J. Elem. s. 977–988

DOI: 10.5601/jelem.2014.19.3.444

INFLUENCE OF COAL ASH FROM FLUIDIZED-BED COMBUSTION AND EM-1 PREPARATION ON THE CONTENT OF Fe AND Mn IN SPRING WHEAT AND BARLEY

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Abstract

The object of the research was to analyze the influence of coal ash from fluidized-bed combustion applied to light soil, and combined with the microbiological preparation Effective Microorganisms (EM-1), on changes of the iron and manganese content in cultivated plants of spring wheat and spring barley. Commissioned by the company Vattenfall, a field study on seven fertilizer variants was carried out in 2007-2009. The experiments were set up in Małyszyn near Gorzów Wielkopolski (Hodowla Roślin Strzelce sp. z o.o. Oddział Małyszyn) on light soil, soil valuation class IVb. Each plot covered 10 m^2. The research was carried out in completely randomized blocks with four replications. Plant samples (grain and straw) were mineralized in a solution of nitric acid(V) and chloric acid(VII); afterwards the total content of iron and manganese was assessed. Application of coal ash to the soil resulted in a decrease of iron and manganese in spring wheat and spring barley grain and straw, especially in the second and third year of the experiment. Additionally, the enrichment of soil with the microbiological preparation EM-1 decreased the concentrations of iron and manganese in the plants. It was noted that the quantities of iron and manganese in the grain and straw of both wheat and barley were decreasing in the subsequent years of the experiment, as a result of which the plant content of these microelements in individual years was varied. To some extent, the above relationship can be explained by the fact that in the last growing season was characterized by the least rainfall. No influence of the applied coal ash on the Fe:Mn weight ratio was determined in grain from cv. Nawra wheat or cv. Lot barley.

Key words: spring wheat, spring barley, coal ash from fluidized-bed combustion, effective microorganisms (EM-1), iron, manganese.

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WPŁYW POPIOŁÓW FLUIDALNYCH Z WĘGLA KAMIENNEGO I PREPARATU EM-1 NA ZAWARTOŚĆ Fe I Mn W PSZENICY I JĘCZMIENIU JARYM

Abstrakt

Analizowano wpływ popiołów fluidalnych z węgla kamiennego wprowadzonych do gleby lekkiej w połączeniu z preparatem mikrobiologicznym efektywne mikroorganizmy (EM-1) na zmiany zawartości żelaza i manganu w pszenicy jarej i jęczmieniu jarym. Doświadczenie zlokalizowano w Małyszynie k. Gorzowa Wielkopolskiego (Hodowla Roślin Strzelce sp. z o.o. Oddział Małyszyn) na glebie lekkiej, klasy bonitacyjnej IVb. Powierzchnia poszczególnych poletek wynosiła 10 m^2. Doświadczenie założono metodą bloków kompletnie zrandomizowanych w 4 powtórzeniach. W próbkach roślinnych (ziarno i słoma) po mineralizacji na mokro w mieszaninie kwasów azotowego(V) i chlorowego(VII) oznaczono ogólną zawartości żelaza i manganu. Wprowadzanie do gleby popiołów fluidalnych z węgla kamiennego spowodowało zmiejszenie ilości manganu w ziarnie i słomie pszenicy jarej oraz jęczmienia jarego. Szczególnie uwidocznienie tego wpływu można było zaobserwować w 2. i 3. roku doświadczenia. Ponadto zanotowano pewną tendencję zmiejszenia się ilości żelaza i manganu w badanych w roślinach w wyniku wprowadzania do gleby preparatu mikrobiologicznego EM-1. W kolejnych latach badań odnotowano zmiejszenie ilości żelaza i manganu w ziarnie i słomie zarówno pszenicy, jak i jęczmienia, co powodowało zróżnicowanie zawartości tych mikroskładników w roślinach w poszczególnych latach. W pewnym stopniu powyższą zależność można tłumaczyć tym, że w ostatnim roku badań okres wegetacyjny charakteryzował się najmniejszą ilością opadów. Nie stwierdzono jednoznacznego wpływu dodanych popiołów fluidalnych na wartość stosunku wagowego Fe:Mn w ziarnie pszenicy odmiany Nawra i jęczmienia odmiany Lot.

