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ASSESSMENT OF CHEMICAL COMPOSITION OF BUSHGRASS (*Calamagrostis epigejos* L.) OCCURRING ON THE LANDFILL SITE OF THE FURNACE WASTE AND CARBIDE RESIDUE LIME
Part 2. CONTENT OF IRON, COBALT MANGANESE, ALUMINIUM AND SILICON

OCENA SKŁADU CHEMICZNEGO TRZCINNIKA PIASKOWEGO (*Calamagrostis epigejos* L.) WYSTĘPUJĄCEGO NA SKŁADOWISKACH ODPADÓW PALENISKOWYCH I WAPNA POKARBIDOWEGO
Cz. 2. ZAWARTOŚĆ ŻELAZA, KOBALTU, MANGANU, GLINU I KRZEMU

Abstract: Furnace ashes and carbide lime deposited on landfills may constitute a valuable raw material, among others for biological reclamation of post-industrial areas. Their environmental management requires the assessment of their suitability not only with respect to concentrations of heavy metals but also other components, including microelements. Ashes originating from hard coal burning are a rich source of microelements, particularly Fe, B, Mn and Co, which is very important for correct growth. However, very high contents of microelements in furnace wastes may influence their excessive uptake by plants, which in consequence lead to their die-back. Although high accumulation of microelements in plants is not always toxic for the plants themselves, it may cause serious pathogenic consequences in people or animals consuming these plants.

The contents of selected elements in bushgrass collected from furnace ash and carbide lime dumps was diversified, ranging from 49.70–1800.0 mg Fe, 0.01–1.17 mg Co, 7.33–146.0 mg Mn, 17.20–120.0 mg Si and 8.68–1500.0 mg Al $\cdot$ kg^{-1} d.m. Higher concentrations of iron, cobalt, manganese and aluminium were registered in plants collected from furnace ash dumps and lower in plants from carbide lime section. Optimal contents of microelements in plants destined for forage are as follows: 40–70 mg Fe, 0.3–1.0 mg Co and 40–60 mg Mn $\cdot$ kg^{-1} d.m. Assessment of the plants according to this criterion revealed over the norm mean content of iron in the samples taken from furnace ashes and carbide lime dump. Optimal content of cobalt was assessed in plants gathered from inactive section of furnace ashes whereas a deficient amount from active section of furnace ashes and carbide lime. Deficient (< 40 mg) manganese contents were found in 13 samples collected from the bowl of furnace ashes and carbide lime landfills. Only in 6 plant samples registered manganese content exceeded its optimal value in fodder. Manganese content in plants gathered from the

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landfill shelves was below the optimal value. Low content of manganese in plants collected from the landfills in comparison with other elements is justified by the fact that in alkaline environment this element passes into compounds unavailable to plants.

Key words: *Calamagrostis epigejos* L. (bushgrass), dumps, incineration ash, lime carbide, Fe, Co, Mn, Al, Si

Considering among others the lack of space for new landfill sites, management of furnace ashes and carbide lime should be a pro-ecological task [1]. Furnace ashes and carbide lime deposited on landfills may be a valuable raw material for among other biological reclamation of post-industrial areas [2–3]. Their environmental applications require an assessment of their usefulness considering not only their heavy metal contents but also with respect to other components including microelements. Ashes originating from hard coal burning provide a rich source of microelements, particularly Fe, B, Mn and Co, which are of key importance for proper plant growth [4–6]. However, very high concentrations of microelements in furnace wastes may also influence their excessive uptake by plants, which in result leads to their dieback [7]. Although high accumulation of microelements in plants is not always toxic for the plants themselves, it may have dangerous pathogenic consequences in people or animals consuming these plants [8].

The investigations aimed at an assessment of Fe, Co, Mn, Al and Si contents in furnace ashes and carbide lime and in bushgrass occurring on these wastes.

Material and methods

The object of investigations was bushgrass (*Calamagrostis epigejos* L.) occurring on furnace waste and carbide lime landfills, the substratum and embankments of these landfills. A detailed description of the above-mentioned landfills was presented in the first part of the paper [9]. The analysis of plant material comprised an assessment of the content of selected elements following their "dry" mineralization. The contents of Fe, Co, Mn, Al and Si in the substratum and bushgrass were assessed using ICP-AES method by sequential spectrometer, JY-238 Ultrace. Statistical computations were made using Statsoft 7.1. programme. Basic statistical parameters: minimum, maximum and medium values as well as variation coefficients were computed. Simple correlation coefficients describing the dependence between the element contents in plants and physical properties (colloidal clay) and chemical properties of the substratum were also calculated.

