties and metal content of plant tissue were determined using ANOVA. The obtained results were subjected to formal evaluation with the assistance of the analysis of variance using the F test. The least significant differences were calculated using the Tukey method at the significant level a=0.05 and then uniform groups within the factor level were established.

RESULTS AND DISCUSSION

Total content of metals

The alkalising effect of wood ash is well documented in the literature (Lucchini *et al*. 2014; Mollon *et al*. 2016; Nabeela *et al*. 2015). Investigations confirmed this effect of wood ash. As can be seen in Figure 1, pH values increased along with the dose of waste applied. However, the application of ash into soil does not have the deacidification effect only. Many authors (Górecka *et al*. 2006; Jones and Quilliam 2014; Lucchini *et al*. 2014; Nabeela *et al*. 2015; Shi *et al*. 2016,) indicate that ash is rich in nutrients, such as P, K, Ca and Mg. Apart from these macronutrients, which are necessary for plants, wood ash also contains microelements. Among other nutrients, Cu, Zn, Mn, Fe and Ni are necessary micronutrients for plants, but their excessive amounts (especially Cu, Zn and Ni) may be toxic to plants. A review of literature presented by Olsson *et al*. (2017) shows that there is a large number of studies which have examined effects of wood ash applications on soil metal content. Most studies cited by the aforementioned authors concern the dependence between the amount of ash applied and the total content (*aqua regia*) of metal in soil. The investigations confirmed that the total content of metals tended to increase along with the amount of ash (Fig. 2). The total content of Mn and Cu in the soil enriched with the largest amount of ash was 1.5 times greater than the amount in soil control. The content of Zn in soil of experimental combination T6 was 25% greater than in soil control. Studies by Górecka *et al.* (2006) and Jones and Quilliam (2014) indicated an even greater increase in the content of Mn, Cu and Zn in soil when wood ash was applied.

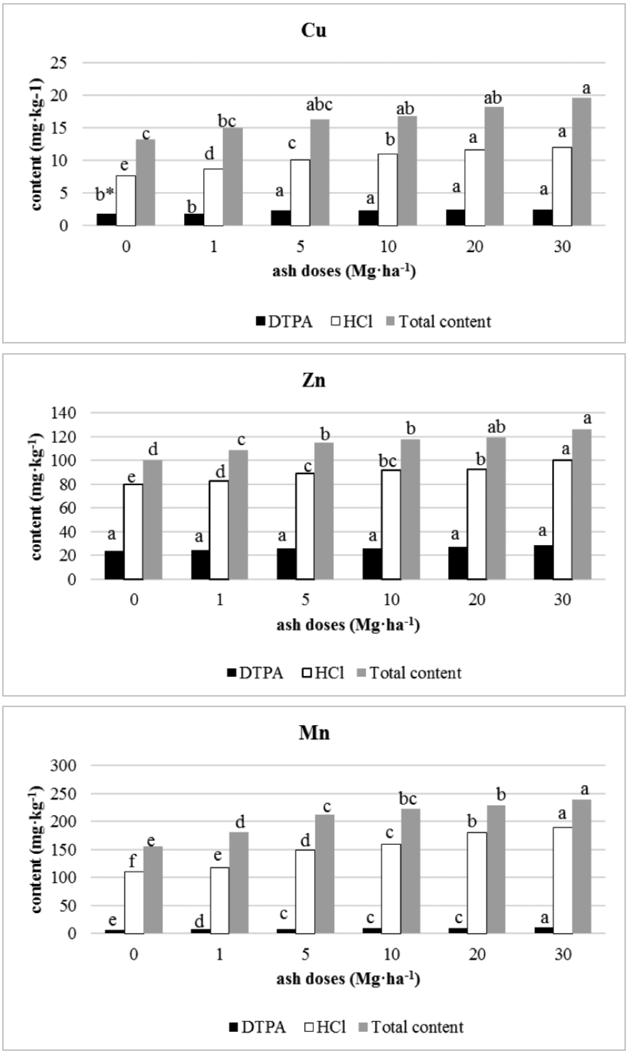


*Values followed by the same letter do not differ significantly at the 5% level

Fig. 1. Changes of soil reaction in relation to applied ash dose

Plant available metals

When using the total amounts, it is assumed that all forms of elements have an identical environmental impact, which is not confirmed in practice. The total content of an element does not provide information on its potential mobility in the environment (Jakubus 2012). In the presented studies single extractants were used, which were chemical solutions of different ionic strength, and thus differ-