Słowa kluczowe: pszenica jara, jęczmień jary, popiół fluidalny, efektywne mikroorganizmy (EM-1), żelazo, mangan.

INTRODUCTION

Being a product of fluidized-bed coal combustion, coal ash is a skeleton -free material containing much iron and manganese. Crystalline grains of ash are built of ferrous phases (Ratajczak et al. 1999). Coal ash originating fluidized-bed combustion is nature friendly, hence its recycling has been broadly studied in Poland and abroad (Nowosielski, Ornowski 1998, Godlewska, Kalembasa 2008, Antonkiewicz 2009, Kováčik et al. 2011).

Metals that perform the function of micronutrients are usually required in trace amounts specific for the species, variety, growth stage or body. Both their deficiency or excess may harm the plant organisms, thus the amounts should be appropriate and never exceed the standards (Pisulewska et al. 1998, Hebbern et al. 2005).

Iron is a significant element of oxidation-reduction processes in plants. Its large quantities are needed in cytochromes, which play a fundamental role in electron transfer during photosynthesis. Iron is also needed to form magnesium and manganese ion bridges between enzymes and the substrate. Iron is particularly important as an activator in the processes of synthesis of chlorophyll and some proteins. Iron takes part in the reduction of nitrogen compounds and metabolism of fatty acids. Metal ions are directed for transport in the xylem and may be complexed by nicotianamine (Von Wiren et al. 1999). Jentschke and Goldbold (2000) pay attention to the impact of fungi causing the release of metal chelating agents from roots into soil, and to the role of iron in maintaining the balance of minerals and hormones in plants.

Iron is a very mobile element, which - under unfavourable conditions - quickly migrates deep into the soil profile, to the detriment of the quantity of forms easily available to plants (Jarociński 2005). Boganegra et al. (2004) indicate that humic complexes present in soil are a good source of iron for plants. Solubility of ferrous compounds depends on their oxidation-reductive potential (El-Fouly et al. 2001, Becker, Asch 2005).

Manganese is a micronutrient necessary for life of plants; it regulates and stimulates their growth and is extremely important for all oxidation-reductive processes. Manganese forms unstable complexes with some enzymes or ATP, acting as an ion bridge between the substrate and enzymes; it takes part in photosynthesis, the metabolism of proteins, carbohydrates and lipids and the scavenging of free radicals (Stadtman et al. 1990). Traditionally, it is assumed that Mn^{2+} can move freely in the xylem and be transported to the transpiration stream in leaves. Ducic and Polle (2005) reported that manganese absorbed through a leaf can be transported back to the roots. In plants, the metal regulates the level of ferrous compounds and exerts influence on the reduction of nitrates(V). Basically, manganese exists in soils in the form of free oxides or silicates. During the weathering of silicates, Mn^{2+} ions are released into the soil solution. Such factors as the content of clayey minerals, pH value or oxidation-reductive potential of the soil play an important role in this process.

Deficits of iron are sometimes coincide with the symptoms of manganese toxicity. The iron to manganese ratio varies significantly in different species of plants.

Effective microorganisms are sold in Poland under the name EM-1 or as a concentrate containing more than 80 different microorganisms, such as lactic acid bacteria, photosynthetic bacteria, yeasts, actinomycetes, fermentations, etc. Professor Teruo Higa of the University of Agriculture in Ryuksyu in Okinawa, Japan, is the creator of the technology of Effective Microorganisms. Microorganisms as an antioxidant agent affect soil and plants directly and indirectly. Higa (2005) points out that controlling the soil microflora in order to reinforce the advantageous impact of beneficial and effective microorganisms can help to improve and sustain the chemical and physical properties of soil.

