Journal of Elementology ISSN 1644-2296

Piekarczyk M., Kobierski M., Jaskulska I., Gałęzewski L. 2018.
Content of available forms of boron, copper, manganese, zinc and iron in sandy soil fertilised with barley, wheat and oilseed rape straw ash.
J. Elem., 23(1): 107-118. DOI: 10.5601/jelem.2017.22.1.1281

ORIGINAL PAPER

CONTENT OF AVAILABLE FORMS OF BORON, COPPER, MANGANESE, ZINC AND IRON IN SANDY SOIL FERTILISED WITH BARLEY, WHEAT AND OILSEED RAPE STRAW ASH*

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Abstract

Ash from incineration of cereal crop and oilseed rape straw can be used for soil fertilisation since it is a source of elements available to plants. At the Experimental Station in Mochełek (53°13′ N; 17°51′ E), owned by the UTP University of Science and Technology in Bydgoszcz, a pot experiment was performed to determine changes in the content of boron, copper, manganese, zinc and iron forms available to plants owing to the application of barley, wheat and rape straw ash at doses corresponding to 0.08-2.68 g kg^{-1}. The pots were filled with loamy sandy soil. The paper provides evidence that the use of ash produced from incinerating straw of cereals and oilseed rape in soil fertilisation is a good way of ash waste management since such ash can be a valuable source of microelements essential for plants. Ash from barley, wheat, and oilseed rape straw can be used as fertiliser. Its application increases the soil pH values after application of a dose of 0.34 g kg^{-1} i.e. 1.0 Mg ha^{-1}. Applied in the pot experiment, barley, wheat and oilseed rape straw ash at doses of 1.34-2.68 g kg^{-1} increased the richness of uncropped soil with forms of microelements available to plants by several to tens of per cent. Ash from straw of barley, wheat and oilseed rape affected similarly the chemical properties of soil. A higher content of microelements was observed in soil fertilised with ash from oilseed rape straw, as compared with the effects of barley straw ash application. Slight differences in the effects of the application of the tested types of ash to soil resulted from the differences in their chemical composition and different ash doses.

Keywords: straw incineration ash, micronutrients.

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* Research project N N310 083536.

INTRODUCTION

The acquisition of energy from fossil fuels leads damage in the environment due to their mining and subsequent use (McKendry 2002, Demirbas 2004, Vamvuka, Karakas 2011). Mining damage, excessive emissions of carbon dioxide, acid rains and vast amounts of mining and incineration waste, often toxic, create the need to implement other methods of acquisition of energy, especially renewable one, which are more friendly for the natural environment, e.g. using the energy of biomass of energy crops, organic waste as well as straw of field-grown plants (Hein, Bemtgen 1998, Zeng et al. 2007, Abbasi, Abbasi 2010).

Unlike brown coal and black coal incineration waste (Demirbas 2005, Kalembasa et al. 2008), plant ash is not toxic (Lima et al. 2008, Piekarczyk et al. 2011) and its alkaline reaction as well as the content of elements essential for the life of plants (Sander, Andren 1997, Werther et al. 2000, Xiao et al. 2011, Vassilev et al. 2013) stimulate its widespread application in agriculture for soil alkalisation and fertilisation of crops (Rautaray et al. 2003, Yeledhalli et al. 2008, Piekarczyk et al. 2012).

The concept for this research came from the results of analyses of the chemical composition and properties of ash from straw of various plants, which had implicated that barley, wheat and oilseed rape straw ash introduced into soil could be a source of microelements available to plants. The aim of this paper has been to determine changes in the content of available forms of boron, copper, manganese, zinc and iron in sandy soil with the grain size composition of loamy sand, induced by different doses of ash produced from incineration of spring barley, winter wheat and winter oilseed rape straw. A more useful measure than a total concentration of trace elements is an estimate of their bioavailability. This way the concentration of a metal in the soil environment can be related to the metal's uptake by plants and mobility.