Results and discussion

A detailed description of physical and chemical properties of furnace ashes and carbide lime was presented in the first part of the paper [9].

The contents of Fe, Co, Mn, Al and Si in wastes. The research revealed that furnace ashes originating from hard coal burning belong to silicate type due to their high concentrations of aluminium, silica and iron [10]. On the other hand, carbide lime is a by-product formed at acetylene production [1].

Total content of selected elements in the samples from the examined landfills ranged quite widely: 1385–38200 mg Fe, 1.00–13.70 mg Co, 28.55–875.0 mg Mn, 264–1285 mg Si and 2545–15950 mg Al · kg^{-1} d.m. (Table 1).

The greatest variability in the content of examined elements was found for iron (V = 87.1 %) and the slightest for aluminium (V = 26.8 %). Experiments have demonstrated that furnace ashes are characterized by a higher content of Fe, Co, Mn, Al and Si in comparison with carbide lime.

In comparison with their total contents, solubility of the tested elements in 1 mol · dm^{-3} HCl solution ranged in limits 0.01–37.38 % Fe, 8.91–36.79 % Co, 13.36–73.53 % Mn and 0.02–42.98 % Al. The greatest solubility in the researched wastes in result of extraction in 1 mol HCl · dm^{-3} was registered for manganese (73 %), then for aluminium (42 %) and the slightest for cobalt and iron (36 %) in relation to total content. For silica greater solubility was registered in 1 mol hydrochloric acid than after a sample digesting in a mixture of nitric(V) and chloric(VII) (3:2) acids.

High contents of microelements in furnace wastes may lead to their excessive uptake by plants [4]. The contents of examined elements in the plants collected from the landfills were diversified and ranged from 49.70 to 1800.0 mg Fe, 0.01–1.17 mg Co, 7.33–146.0 mg Mn, 17.20–120.0 mg Si and 8.68–1500.0 mg Al · kg^{-1} d.m. (Table 1). Among the investigated elements the greatest diversification was registered for aluminium (V = 151.0 %) assessed in bushgrass growing in furnace ashes section and the smallest for iron (V = 28.5 %) in plants occurring in carbide lime section. Similar as in the substratum, higher contents of iron, cobalt and aluminium were assessed in plants collected from furnace ashes dumps, whereas lower from carbide lime section. Manganese contents were on an approximately similar level in the bushgrass gathered from the landfills, whereas greater amounts of silica were registered in bushgrass growing in carbide lime section.

Optimal contents of microelements in plants destined for forage are: 40–70 mg Fe, 0.3–1.0 mg Co and 40–60 mg Mn · kg^{-1} d.m. [11–12]. Assessment of the plants according to this criterion revealed over the norm mean content of iron in the samples taken from furnace ashes and carbide lime dump. Optimal content of cobalt was assessed in plants gathered from inactive section of furnace ashes whereas a deficient amount from active section of furnace ashes and carbide lime. Deficient manganese contents (< 40 mg · kg^{-1}) were found in 13 samples collected from the bowl of furnace ashes and carbide lime landfills. Only in 6 plant samples registered content of manganese exceeded optimal value. Manganese content in plants gathered from the landfill shelves was below the optimal value. Optimal Fe to Mn ratio is 1.5–2.5:1 [12]. Symptoms of manganese toxicity and iron deficiency occur when this value falls below 1, whereas when Fe:Mn ratio is above 2.5 a manganese deficiency and iron excess are noted in plants. The conducted research confirms that mean Fe to Mn ratio in bushgrass occurring on landfill exceeds the optimal value, which demonstrates Fe excess and Mn deficiency.

Table 1

Element contents in plants and substratum of investigated landfills [mg · kg^{-1} d.m.]

Parameter	Plant	Total*	Soluble**	Plant	Total	Soluble	Plant	Total	Soluble
	Fe			Co			Mn		
Quarters incineration ash (N = 30)									
Minimum	49.70	1515.00	193.00	0.01	1.00	0.16	7.33	28.55	8.44
Maximum	1800.00	34900.00	5140.00	1.17	13.70	3.20	129.00	655.00	312.00
Mean	329.99	15754.00	2847.90	0.21	9.44	1.87	32.82	309.97	151.59
V%***	116.16	48.71	39.62	132.11	29.35	31.99	82.09	46.31	48.37
Quarters lime carbide (N = 20)									
Minimum	74.80	1385.00	0.20	0.02	1.00	0.11	8.04	79.00	13.80
Maximum	275.00	38200.00	5210.00	0.22	12.55	2.20	146.00	875.00	339.00
Mean	156.27	10863.50	1740.56	0.09	6.36	1.13	31.26	277.43	121.44
V%	28.54	87.10	108.98	51.61	66.89	75.39	115.10	67.14	78.60

Table 1 contd.