The aim of this study was to assess the suitability of coal ash obtained from fluidized-bed combustion for the de-acidification of mineral soil. The analysis was based on a comparison of its effect versus and the traditional calcium and magnesium fertilizers. The object was to examine the influence of coal ash applied to light soil, combined with the microbiological preparation Effective Microorganisms (EM-1), and the impact of the above on changes of the iron and manganese content in cultivated crops, such as spring wheat and spring barley.

MATERIAL AND METHODS

Experimental conditions

Commissioned by the company Vattenfall, a field study on seven fertilizer variants was conducted in 2007-2009 (Table 1). The experiments were set up in Małyszyn near Gorzów Wielkopolski (Hodowla Roślin Strzelce sp. z o.o. Oddział Małyszyn) on light soil, which belonged to soil valuation class IVb. The area of each plot was 10 m^2. The experiment was carried out in completely randomized blocks with four replications. Chemical and physicochemical parameters of the materials used in the experiment are given in Table 2. Dolomite calcium and ash were used once, in 2007, split into two doses equal 1.0 and 1.5 of hydrolytic acidity. Doses of calcium fertilizer and coal ash were established according to their content of calcium and magnesium. In order to neutralize the soil's acidity, each plot covering 10 m^2 was treated with two doses of 13.50 and 20.75 kg of coal ash. Dolomite lime in the doses of 4.74 and 7.11 kg was used to neutralize the hydrolytic acidity. Coal ashes from the Żerań Power Plant was supplied by Vatenffal and incorporated into the soil in the spring of 2007.

Table 1

The design of the experiment

The variant	The fertilization
1	control - soil
2	soil + 1 $CaCO_3 \times MgCO_3$
3	soil + 1,5 $CaCO_3 \times MgCO_3$
4	soil + 1 coal ash
5	soil + 1.5 coal ash
6	soil + 1 coal ash + **e**ffective microorganisms EM-1
7	soil + 1.5 coal ash + **e**ffective microorganisms EM-1

Table 2

Chemical and physicochemical parameters of the materials used in the experiment

Parameter	pH in KCl	pH in H_2O	Hydrolytic acidity	Iron (%)	Manganese (%)	Calcium (%)	Magnesium (%)
Soil at the A_p	4.30	5.13	32.0 mmol H^+ kg^{-1}	0.4	0.02.	0.26	0.06
Coal ash	12.32	12.21	-	4.4	0.05	8.40	1.40
Dolomite lime			-	1.5	0.1	21.50	1.70

During the three-year long experiment, the following crops were grown: spring wheat cv. Nawra, spring barley cv. Lot and bean cv. Martin. However, only wheat and barley were submitted to analyses, as the bean crop was unrepresentative due to the drought which occurred at the flowering stage.

Phosphorus and potassium were applied in spring each year, in the form of Polifoska®5 NPK (Mg-S) 5-15-30-(2-7) dosed at 250 kg per ha. Nitrogen fertilizers were applied in three doses (before sowing, in the flowering stage and in the stem elongation), totalling 120 kg N ha^{-1} each year. In each year, samples of plants were taken on the day of harvest.

In the experiment, the microbiological preparation Effective Microorganisms (EM-1) was used once, on May 15, during rainfall which supplied 15 dm^3 of water ha^{-1}. Additionally, 600 dm^3 ha^{-1} of water was poured.

Methodology of chemical analyses

Plant samples (grain and straw) were first mineralized in a solution of nitric acid(V) and chloric acid(VII). Afterwards, the total content of iron and manganese was determined. The analyses were carried out on an atomic absorption spectrometer Solaar AA Series.

The concentrations of calcium, magnesium, iron and manganese in soil, dolomite lime and coal ash were additionally determined by spectrophotometry following wet mineralization. Soil pH was determined potentiometrically (pH_{H2O} and pH_{KCl}) according to the PN-ISO 10390/1997 standard. The soil hydrolytic acidity was determined using extraction by calcium acetate(II) (PN-R-04027/1997).

The results were analysed with one-way variance for a randomized block design and for values of Tukey's confidence half-intervals at the significance level of α=0.05. An FR – Analwar 5 statistical software package was used for calculations as well as an original programme written by prof. Franciszek Rudnicki.