RESEARCH METHODS

In 2010-2011, a two-factor pot experiment, set up in a completely randomised design, was performed with four replications at the Experimental Station in Mochełek (53°13′ N; 17°51′ E), owned by the UTP University of Science and Technology in Bydgoszcz. The amount of soil material per pot was about 15 kg. Values of the coefficients of variation for the various soil parameters were below 5%, which indicates the homogeneity of soil material used in the experiment. The first factor (A) was ash produced by incinerating straw of barley, wheat and oilseed rape. The second factor (B) consisted of doses of ash such as 0.08, 0.17, 0.25, 0.34, 0.67, 1.34 and 2.68 g kg^{-1}. The lowest dose of ash applied was approximately the mass of ash which can be obtained from burning straw harvested from one hectare.

The soil material used in the experiment was sampled from the arable horizon of Luvisols (IUSS Working Group WRB 2014) with the grain size composition of loamy fine sand, containing the following percentages of fractions (Table 1): sand (2.0-0.05 mm) – 78.1%, silt (0.05-0.002 mm) – 19.9%,

Table 1

Properties of soil used in pots (n = 5)

Parameters	pH (1M KCl)	C_{org} (g kg^{-1})	N_t (g kg^{-1})	EC (µS cm^{-1})	TEB (cmol kg^{-1})	Sand (%)	Silt (%)	Clay (%)
Mean	6.6	7.9	0.7	117	7.3	78.1	19.9	2.0
SD	0.14	0.16	0.03	3.58	0.34	1.06	0.17	0.07
CV (%)	2.2	2.1	4.3	3.1	4.7	1.4	0.9	3.5

SD – standard deviation, CV – coefficient of variation, EC – electrical conductivity, TEB – total exchangeable bases

clay (<0.002 mm) – 2.0% (light soil in the agronomic soil categories). A Mastersizer 2000 laser diffraction particle size analyser (Malvern Instruments) was used to determine the textural composition. Soil pH was determined potentiometrically in a 1M KCl solution (soil : solution ratio 1 : 2.5). The pH of soil was 6.6 and the mean total content of organic carbon was 7.9 g kg^{-1}, while total nitrogen equalled 0.7 g kg^{-1} (Table 1). The content of total organic carbon and nitrogen was assayed with a Vario Max CN elemental analyser. The determination of electrical conductivity (EC) was made by measuring the electrical resistance of a 1 : 5 soil : distilled water suspension. The value of electrical conductivity was 117.4 µS cm^{-1}. Total exchangeable bases (TEB) were calculated by adding the content of exchangeable cations Ca^{2+}, Mg^{2+}, K^+, Na^+ following the barium chloride method (PN-EN ISO 11260, 2011). The concentration of the analysed cations was 7.3 cmol kg^{-1}. Applying the atomic absorption spectrometry method, on a Philips PU 9100 X, the total content of metals and their forms available to plants were determined. To determine the total content of metals, soil samples were mineralised in a mixture of hydrofluoric acid and perchloric *acid*. The mean total metal content was: B – 19.9 mg kg^{-1}, Mn – 518 mg kg^{-1}; Zn – 28.7 mg kg^{-1}, Fe – 9.18 g kg^{-1} (Table 2). Under the *Regulation of the Minister of the Environment* (2002)

Table 2

Total content of metals in soil used in pots (n = 5)

Parameters	B (mg kg^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	Fe (g kg^{-1})
Mean	19.9	5.1	518	28.7	9.19
SD	0.34	0.11	12.3	1.15	0.43
CV (%)	1.7	2.2	2.4	4.0	4.7

SD – standard deviation, CV – coefficient of variation concerning soil quality standards, the total concentration of metals in soil material was lower than the admissible values (geochemical background level). The content of available form of metals was determined after the extraction with the solution of 1 M HCl. The mean concentration of available forms of the metals was: B – 0.74 mg kg^{-1}, Cu – 1.84 mg kg^{-1}, Mn – 157 mg kg^{-1}, Zn – 6.65 mg kg^{-1}, Fe – 517 mg kg^{-1}. According to the Polish standard (IUNG Puławy), the content of the above metals was low, medium, medium, high and low, respectively

Perforated-bottom pots, with the bottom surface of 0.05 m^2 and 0.22 m deep, were filled with soil and then, in autumn 2009, placed on the surface layer of an arable field. Considering the dimensions of pots and the average density and the weight of soil in the arable layer, ash was added to soil (at the beginning of April 2010 and 2011) in the amounts dictated by the experimental design. After the application of ash, soil in the pots was mixed to the depth of about 10 cm. Soil material was disturbed down to 10 cm by analogy to a reduced tillage production system with minimum soil disturbance. No plants were grown in the pots.

