ACTA Acta Sci. Pol., Agricultura 10(2) 2011, 97-104

THE ELEMENTAL COMPOSITION OF ASH FROM STRAW AND HAY IN THE CONTEXT OF THEIR AGRICULTURAL UTILIZATION*

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Abstract. The paper presents the results of the elemental composition of the ash produced during combustion of straw and hay. Test samples of ash were characterized by alkaline pH (pH 10.2) and a substantial overall potassium content (155,7 g·kg^{-1} K), calcium (124,0 g·kg^{-1} Ca), phosphorus (15,1 g·kg^{-1} P) and magnesium (7,3 g·kg^{-1} Mg). In addition, presence of essential micronutrients for plants was found in them (Fe > Mn > Zn > Cu). A small natural content of heavy metals (Cr > Pb > Ni > Cd > Hg) in the ash is not a contraindication for the agricultural use of ash from the plant biomass.

Key words: macroelements, microelements, heavy metals

INTRODUCTION

Cereal straw and rape straw as well as the biomass of other plants more and more frequently are used in Poland for fuel purposes [Budzyński and Bielski 2004, Hołubowicz-Kliza 2007, Denisiuk 2009]. Combusted in boilers which sometimes heat whole cities, they intensify the negative balance of the soil organic matter, especially on farms selling by-product yield of plants [Harasimowicz-Hermann and Hermann 2007]. With the increasing mass of combusted straw and biomass of other fuel plants, there occurs a problem of environmentally-safe storage and possible agricultural utilization of the produced ash [Kalembasa 2006].

In literature, relatively rare are studies devoted to chemical composition and the agricultural utilization of ash from the plant biomass [Blander and Pelton 1997, Kalembasa 2006]. The results concerning chemical composition, fertilizer application as well as landfill remediation of hearth wastes formed during the combustion of brown coal and hard coal [Antonkiewicz 2005, 2007, Gibczyńska et al. 2007, Kalembasa et al. 2008, Właśniewski 2009], wood or sludges [Białowiec and Janczukowicz 2009] are

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* Scientific paper financed from education means in the years 2009-2012 as a research project PB 0835/B/P01/2009/36

published more frequently. Ash has an alkaline reaction and contains in its composition different amounts of macro- and microelements, sometimes also a harmful content of heavy metals [Greinert and Greinert 1999, Maciak 1999, Antonkiewicz and Radkowski 2006].

Research hypothesis assumes that ash from the combustion of cereal straw, rape straw and from hay from the seed forage grass has great fertilizing advantages, and trace content of heavy metals does not limit the possibilities of its application in the field plant production. The aim of the research was the evaluation of chemical properties of ash from straw and hay coming from different sources in the context of fertilization.

MATERIAL AND METHODS

Research material included collected in 2009 representative samples of ash from combustion of wheat straw and rape straw as well as of hay from the seed forage grasses stored in heaps at municipal-communal boiler in Kisielice (53°60' N; 19°25' E), Iława district, Warmian-Masurian Voivodeship. Ash obtained at the Experimental Station Mochełek (53°13' N; 17°51' E) near Bydgoszcz from freshly combusted wheat straw, barley straw and winter rape straw was also used for research purposes. From each place 8 samples were collected and detailed chemical tests were conducted on collective samples of ash from a particular plant and town. All ash samples were subjected to analysis of: their reaction, content of total forms of macro- and microelements as well as the content of total forms of heavy metals. The tests were conducted at the Regional Chemical-Agricultural Station in Bydgoszcz according to standard methods. The content of total forms of phosphorus, potassium, calcium and magnesium were determined with the use of the flame photometric method (PB 57). The total content of the rest of elements was tested with the atom absorption spectrometry method: Cu (PB 10), Mn (PB 10), Zn (PB 10), Fe (PB 10), Pb (PB 12), Cd (PB 12), Ni (PB 12), Cr (PB 14), whereas the total content of mercury (Hg) was determined with the use of AMA-254 analyser (PB 59).