The meteorological data

The development of plants and uptake of macronutrients are largely dependent on the amount of precipitation, which should ensure adequate soil moisture. The normal plant growth during vegetation and intake of macroelements are to a large extent governed by the amount of precipitation which ought to maintain an adequate soil moisture content.

From the data provided by the Meteorological Station Plant Breeding, Strzelce Ltd. (http://home20.static.kutno68.tnp.pl), the plant growing period in 2007 was humid. For example, precipitations in May were much above the multi-year mean. The season in 2008 was dry due to relatively scanty rainfalls in May and June. In the last year, in 2009, the growing season was dry despite higher precipitation in May than in the multi-year period.

RESULTS AND DISCUSSION

The content of iron in wheat and barley

The content of iron in grain is important for two reasons: broad use of grains and significant role of iron in living organisms. However, the content of iron in plants should not exceed the set norms. In 2001-2003, Szteke et al. (2004) studied the content of iron in grain of wheat grown in Poland, and reported a wide range of results: from 18.7 to 167.0 mg Fe kg^{-1} in dry mass.

In first year of our experiment, the content of iron in wheat grain was 46.0-50.4 mg Fe kg^{-1} in dry mass, falling by half in the second year. During the first two years, no influence was observed of the applied liming agents or the microbiological preparation EM-1 on changes in the iron content in wheat grain. In the third year of the experiment, some influence of coal ash and microbiological preparation EM-1 was found, namely the iron content in wheat grain decreased (Table 3). Wheat grain harvested in the third year had the lowest content of iron. To a certain extent, this effect can be attributed to the fact that the plant growing season in that year was characterized by the lowest precipitation.

The composition of grain from wheat grown in this experiment corresponds to the data presented in the subject literature (Jackowska, Borkowska 2002, Rachoń, Szumiło 2009, Kozłowska-Strawska 2010, Ciołek et al. 2012, Rachoń et al. 2012).

The content of iron in the straw of spring wheat grown in the experiment ranged from 13.4 to 60.2 mg Fe kg^{-1} dry mass, i.e. less than the one indicated by Kozłowska-Strawska (2010), who received results ranging from 109.6 to 204.0 mg Fe kg^{-1}. The liming agents or the microbiological preparation EM-1 did not cause significant changes in the content of iron in spring wheat straw (Table 3).

Table 3

The content of iron in cv. Nawra spring wheat (mg Fe kg^{-1} d.m.)

The variant	Years of experiment					
	2007		2008		2009	
	grain	straw	grain	straw	grain	straw
1	48,6	42.5	24,9	21.0	32,4	14.8
2	46,1	49.7	24,7	29.4	23.5	24.4
3	46.0	45.5	29.0	21.2	22.6	13.4
4	50.4	46.9	24.3	29.1	17.9	16.4
5	48.1	43.4	26.6	25.8	10.8	23.0
6	44.5	45.3	16.4	27.9	8.8	25.7
7	46.1	60.2	18.1	29.2	9.8	28.1
Average	47.1	47.6	23.4	26.2	18.0	20.8
$LSD_{0.05}$	n.s.	n.s.	n.s.	n.s.	7.46	n.s.

Table 4

The content of iron in cv. Lot spring barley (mg Fe kg^{-1} d.m.)

The variant	Years of experiment					
	2007		2008		2009	
	grain	straw	grain	straw	grain	straw
1	62,9	60.1	31,4	28.7	30.0	26.8
2	57.6	60.8	31.4	34.3	24.1	32.7
3	57.2	59.5	29.4	34.8	25.0	43.1
4	64.3	72.9	33.8	16.3	17.2	38.6
5	69.4	52.4	31.8	15.8	23.6	30.6
6	55.2	53.4	30.4	28.5	18.8	24.3
7	64.1	52.3	33.6	24.4	21.5	28.1
Average	61.5	58.8	31.7	26.1	22.9	32.0
$LSD_{0.05}$	n.s.	n.s.	n.s.	13.25	11.60	18.72

Spring barley grain and straw contained a similar amount of iron: from 15.8 to 72.9 mg kg^{-1} in dry mass. The results gathered in the experiment do not suggest that the applied liming agents or the microbiological preparation EM-1 affected changes in the iron content in barley grain and straw (Table 4).