The ash applied in the experiment, which originated from barley, wheat and oilseed rape straw incineration, had alkaline reaction, with pH in 1 M KCl: 10.0, 10.2 and 10.7, respectively. The total content of microelements was as follows: boron 45, 49, 74 mg B kg^{-1}, copper 31, 33, 39 mg Cu kg^{-1}, manganese 1036, 1229, 539 mg Mn kg^{-1}, zinc 289, 265, 194 mg Zn kg^{-1}, and iron 2.20; 3.49; 6.19 g Fe kg^{-1}, respectively. Table 3 presents the amounts of boron, copper, manganese, zinc and iron, applied into soil together with a straw ash dose of 0.34 g kg^{-1}, which corresponds to a dose of 1 Mg ha^{-1}. The amounts of metals introduced into the pots are respectively lower or higher depending on the dose of ash.

Table 3

Amounts of microelements (mg kg^{-1}) introduced at a dose 0.34 (g kg^{-1}) of soil in pot

Specification	Straw ash		
	Barley	Wheat	Rape
Boron	15.4	16.7	25.2
Copper	10.5	11.2	13.3
Manganese	352	418	183
Zinc	98.3	90.1	66.0
Iron	748	1187	2105

The soil material was sampled 3 times during the plant growing season of 2010 and 2011. The content of available forms of microelements was investigated on an atomic absorption spectrometer. Respectively to the assumed experiment design, the research results were statistically verified. Synthesis of the analysis of variance was made and the significance of differences between means of the studied characteristics was estimated with the Tukey’s test at a significance level p = 0.05. The calculations were supported by a statistics software package FR – ANALWAR 5.2. Microsoft Office Excel helped to make calculations of values of the coefficients of simple correlation between doses of barley, wheat and oilseed rape straw ash versus the content of phytoavailable boron, copper, manganese, zinc and iron in soil.

RESULTS AND DISCUSSION

Soil incoporation of ash obtained from straw led to alkalinisation of the soil environment (Table 4) and an increase in electrolytic conductivity (Table 5). The highest dose of ash (2.68 g kg^{-1}) resulted in an increase of soil pH to 7.7-7.8 and soil EC from 297 to 340 (μS cm^{-1}). High doses of straw ash did not cause excessive salinity of the soil.

In the pot experiment, the control soil showed a low content of boron available to plants, i.e. 0.74 mg B kg^{-1} on average (Table 6). An increase in the content of this element, due to the application of barley, wheat and oilseed rape straw ash, was recorded starting from the dose of 1.34 g kg^{-1}. A considerable increase in the content of available forms of boron in soil, as compared with the control pot soil, was 0.33 and 0.57 mg B kg^{-1}, accounting

Table 4

Soil pH (1 M KCl) after application of straw ash

The dose of ash (g kg^{-1})	Straw ash		
	Barley	Wheat	Rape
0	6.6	6.6	6.6
0.08	6.6	6.7	6.8
0.17	6.8	6.9	6.9
0.25	6.8	6.9	7.0
0.34	6.9	7.0	7.0
0.67	6.9	7.0	7.0
1.34	7.1	7.2	7.3
2.68	7.8	7.7	7.7

Table 5

Soil EC (μS cm^{-1}) after application of straw ash

The dose of ash (g kg^{-1})	Straw ash		
	Barley	Wheat	Rape
0	117	115	120
0.08	121	119	136
0.17	132	135	144
0.25	149	151	157
0.34	167	159	171
0.67	201	220	207
1.34	260	275	230
2.68	331	340	297

Table 6

Content of available forms of boron in the soil fertilised with straw ash (mg B kg^{-1})