Obtained results were subjected to comparative evaluation and evaluation concerning utilization of fertilizers. Variation coefficients of pH and the content of particular elements in ash, taken from different places, from straw from different plants were calculated with Microsoft Office Excel 2007 spreadsheet. The mean values were also determined for particular elements introduced into the soil with an ash dose of $1\ t \cdot ha^{-1}$.

RESULTS

Analyzed samples of ash from straw were characterized by alkaline reaction. pH indicator in KCl was on average 10.2, oscillating from 9.8 for wheat straw ash taken from a heap in Kisielice to 10.7 – winter rape straw ash from Mochełek. Variation of the pH indicator was very low, oscillating on the level of 3.2% (Table 1). The total phosphorus content was on average 15.1 $g \cdot kg^{-1}$ P, oscillating between 5.8 $g \cdot kg^{-1}$ P in wheat straw ash from a heap in Kisielice and 22.6 $g \cdot kg^{-1}$ P in ash from freshly combusted rape straw in Mochełek. The variation coefficient of phosphorus content in ash was 44.2%. Ash subjected to analysis had a relatively large, 155.7 $g \cdot kg^{-1}$ K, though diversified from 75.0 g·kg^{-1} K to 247.3 g·kg^{-1} K content of total potassium, characterized by variation of 46.2%. Moreover, the ash contained 124.0 g·kg^{-1} Ca, with its concentration oscillating in the range from 64.9 g·kg^{-1} Ca in wheat straw from Kisielice to 207.3 g·kg^{-1} Ca in rape straw from Mochełek. The total magnesium content was on average 7.3 g·kg^{-1} Mg and oscillated from 5.2 g·kg^{-1} Mg in barley straw ash to 14.7 g·kg^{-1} Mg in hay ash (Table 1). Variation coefficient of the content of total forms of calcium and magnesium was 48.6% and 50.5%, relatively. The mean total content of macroelements in ash was arranged in a descending order of values K > Ca > P > Mg.

Ash from cereal straw and from grass hay also contained microelements in its chemical composition (Table 2). The mean total content of copper was 34.3 mg·kg^{-1}, oscillating from 25.6 mg·kg^{-1} in straw ash from a heap in Kisielice to 43.4 mg·kg^{-1} in hay ash. The total content of other microelements in ash was on average: Zn – 185.0 mg·kg^{-1}, Mn – 836.4 mg·kg^{-1}, Fe – 3661.7 mg·kg^{-1}. Variation coefficient of the total content of copper (Cu) in ash was relatively low – 18.1%, whereas for zinc (Zn), manganese (Mn) and iron (Fe) it reached the level of 45.2%, 48.6% and 37.9%, respectively. The mean total content of microelements in ash was arranged in a descending order of values Fe > Mn > Zn > Cu.

The total content of heavy metals in ash was very low, although variable in its particular samples, and was on average: 3.5 mg·kg^{-1} lead (Pb), 1.2 mg·kg^{-1} cadmium (Cd), 2,8 mg·kg^{-1} nickel (Ni), 10.1 mg·kg^{-1} chromium (Cr), 0.0041 mg·kg^{-1} mercury (Hg). Variation coefficient of the heavy metal content in ash from straw and hay oscillated from 43.3% in case of lead (Pb) up to 93.3% for nickel (Ni). The mean total content of heavy metals in ash was arranged in a descending order of values Cr > Pb > Ni > Cd > Hg (Table 3).

Table 4 presents amounts of total forms of macroelements, microelements and heavy metals introduced into the soil with an ash dose of 1 t·ha^{-1}. From the table it follows that the element that might reduce application of large doses of straw ash is potassium. With the dose of dry ash being 1 t·ha^{-1}, approximately 155.7 kg K·ha^{-1}, 124.0 kg Ca·ha^{-1}, 15.1 kg P·ha^{-1} and 7.3 kg Mg·ha^{-1} are introduced into the soil. With such an amount of ash, microelements are also introduced into the soil in the amount of 34.4 g copper (Cu), 185.2 g zinc (Zn), 836.4 g manganese (Mn) and 3661.6 g iron (Fe). The amount of introduced into the soil heavy metals, even with relatively large doses of ash, does not pose a threat for natural environment. The dose of 1 t·ha^{-1} ash contains approximately 10 grams of chromium (Cr), several grams of lead (Pb), cadmium (Cd), nickel (Ni) and less than 0,01 g mercury (Hg) (Table 4).