It should be noted that in the subsequent years of the experiment the content of iron in grain and straw of spring wheat and barley was declining, which resulted in varied levels of this micronutrient in plants in individual years (Tables 3 and 4). The study by Borkowska (2004) on the influence of nitrogen fertilization on the content of selected micronutrients in spring wheat grain also validates the findings concerning big differences in the content of copper, zinc, iron and manganese in wheat grain observed in individual years of the experiment.

The content of iron determined in this experiment was in the range of most frequently observed concentrations, being much lower that those regarded toxic to animals (Wysokiński 2011).

The content of manganese in wheat and barley

Manganese takes part in physiological processes, mainly as the activator of enzymes regulating the metabolism of carbohydrates, lipids and proteins. Szteke et al. (2004), in their research carried out in 2001-2003 to determine the content of manganese in grain of wheat grown in Poland, obtained a wide range of results: from 9.2 to 69.1 mg Mn kg^{-1} in dry mass.

In the first year of the experiment, the content of manganese in spring wheat grain was on the level of 81.0-93.9 mg Mn kg^{-1} in dry mass. Particularly in the first year, the straw from spring wheat grown in ash fertilized soil with an addition of EM-1 preparation had about 30% lower content of manganese compared to the crops from the control (Table 5).

Table 5

The content of manganese in cv. Nawra spring wheat (mg Mn kg^{-1} d.m.)

The variant	Years of experiment					
	2007		2008		2009	
	grain	straw	grain	straw	grain	straw
1	90.9	367	52.6	148	34.9	75.5
2	92.5	307	46.6	86	30.5	67.3
3	83.9	273	49.3	133	27.0	51.6
4	93.9	256	39.1	105	27.2	73.3
5	92.4	296	31.3	92	24.0	26.5
6	83.5	227	40.7	56	24.7	66.2
7	81.0	196	50.5	121	23.5	90.9
Average	88.3	274	44.3	106	27.4	64.5
$LSD_{0.05}$	n.s.	n.s.	n.s.	n.s.	3.18	23.06

In the following years of the experiment, a gradual decrease of the manganese content in spring wheat grain and straw was achieved; the minimum amount was 23.5 mg Mn kg^{-1} in dry mass (Table 5). Similarly to the changes in the amount of iron in wheat grain, this relationship can be attributed to the fact that the last plant growing period had the smallest amount of atmospheric precipitation.

The content of manganese in spring barley grain grown in the experiment ranged from 14.6 to 80.5 mg Mn kg^{-1} in dry mass. It has to be emphasized that barley straw was much richer in manganese and the determined amount of that element varied from 36.5 to 345 mg Mn kg^{-1} in dry mass. Błaziak (2007), while assessing changes of the microelemental composition of grain due to soil liming and magnesium enrichment of soil, reports analogous concentrations of microelements in grain and straw from cv. Aramir spring barley. The amount of manganese was between 24-60 mg Mn kg^{-1} d.m. in grain and from 684 to 357 mg Mn kg^{-1} d.m. in straw.

In the first year, no influence of the applied liming agents or the microbiological preparation EM-1 on changes of the content of manganese in barley grain and straw was observed (Table 6). The results gathered during the next two years indicate that the application of the microbiological preparation and coal ash causes a decrease of the manganese content in spring barley. Similar relations were observed by Błaziak (2007), who concluded that liming and magnesium enrichment of soil led to a significant decrease of microelements, especially manganese (by 25–90%), in the aerial parts and roots of cereals.

Similarly to wheat, in the subsequent years of the trials, a decrease of the manganese content in spring barley grain and straw was noted, down to the lowest concentration in the third year (Tables 5 and 6).

Table 6

The content of manganese in cv. Lot spring barley (mg Mn kg^{-1} d.m.)