(B) The dose of ash (g kg^{-1})	(A) Straw ash			Mean (SD)
	Barley	Wheat	Rape	
0	0.74	0.74	0.74	0.74 (0.14)
0.08	0.68	0.72	0.76	0.72 (0.12)
0.17	0.76	0.79	0.84	0.80 (0.09)
0.25	0.78	0.81	0.89	0.83 (0.10)
0.34	0.81	0.88	0.91	0.87 (0.12)
0.67	0.77	0.91	1.05	0.91 (0.17)
1.34	0.97	0.94	1.31	1.07 (0.26)
2.68	1.03	0.98	1.91	1.31 (0.61)
Mean (SD)	0.82 (0.16)	0.85 (0.12)	1.05 (0.47)	0.91 (0.32)
$LSD_{(0.05)}$	A – 0.09; B – 0.192; B/A – 0.333; A/B – 0.254			
Coefficient of simple correlation	0.927	0.836	0.998	0.987

SD – standard deviation

for 44.6 and 77% respectively, for the doses of 1.34 and 2.68 g kg^{-1} of the ash introduced to soil. Likewise, the type of ash, depending on incinerated straw, significantly differentiated the amount of boron forms available to plants in soil, and a higher boron content in soil was demonstrated following the application of oilseed rape straw ash, as compared with the cereal straw ash. The statistical analysis of the research results revealed a significantly positive correlation between the content of available boron and the amount of barley, wheat and oilseed rape straw ash introduced into soil.

The content of available copper in soil not fertilised with ash was moderate, reaching 1.84 mg Cu kg^{-1} on average. The increase in the content of copper owing to the application of barley, wheat and oilseed rape straw ash was confirmed only for the dose of 2.68 g kg^{-1}, where it equalled 0.52 mg Cu kg^{-1} on average, which accounts for 28.3% (Table 7). The type of ash

Table 7

Content of available forms of copper in the soil fertilised with straw ash (mg Cu kg^{-1})

(B) The dose of ash (g kg^{-1})	(A) Straw ash			Mean (SD)
	Barley	Wheat	Rape	
0	1.84	1.84	1.84	1.84 (0.21)
0.08	1.70	1.95	1.62	1.76 (0.30)
0.17	1.70	1.96	1.88	1.84 (0.39)
0.25	1.95	1.90	1.83	1.89 (0.36)
0.34	2.20	1.92	1.92	2.01 (0.36)
0.67	2.14	2.06	2.12	2.11 (0.40)
1.34	2.23	2.07	2.25	2.18 (0.32)
2.68	2.47	2.25	2.36	2.36 (0.36)
Mean (SD)	2.03 (0.36)	1.99 (0.41)	1.98 (0.38)	2.00 (0.38)
$LSD_{(0.05)}$	A – n.s. ; B – 0.392; A x B – n.s.			
Coefficient of simple correlation	0.839	0.941	0.882	0.927

n.s. non-significant differences, SD – standard deviation depending on the incinerated straw did not differentiate significantly the amounts of plant available forms of copper in soil; no significant interactions between the tested factors were recorded either. The statistical analysis of the research results confirmed a significantly positive correlation between the content of available copper and the amount of barley, wheat and oilseed rape straw ash introduced into soil.

Cereal and oilseed rape straw incineration waste enhanced the content of available manganese in sandy soil. The richness of the control soil in the experiment with available manganese was average (157 mg Mn kg^{-1}). A significant increase in the content of manganese available to plants by 10 mg Mn kg^{-1}, i.e. by 6.4%, was caused by a dose of barley, wheat and oilseed rape straw ash as low as 0.34 g kg^{-1}. Providing soil with incineration waste from straw at doses of 0.67, 1.34 and 2.68 g kg^{-1} increased the content of this metal by 13, 16 and 21 mg Mn kg^{-1}, respectively, which accounts for 8.3, 10.2 and 13.4%, as compared with the control. However, the above increase did not translate to a change of the soil Mn richness class (Table 8). The correlation between the dose of ash from cereal and oilseed rape straw and the content of plants available forms of manganese in soil was significantly positive.