Table 1. Macroelement content and pH in ash from straw and hay
Tabela 1. Zawartość makroelementów i pH w popiele ze słomy i siana

Specification Wyszczególnienie	Ash from the boiler Kisielice Popiół z kotłowni Kisielice			Ash from Mochełek Experimental Station Popiół ze Stacji Badawczej Mochełek			Mean Średnia	Variation coefficient Współczynnik zmienności %
	wheat straw słoma pszenicy	rape straw słoma rzepaku	hay siano	wheat straw słoma pszenicy	barley straw słoma jęczmienia	rape straw słoma rzepaku		
pH w 1 N KCl	9.8	10.2	10.5	10.2	10.0	10.7	10.2	3.2
Total forms – Formy ogólne								
Phosphorus – Fosfor (P), $g \cdot kg^{-1}$	5.8	8.4	16.2	16.7	20.7	22.6	15.1	44.2
Potassium – Potas (K), $g \cdot kg^{-1}$	75.0	161.0	127.8	232.4	247.3	90.5	155.7	46.2
Calcium – Wapń (Ca), $g \cdot kg^{-1}$	64.9	145.9	174.5	71.5	80.1	207.3	124.0	48.6
Magnesium – Magnez (Mg), $g \cdot kg^{-1}$	5.3	5.9	14.7	5.4	5.2	7.4	7.3	50.5

Table 2. Microelement content in ash from straw and hay
Tabela 2. Zawartość mikroelementów w popiele ze słomy i siana

Specification Wyszczególnienie	Ash from the boiler Kisielice Popiół z kotłowni Kisielice			Ash from Mochełek Experimental Station Popiół ze Stacji Badawczej Mochełek			Mean Średnia	Variation coefficient Współczynnik zmienności %
	wheat straw słoma pszenicy	rape straw słoma rzepaku	hay siano	wheat straw słoma pszenicy	barley straw słoma jęczmienia	rape straw słoma rzepaku		
Total forms – Formy ogólne								
Copper – Miedź (Cu), $mg \cdot kg^{-1}$	25.6	33.0	43.4	33.5	31.3	39.0	34.3	18.1
Manganese – Mangan (Mn), $mg \cdot kg^{-1}$	606.8	310.1	1297.7	1228.7	1035.8	539.2	836.4	48.6
Zinc – Cynk (Zn), $mg \cdot kg^{-1}$	64.9	133.8	162.6	265.4	289.2	194.2	185.0	45.2
Iron – Żelazo (Fe), $mg \cdot kg^{-1}$	3158.0	2861.0	4068.0	3491.0	2200.0	6192.0	3661.7	37.9

Table 3. Heavy metal content in ash from straw and hay
Tabela 3. Zawartość metali ciężkich w popiele ze słomy i siana

Specification Wyszczególnienie	Ash from the boiler Kisielice Popiół z kotłowni Kisielice			Ash from Mochełek Experimental Station Popiół ze Stacji Badawczej Mochełek			Mean Średnia	Variation coefficient Współczynnik zmienności %
	wheat straw słoma pszenicy	rape straw słoma rzepaku	hay siano	wheat straw słoma pszenicy	barley straw słoma jęczmienia	rape straw słoma rzepaku		
Total forms – Formy ogólne								
Lead – Ołów (Pb), $mg \cdot kg^{-1}$	5.8	2.6	2.5	4.7	1.9	3.2	3.5	43.3
Cadmium – Kadm (Cd), $mg \cdot kg^{-1}$	1.8	1.4	2.4	0.8	0.4	0.2	1.2	71.5
Nickel – Nikiel (Ni), $mg \cdot kg^{-1}$	0.3	1.2	7.1	1.6	1.7	5.1	2.8	93.3
Chromium – Chrom (Cr), $mg \cdot kg^{-1}$	18.7	8.3	12.4	6.8	5.8	8.6	10.1	47.2
Mercury – Rtęć (Hg), $mg \cdot kg^{-1}$	0.0043	0.0077	0.0089	0.00082	0.00086	0.00202	0.0041	85.6