*Values followed by the same letter do not differ significantly at the 5% level

Fig. 2. Total and available amounts of metals in soil amended with ash doses

ent properties and extractabilities. These include hydrochloric acid and chelating agent DTPA. Acid is considered to be strong extraction solution, with particularly high extractability, separating components bound with the exchangeable fraction, the carbonate fraction, with Fe-Mn oxides and organic matter.

Since acids, particularly 1 mol·dm^{-3} HCl, do not provide the actual amounts of microelements which may be absorbed by plants, alternatives include application of DTPA. This agent forms a strong complex with the extracted metal, which enhances their efficiency (Jakubus 2009; Zou *et al*. 2009). Taking into account agricultural practice a greater applicability is ascribed to the chelate

DTPA, which facilitates determination of the current availability of micronutrients bound mainly to the exchangeable and carbonate fractions of the tested matrix. Moreover, it is recommended by the International Organization for Standardization (ISO) (Jakubus 2009).

The data shown in Figure 2 reflect differences between solutions. More metals were extracted from soil with HCl than with DTPA. Increasing amounts of ash considerably increased the content of metals in soil. The effect was the least noticeable for Zn, whereas it was the most noticeable for Mn. The application of the smallest dose of ash (1 Mg·ha^{-1}) caused a significant increase in the content of Cu, Mn and Zn, but the differences were more evident when HCl was used for extraction. In comparison with the content in soil control, the maximum dose of ash (30 Mg·ha^{-1}) increased the content of Mn by 65% (DTPA) and 79% (HCl), Cu – by 36% (DTPA) and 57% (HCl) and Zn – by 22% (DTPA) and 26% (HCl) (Fig. 2). These tendencies are confirmed by reference publications (Górecka *et al*. 2006; Lucchini *et al*. 2014; Olsson *et al*. 2017; Shi *et al*. 2016). The analysis of the percentage share of available amounts in the total content did not confirm the specific effect of wood ash so definitely. Regardless of the experimental combinations there were similar percentage shares of metals extracted with DTPA and HCl, i.e. Cu DTPA – 12.1–14.1%, Cu HCl – 57–65%; Zn DTPA – 22–23%, Zn HCl – 77–80%; Mn DTPA – 4%, Mn HCl – 65–79%.

Metals fractionation in soil

Sequence analysis is undoubtedly a valuable supplement to single extractions, because it describes the character of bonds between metal and soil solid phase in more detail. A much greater practical importance is attributed to the identification of chemical forms of nutrients in soil, facilitating an assessment of the degree of their solubility, and thus their bioavailability. Bioavailability for plants is connected with its solubility and decreases in the following order: water-soluble forms > adsorbed on Mn and Fe oxides > organic forms > residual forms.

When applying methods of sequential extraction, changes and the degree of bioavailability for a given nutrient may be assessed more reliably. In the sequential method applied in this study, fractions I and II can be ascribed to metal combinations readily released in the environment, i.e. potentially bioavailable. In turn, fractions III and IV indicate the amounts of the element strongly bound with organic matter and the mineral portion of the analyzed matrix, and thus hardly available for plants.