The content of phytoavailable forms of zinc in soil material of the control pots was high, at 6.65 mg Zn kg^{-1}. Adding straw ash in the doses of 0.67, 1.34 and 2.68 g kg^{-1}, which are 2.0; 4.0 and 8.0 Mg ha^{-1} respectively, clearly increased the content of this metal by 1.36, 1.93 and 2.75 mg Zn kg^{-1}, respectively, which is higher by 20.5; 29.0 and 41.3% than in the control. The dose of 0.34 g kg^{-1} of the incineration waste was enough to improve the richness with this microelement (Table 9). The experiment did not demonstrate any differences in the content of bioavailable zinc depending on the type of ash applied. However, a tendency was observed towards a lower content of this element in soil following the application of oilseed rape straw ash as compared with the effects of applying barley and wheat straw ash. The research

Table 8

Content of available forms of manganese in the soil fertilised with straw ash (mg Mn kg^{-1})

(B) The dose of ash (g kg^{-1})	(A) Straw ash			Mean (SD)
	Barley	Wheat	Rape	
0	157	157	157	157 (8.4)
0.08	157	158	156	157 (11.1)
0.17	156	161	157	158 (9.5)
0.25	163	164	162	163 (12.1)
0.34	167	170	164	167 (9.7)
0.67	173	173	165	170 (10.7)
1.34	176	176	168	173 (10.1)
2.68	180	180	173	178 (12.2)
Mean (SD)	166 (12.4)	167 (13.7)	163 (1.6)	165 (12.6)
$LSD_{(0.05)}$	A – 3.2; B – 9.2; A x B – n.s.			
Coefficient of simple correlation	0.869	0.860	0.907	0.890

n.s.– non-significant differences, SD – standard deviation

Table 9

Content of available forms of zinc in the soil fertilised with straw ash (mg Zn kg^{-1})

(B) The dose of ash (g kg^{-1})	(A) Straw ash			Mean (SD)
	Barley	Wheat	Rape	
0	6.65	6.65	6.65	6.65 (0.76)
0.08	6.67	6.65	6.54	6.62 (0.84)
0.17	6.74	6.62	6.57	6.64 (0.91)
0.25	7.03	6.67	6.81	6.84 (1.01)
0.34	7.57	7.53	7.61	7.57 (0.91)
0.67	8.08	8.06	7.88	8.01 (0.75)
1.34	8.71	8.82	8.22	8.58 (0.77)
2.68	9.88	9.54	8.77	9.40 (1.02)
Mean (SD)	7.67 (1.41)	7.57 (1.33)	7.38 (1.22)	7.54 (1.31)
$LSD_{(0.05)}$	A – n.s. ; B – 0.750; A x B – n.s.			
Coefficient of simple correlation	0.967	0.937	0.895	0.942

n.s. – non-significant differences, SD – standard deviation

did not record any interaction between the factors of the experiment, although significantly positive values of the correlation coefficient were obtained the between the amount of ash introduced to soil and the content of zinc available to plants.

Soil in the control pots, with the grain size composition of loamy sand, contained 517 mg Fe kg^{-1} of available iron, which corresponds to low soil richness. The application of ash from incinerated straw of barley, wheat and oilseed rape at the doses of 1.34 and 2.68 g kg^{-1} to soil increased the content of available iron, by 57 and 81 mg Fe kg^{-1}, respectively, which is by 11 and 15.7% as compared with the control. Moreover, However, the application of 0.34 g kg^{-1} and 0.64 g kg^{-1}, i.e. doses of 1.0 and 2.0 Mg of ash per 1 ha, was sufficient to raise the content of plant available Fe forms by 5.0 and 8.3%, respectively (Table 10). A higher content of this element was observed in soil fertilised with ash from oilseed rape straw, as compared with the effects of the application of barley straw ash. The interactions of the dose and type of ash used were not significant. The coefficient of correlation between the total content of iron and the dose of ash applied ($r = 0.943$) was highly significant, which shows very strong dependencies.