Table 4. Mean rate of total forms of macroelements, microelements and heavy metals in the ash dose 1 $t \cdot ha^{-1}$
Tabela 4. Średnia ilość ogólnych form makroelementów, mikroelementów i metali ciężkich w dawce popiołu 1 $t \cdot ha^{-1}$

Macroelements – Makroelementy		Microelements – Mikroelementy		Heavy metals – Metale ciężkie	
Phosphorus – Fosfor (P), $kg \cdot ha^{-1}$	15.1	Copper – Miedź (Cu), $g \cdot ha^{-1}$	34.4	Lead – Ołów (Pb), $g \cdot ha^{-1}$	3.44
Potassium – Potas (K), $kg \cdot ha^{-1}$	155.7	Manganese – Mangan (Mn), $g \cdot ha^{-1}$	836.4	Cadmium – Kadm (Cd), $g \cdot ha^{-1}$	1.16
Calcium – Wapń (Ca), $kg \cdot ha^{-1}$	124.0	Zinc – Cynk (Zn), $g \cdot ha^{-1}$	185.2	Nickel – Nikiel (Ni), $g \cdot ha^{-1}$	2.84
Magnesium – Magnez (Mg), $kg \cdot ha^{-1}$	7.3	Iron – Żelazo (Fe), $g \cdot ha^{-1}$	3661.6	Chromium – Chrom (Cr), $g \cdot ha^{-1}$	10.08
				Mercury – Rtęć (Hg), $g \cdot ha^{-1}$	0.00408

DISCUSSION

Fertilizing properties of ash have been known for a long time and have constituted basis of slash-and-burn cultivation in primitive agriculture. Nowadays, activities aiming at utilization of ash produced in boilers are necessary, and agricultural utilization may be one of them, as it has a lot of beneficial properties. The reaction of ashes from hard coal and brown coal is alkaline, with pH indicator from 8.0 to 11.1 [Greinert and Greinert 1999, Maciak 1999]. Also the studied straw ash, regardless of the plant species, was characterized by alkaline reaction. Properties of the ash from the plant biomass are diversified and depend on the kind of combusted biomass, its chemical composition, as well as on the combustion technology itself [Olanders and Steenari 1995, Blander and Pelton 1997, Bakisgan et al. 2009]. These ashes are richest in potassium and calcium. Potassium content in ash from the plant biomass may reach up to 40% K_2O (332 $g \cdot kg^{-1}$ K), and calcium may even exceed 60% CaO (429 $g \cdot kg^{-1}$ Ca) [Kalembasa 2006, Kowalczyk-Juśko 2009]. Studied straw ash confirms these relations. In some of its samples, the content of potassium and calcium exceeded 200 $g \cdot kg^{-1}$. Alkaline reaction and the relatively large amount of calcium with large doses of ash, may favorably influence the pH and the physical-chemical properties of the soil [Właśniewski 2009]. Not less significant ash component, from the point of view of plant nutrition and soil properties, is magnesium. Its total content in ash may reach 5.33% MgO (32.1 $g \cdot kg^{-1}$ Mg) [Kalembasa 2006], 5.2% MgO (31.4 $g \cdot kg^{-1}$ Mg) [Bakisgan et al. 2009], 7.85% MgO (47.3 $g \cdot kg^{-1}$ Mg) [Kowalczyk-Juśko 2009]. In own research on straw ash, the content of magnesium was lower and oscillated between 5.2 and 14.7 $g \cdot kg^{-1}$ Mg. Nevertheless, with the applied dose of 1 t of ash per ha, from 5.2 to 14.7 kg $Mg \cdot ha^{-1}$ is introduced into the soil. With the confirmed in research total content of 15.1 g $P \cdot kg^{-1}$, however, the amount of introduced into the soil phosphorus is greater. Other authors report that the content of this macroelement in ash may be significantly greater, even up to 16.5% (71.9 g $P \cdot kg^{-1}$) [Kalembasa 2006, Bakisgan et al. 2009, Kowalczyk-Juśko 2009]. Moreover, ashes obtained during combustion of the plant biomass have in its chemical composition rich and at the same time diversified set of microelements [Olanders and Steenari 1995, Blander and Pelton 1997, Kalembasa 2006, Bakisgan et al. 2009], which was also proved when analyzing samples of cereal straw, rape straw and grass hay.