The data in Table 4 show that regardless of the metal, its amounts in fractions I–III significantly differed, although the differences were more noticeable when the greatest dose of wood ash was applied. On the other hand, the differences identified in the content of Cu, Zn and Mn in fraction IV of soil fertilised with increasing doses of ash were statistically insignificant. It is noticeable that the application of ash into soil did not change the preferential creation of bonds between metals and soil solid phase, which results from the geochemical character of individual elements. Cu is considered to be a metal which does not bind into water-soluble forms easily, so it is not easily activated in the soil environment and simultaneously complexes formed by Cu with organic matter are characterised by high durability (Kumpiene *et al*. 2008; Rao *et al*. 2008). However, according to Whittle and Dyson (2002), Cu exhibits amphoteric properties and forms compounds that are soluble both in an alkaline and acidic environment. Brümmer *et al*. (1986) reported that at pH=7 Cu was easily bound by soluble substances. It may have caused the growth of water-soluble forms. This option results from our study. As can be seen in Table 4, the largest amounts of Cu (2.62–12.79 mg·kg^{-1}) were identified in oxidisable (Fr. III) and reducible fractions (Fr. II). The largest dose of wood ash caused the gain of Cu content by 45% (Fr. II) and 66% (Fr. III) in relation to the amount obtained in control soil. However, after wood ash application, the greatest increase (3.5 times) in the content of this element was noted in fraction I (from 0.1 to 0.35 mg·kg^{-1}). This trend was also reflected by Cu share of fraction I in its total content. This percentage values in fraction I increased from 0.8% (T1) to 1.8% (T6). In the case of Cu content in fractions II and III, the percentage shares were comparable to soil in individual experimental combinations and they ranged from 17.3% (T5) to 22% (T3) (Fr. II) and from 58% (T1) to 65% (T6) (Fr. III). The considerable increase in the content of Cu in water-soluble fractions can be explained with high pH values, which were accompanied by an increase in pH-dependent

TABLE 4. CONTENT OF METALS IN EXTRACTED FRACTIONS OF SOIL

	Experiment treatments					
Fraction	T1	T2	T3	T4	T5	T6
			Cu			
Fr I	0.1 c*	0.13c	0.21b	0.24b	0.33a	0.35a
Fr II	2.62b	2.83b	2.80b	3.03b	3.15b	3.81a
Fr III	7.69c	8.99bc	10.1abc	10.28abc	11.79ab	12.79a
Fr IV	2.85a	3.04a	3.25a	3.24a	2.96a	2.75a
			Zn			
Fr I	27.04c	27.12c	27.98c	28.68c	32.34b	35.37a
Fr II	28.97e	31.79d	37.75c	39.64b	40.30b	43.51a
Fr III	26.07b	29.29ab	29.58ab	29.15ab	29.21ab	31.31a
Fr IV	17.74a	17.89a	18.05a	18.72a	19.66a	20.05a
			Mn			
Fr I	50.16c	56.42bc	63.44ab	68.54a	66.29a	69.37a
Fr II	52.30d	58.47d	78.62c	85.35bc	91.13ab	98.70a
Fr III	27.45c	38.40b	41.64a	41.66a	43.6a	43.86a
Fr IV	26.59a	27.51a	29.11a	26.23a	28.01a	28.20a

*Values followed by the same letter do not differ significantly at the 5% level negative charge. According to Lindsay (2001) (cited after Lucchini *et al*. 2014), increase the pH-dependent negative charge on soil surfaces stimulating further sorption as well as promoting metal precipitation which readily occurs for several metals above pH 6.5. Simultaneously, due to the high cation content of the wood ash (data not presented), particularly K, Ca, Mg, we hypothesized that ash addition would stimulate desorption of the native metals, increasing their bioavailability.