The acquisition of renewable energy from energy plant biomass is accompanied by generation of high amounts of incineration waste, which could be used as fertiliser in agriculture and forest management (James et al. 2012). A good use of ash produced from plants should be supported by research into the production and environmental consequences of soil application of plant ash. Of all nutrients, plant biomass ash contain mostly potassium, calcium, phosphorus and magnesium, the macroelements which are essential for plants (Piekarczyk et al. 2011, Meller, Bilenda 2012, Stankowski et al. 2014). Plant incineration waste also contains numerous microelements, which – while occurring in low amounts – can significantly affect the nutrition of

Table 10

Content of available forms of iron in the soil fertilised with straw ash (mg Fe kg^{-1})

(B) The dose of ash (g kg^{-1})	(A) Straw ash			Mean (SD)
	Barley	Wheat	Rape	
0	517	517	517	517 (26.5)
0.08	516	517	519	517 (36.2)
0.17	519	518	522	520 (34.8)
0.25	526	523	534	528 (41.7)
0.34	534	538	558	543 (37.3)
0.67	549	553	578	560 (36.5)
1.34	554	566	602	574 (36.8)
2.68	563	591	639	598 (43.0)
Mean (SD)	535 (40.7)	540 (43.8)	559 (48.8)	545 (45.3)
$LSD_{(0.05)}$	A – 21.0; B – 45.0; A x B – n.s.			
Coefficient of simple correlation	0.890	0.956	0.949	0.943

n.s. – non-significant differences, SD – standard deviation

plants and the balance of biogenic elements in soil (Lima et al. 2008, Meller et al. 2009, Ciesielczuk et al. 2011, Ingerslev et al. 2011). The cereal and oilseed rape straw ash applied in the pot experiment at the doses of 1.34 and 2.68 g kg^{-1} increased the richness of uncropped soil with plant available forms of microelements by several up to tens of per cent. Higher amounts of nutrients following the soil application of ash have been reported in the papers published earlier by Gibczyńska et al. (2014), Park et al. (2005) and Piekarczyk et al. (2013, 2014a). The range of changes in soil richness depends on the amount of ash introduced to soil as well as the origin and the elemental composition of ash, which varies greatly (Olanders, Steenari 1995, Blander, Pelton 1997, Demirbas 2005, Kalembasa 2006, Bakisgan et al. 2009).

A relatively low content of microelements in the barley, wheat and oilseed rape straw ash applied to soil slightly but significant increased the soil richness with available boron, copper, manganese, zinc and iron. Even if relatively low amounts of elements are introduced to soil with incineration waste and the result such as increased soil richness is not visible immediately (Piekarczyk et al. 2014*b*, 2015), the application of such substance inhibits the soil depletion of these nutrients removed from fields together with energy crop yields (Ohno, Erich 1990, Park et al. 2005). The application of ash to the soil environment can also significantly enhance all physical and chemical properties of soil (Yeledhalli et al. 2008). Trace elements in soil are most soluble under acidic conditions and thus more available to plants. The ash doses used in the pot experiment resulted in a significant increase in the concentration of trace elements, despite the concomitant alkalinisation of the soil environment occurred. This confirms that ash from straw of cereals and oilseed rape is a very good source of trace elements.

CONCLUSIONS

1. Ash from barley, wheat, and oilseed rape straw can be used as a fertiliser. Results of ash application include a pronouced increase in the soil pH at a dose of 0.34 g kg^{-1} (1.0 Mg ha^{-1}). The use of ash caused a significant increase in available forms of metals in the soil, which indicates that ash is a very good source of these elements.

2. The use of ash produced from incinerating cereals and oilseed rape straw in soil fertilisation is a good ash waste management solution since such ash is a valuable source of microelements essential for plants.

3. Barley, wheat and oilseed rape straw ash at the doses of 1.34 and 2.68 g kg^{-1}, which are respectively 4.0 and 8.0 Mg ha^{-1}, applied in this pot experiment increased the richness of soil with phytoavailable forms of microelements by several up to tens of per cent.

4. Slight differences in the effects of the application of the tested types of ash to soil resulted from the differences in their chemical composition and different ash doses.

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