The variant	Years of experiment					
	2007		2008		2009	
	grain	straw	grain	straw	grain	straw
1	54.7	268	19.1	224	19.3	82.3
2	58.2	323	20.4	114	16.2	49.2
3	52.8	220	17.6	80	14.6	60.2
4	64.3	318	19.9	166	14.9	40.9
5	80.5	345	18.7	140	16.0	36.5
6	65.7	317	16.8	111	15.6	58.7
7	61.7	318	24.5	100	16.8	54.3
Average	62.6	301	19.6	133	16.2	54.7
$LSD_{0.05}$	6.56	n.s.	1.98	13.58	2.59	15.35

Iron and manganese weight ratio in spring wheat and spring barley grain

Iron is present in plants in the oxidation state +2 and +3. Manganese occurs in plants in different oxidation states: from +2, through +3 and +4 up +7. In certain conditions, the sum of cations in a plant changes insignificantly. An increase in absorption of one of the nutrients results in a decreased absorption of others. In this context, it is interesting that manganese and iron can act as biochemical antagonists and can compete with each other in terms of the absorption from soil (Gudmundsdóttir et al. 2006). The discussed elements occur in different oxidation states in plants; to compare them, we can only use weight ratios, i.e. a simple quotient of their amounts in plants (Table 7).

The Fe:Mn weight ratio in cv. Nawra spring wheat grain ranged from 0.36 to 0.93, and its value indicates a higher concentration of manganese than iron in wheat grain (Table 7). The Fe:Mn ratio in cv. Lot spring barley grain ranged between 0.84-1.81, which means its value was near the lower limit considered optimal. In healthy fodder plants, the Fe:Mn ratio should range between 1.5-2.5. Below the value of 1.5, the symptoms of manganese toxicity and iron deficit are observed, whereas above 2.5 the excessive amount of iron becomes harmful and is followed by the symptoms of manganese deficit (Motowicka-Terelak 1978, Mazur 1990, Błaziak 2007).

The chemical composition of barley grain had an increasing value of the Fe:Mn weight ratio over time. The results indicate that the decrease of manganese in barley grain in the subsequent years of the experiment was more significant than that of iron.

The results of the experiment did not allow us to formulate an unequivocal conclusion on the influence of added coal ash on the Fe:Mn weight ratio.

Table 7

Fe:Mn weight ratio in grain of wheat and barley

The variant	Years of experiment					
	2007	2008	2009	2007	2008	2009
	spring wheat			spring barley		
1	0.53	0.47	0.93	1.15	1.64	1.55
2	0.50	0.53	0.77	0.99	1.54	1.49
3	0.55	0.59	0.84	1.08	1.67	1.71
4	0.54	0.62	0.66	1.00	1.70	1.15
5	0.52	0.85	0.45	0.86	1.70	1.48
6	0.53	0.40	0.36	0.84	1.81	1.21
7	0.57	0.36	0.42	1.04	1.37	1.28
Average	0.53	0.55	0.63	0.99	1.63	1.41

CONCLUSIONS

Some influence of ash from fluidized-bed combustion of was obserevd only in the third year of the experiment. Namely, the amount of iron in cv. Nawra wheat grain decreased.

2. The results of the experiment do not indicate that coal ash from fluidized-bed combustion applied to soil exert influence on changes in the iron content in cv. Lot barley grain and straw. Some impact was observed only in the first year of experiment.

3. The application of coal ash to soil resulted in a decrease of iron and manganese in spring wheat and spring barley grain and straw, especially in the second and third year of the experiment.

4. When the microbiological preparation EM-1 was applied into soil, the levels of iron and manganese in the studied plants tended to decrease.

5. It should be emphasized that in the subsequent years of the research the concentrations of iron and manganese were decreasing in grain and straw of both wheat and barley, causing variation in the content of these micronutrients in plants between individual years. This trend was more evident in the case of manganese than iron.

6. No influence of the applied coal ash on the Fe:Mn weight ratio was determined in cv. Nawra wheat grain or cv. Lot barley grain.

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