The greatest contents of Zn and Mn are most often revealed in fractions I and II, whereas the smallest contents of these elements are in fraction III (Jakubus 2004; Rao *et al*. 2008; Sofianska and Michailidis 2015). Our study also showed a similar distribution of metals among particular fractions in soil enriched with ash. Despite considerable affinity between Zn and organic matter, it forms less stable organic ligands than copper (Brümmer *et al*. 1986). Therefore, its content in oxidisable fractions is low (26.07–31.31 mg·kg^{-1}) (Table 4). The increase in the Zn content in fraction III from combination T6 was relatively small. In comparison with the control soil, the maximum dose of ash increased the content of the metal in soil by 18%. Greater affinity between Zn and fulvic acids, formation of easily soluble metal-organic complexes and the easiness of adsorption on Fe and Mn oxides may explain the high content of the metal in fraction I (27.04–35.30 mg·kg^{-1}) and II (28.97–43.50 mg·kg^{-1}) (Table 4). Apart from that, as Brümmer *et al*. (1986) proved, the neutral soil pH favours and intensifies these phenomena. Zn content in fractions I and II was chiefly modified by ash at doses of 20 and 30 Mg·ha^{-1} (Table 4). The content of the metal in these fractions from combination T6 was 25% (Fr. I) and 1.5 times (Fr. II) greater than in the control soil. However, it was not reflected by Zn share in these fractions in the total Zn content. The percentage share of Zn in fraction I ranged from 24% (T3) to 28% (T6), whereas in fraction II it ranged from 29% (T1) to 35% (T5). Mollon *et al*. (2016) made similar observations. In their opinion, the mechanisms of desorption and adsorption play a significant role in controlling the solubility and availability of Zn in soil enriched with wood ash.

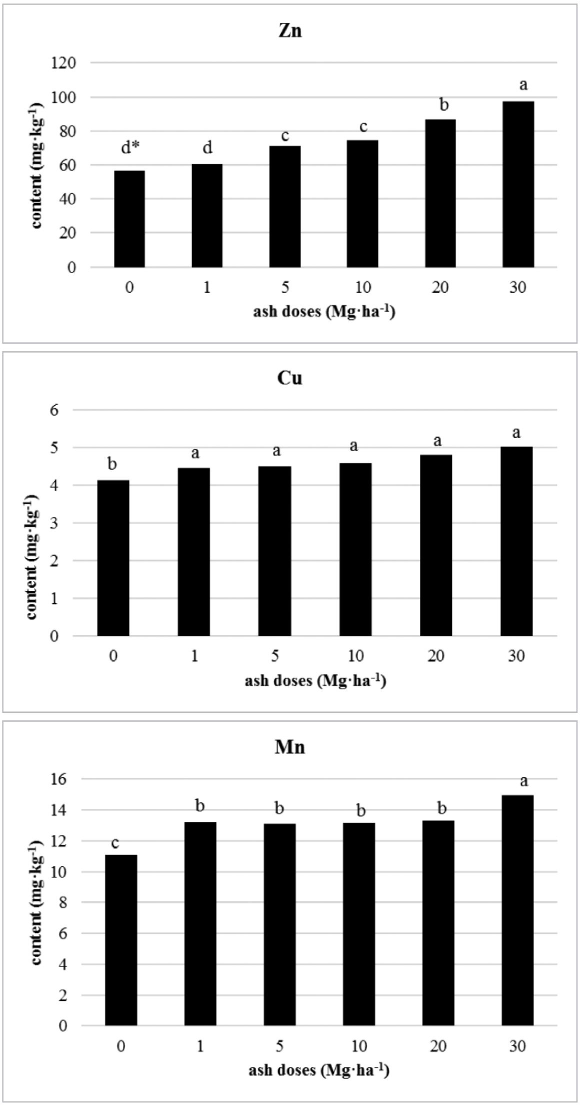
The distribution of manganese among fractions was similar to the distribution of zinc. As Kabata-Pendias and Pendias (1999) reported, Mn forms complex mobile ions $MnHCO_3^+$ and it is poorly adsorbed by organic matter, but more strongly by Fe and Al oxides and hydroxides. It is chiefly stressed that Mn forms complexes with humic compounds with low molecular weight, which have the nature of fulvic acids (Soumarė *et al*. 2003). According to Herms (1982), this reaction is stimulated by pH of 7–8. Apart from that, the study by Párraga-Aguado *et al*. (2017) shows that in soils with pH of 6–8, the solubility of Mn oxides increases and it results in greater content of this element in water-soluble fractions. This observation was confirmed in our study. The highest content of the element was observed in reducible (Fr. II) (52.30–