Straw ash as a waste material may be used for soil fertilization. Results of the studies of chemical composition and defined amounts of introduced components, even with relatively large doses, confirm this possibility. Ash also in this field meets requirements of mineral fertilizers, which is precisely regulated by law [Ustawa... 2001, 2007, Rozporządzenie (WE)... 2003, Rozporządzenie MRiRW... 2008]. One of the many conditions is, among others, the minimum content of phosphorus (2% P_2O_5) and potassium (2% K_2O) in mineral fertilizers in the solid state. Maximum content of heavy metals in the dry matter of mineral fertilizer is also determined, and it amounts to: arsenic (As) – 50 $mg \cdot kg^{-1}$, cadmium (Cd) – 50 $mg \cdot kg^{-1}$, lead (Pb) – 140 $mg \cdot kg^{-1}$, mercury (Hg) – 2 $mg \cdot kg^{-1}$. Whereas for organic-mineral fertilizers maximum content in the dry matter of fertilizer is as follows: chromium (Cr) – 100 $mg \cdot kg^{-1}$ and nickel (Ni) – 60 $mg \cdot kg^{-1}$ [Rozporządzenie MRiRW... 2008].

CONCLUSIONS

1. Properties of straw ash, despite variation depending on the conditions of obtaining it, indicate the possibility to utilize this waste material for fertilization and enrichment of the soils.

2. On average, studied samples of ash from wheat straw, barley straw, rape straw and hay from the seed forage grasses were characterized by alkaline reaction (pH 10.2) as well as by the substantial total content of potassium – 155.7 $g \cdot kg^{-1}$ K, calcium – 124.0 $g \cdot kg^{-1}$ Ca, phosphorus – 15.1 $g \cdot kg^{-1}$ P and magnesium – 7.3 $g \cdot kg^{-1}$ Mg.

3. Ash from straw contained in its chemical composition microelements applied in plant fertilization in a descending amount Fe > Mn > Zn > Cu. Low, though variable, natural content of heavy metals (Cr > Pb > Ni > Cd > Hg) is not a contraindication to its agricultural utilization.

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SKŁAD ELEMENTARNY POPIOŁU ZE SŁOMY I SIANA W ASPEKCIE JEGO ROLNICZEGO WYKORZYSTANIA

Streszczenie. W pracy przedstawiono wyniki badań składu elementarnego popiołu ze spalania słomy pszenicy, jęczmienia, rzepaku i siana traw nasiennych. Badane próbki popiołu miały odczyn alkaliczny (średnio pH 10,2) oraz znaczną ogólną zawartość potasu (155,7 $g \cdot kg^{-1}$ K), wapnia (124,0 $g \cdot kg^{-1}$ Ca), fosforu (15,1 $g \cdot kg^{-1}$ P) i magnezu (7,3 $g \cdot kg^{-1}$ Mg). Stwierdzono w nich ponadto obecność niezbędnych dla roślin mikroelementów (Fe > Mn > Zn > Cu). Niewielka naturalna zawartość metali ciężkich (Cr > Pb > Ni > Cd > Hg) w popiele z badanej słomy i siana traw nasiennych nie stanowi przeciwwskazań do jego rolniczego wykorzystania.

Słowa kluczowe: makroelementy, mikroelementy, metale ciężkie

Accepted for print – Zaakceptowano do druku: 09.02.2011