98.70 mg·kg^{-1}) and water-soluble combinations (Fr. I) (50.16–68.37 mg·kg^{-1}). It is noteworthy that although the content of Mn in oxidisable fraction was low (27.45–43.86 mg·kg^{-1}), it increased considerably (by 60% in T6) after wood ash application (Table 4). When ash was applied at a dose of 30 Mg·ha^{-1}, the content of Mn increased by 40% in Fr. I and by 89% in Fr. II, as compared with control soil. The considerable increase in the Mn content in Fr. II was not reflected by the percentage share of this metal in the total content, which ranged from 32% (T2) to 41% (T6). Also, increasing doses of wood ash did not influence on the percentage share of Mn content in oxidisable fraction in the total content, because these values were comparable, ranging from 18% (T1) to 21% (T2).

Metal in test plant tissue

Wood ash which is a product of incomplete combustion of wood containing organic and inorganic products is considered as an important source of minerals. It can be utilized as a source of plant nutrition to save fertilisers and to realize nutrient cycling in agriculture (Nabeela *et al.* 2015). In view of this fact, it is interesting to know what quantities of elements will be accumulated in plant tissues.

Usually the concentration of metals in the test plant tissues increased along with the amount of wood ash applied to the soil. This dependence can be seen in Figure 3. It was most strongly accented for Zn and weakly for Cu. Fertilising the soil with wood ash at a dose of 30 Mg·ha^{-1} increased the content of Zn by 72%, Mn by 35% and Cu by 21% in the test plants in comparison with the control plants. However, it is necessary to stress the fact that when small doses (1–5 Mg·ha^{-1}) were applied, the differences in the content of Zn in the plants were statistically significant. As far as Cu is concerned, only a dose of 20 Mg·ha^{-1} caused a statistically significant increase in the content of this element in the plant tissues (Fig. 3). The study by Jones and Quilliam (2014) also confirmed the increase in the Cu content in plant tissues. However, this dependence was not observed for Zn or Mn by cited authors. Nabeela *et al*. (2015) analysed the influence of different doses of wood ash on the development of *Brassica napus*. They observed considerable accumulation of Zn and lesser content of Cu in the plants. However, the absolute values of metals in plants may not give much information on the plant reaction to increasing metal concentration in soil. Therefore, a BCF ratio of a metal concentration in plant to that in soil at different doses of wood ash was calculated for the analysed metals (Table 5). Despite the increase in the content of metals in the available forms to plants and in spite of the increase in the concentration of these metals in plant tissues, BCF values did not confirm that the accumulation of Cu and Mn increased along with greater doses of wood ash. This tendency was only observed for Zn.



*Values followed by the same letter do not differ significantly at the 5% level

Fig. 3. Content of metals in test plant tissues

TABLE 5. BIOCONCENTRATION FACTOR OF METALS DERIVED AT DIFFERENT DOSES OF WOOD ASH

Metal	T1	T2	T3	T4	T5	T6
Cu	0.312	0.298	0.275	0.274	0.263	0.256
Zn	0.565	0.554	0.617	0.630	0.729	0.773
Mn	0.071	0.073	0.061	0.059	0.058	0.063

CONCLUSIONS

The micronutrients in wood ash make it a valuable source of plant nutrition but particularly high application rates may pose metal increment in soil. Our results have shown that wood ash can increase concentrations of total as well as available Cu, Zn, Mn and lead to significant uptake by plants. In general, ash did not change the distribution of metals in sequentially obtained fractions. However, the increasing doses of ash increased the content of Cu, Zn and Mn in rapidly soluble fractions in the soil environment, which are potentially available to plants. Despite these conclusions, only in the case of Zn, bioconcentration factor marked its accumulation in plant tissues.

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