Parameter	Plant	Total	Soluble	Plant	Total	Soluble	Fe:Mn ratio in plants
	Si			Al			
Quarters incineration ash (N = 30)							
Minimum	17.20	394.00	158.00	8.68	2545.00	518.00	1.83
Maximum	73.00	1285.00	9890.00	1500.00	15300.00	5580.00	26.35
Mean	35.81	658.15	5013.23	217.65	11005.83	3518.60	9.65
V%	35.64	28.69	43.46	151.04	26.84	34.34	61.29
Quarters lime carbide (N = 20)							
Minimum	25.40	264.50	203.00	15.20	4845.00	1.04	0.73
Maximum	120.00	735.00	6810.00	309.00	15950.00	4890.00	20.40
Mean	52.31	442.55	3058.55	104.83	10430.50	2115.30	10.09
V%	51.23	34.92	92.82	78.68	39.00	103.20	65.71

* Total content in waste, ** Content of forms soluble in 1 mol HCl $\cdot$ dm^{-3}; *** Variability coefficient.

Correlation coefficients. Occurrence of statistically significant relationships between the contents of Fe, Co, Mn, Si and Al in bushgrass and their amounts in wastes and chemical properties were established by computing simple correlation coefficients at significance level p=0.001 (Table 2 and 3). Fe and Co contents in bushgrass growing on furnace ashes were most strongly affected by the aluminium in plant (Table 2). Total Fe content in the ashes was strongly correlated with total content of manganese and amount its soluble forms. Total Mn content and amount its soluble forms in the ashes were also determined by Co content in this waste. Moreover total content of aluminium and its soluble forms in the ash affected Fe and Co content in this waste. Significant relationships were also found between the contents of Si soluble in 1 mol HCl · dm^{-3} in ash and Fe and Co content. In carbide lime the contents of Co, Mn and Al were strongly correlated with iron content, moreover Mn and Al contents depended on the total content and amount of soluble forms of cobalt in this lime. It was also found that aluminium contents in carbide lime depended on Mn and Si in this waste.

Table 2

Significant (p = 0.001) simple correlation coefficients (r) between element content of plant and wastes

Specification		Plant	Total	Soluble	Plant	Total	Soluble	Soluble	Soluble	Total
		Fe			Co			Mn	Si	Al
Quarters incineration ash (N = 30)										
Soluble**	Fe		0.71						0.68	0.74
Plant	Co	0.95								
Total*	Co		0.64	0.73					0.71	0.75
Soluble	Co					0.70			0.83	
Total	Mn		0.93	0.85		0.71		0.77		
Soluble	Mn		0.65	0.91		0.66				0.82
Plant	Al	0.98			0.97					
Soluble	Al			0.69		0.79	0.86		0.93	0.66
Quarters lime carbide (N = 20)										
Soluble	Fe		0.78						0.92	
Total	Co		0.85	0.90					0.95	
Soluble	Co			0.93		0.96			0.97	
Total	Mn		0.87							
Soluble	Mn		0.85	0.89		0.89	0.83		0.87	
Total	Al		0.77	0.89		0.97	0.97	0.84	0.96	
Soluble	Al			0.96		0.94	0.98	0.86	0.99	0.95

* Total content in waste; ** Content of forms soluble in 1 mol HCl · dm^{-3}.

Table 3 presents correlation relationships between Fe, Co, Mn, Si and Al contents in bushgrass and wastes with physical and chemical properties of the waste.

Table 3

Significant ($p = 0.001$) simple correlation coefficients (r) between element content of plant and soil and some of its properties

Specification	Plant	Soluble**	Plant	Total*	Soluble	Plant	Soluble	Plant	Soluble	Plant	Total	Soluble
	Fe		Co			Mn		Si		Al		
Quarters incineration ash (N = 30)												
pH_{KCl}						0.64					–0.61	
available K	0.73		0.77							0.78		
Quarters lime carbide (N = 20)												
Clay coloid								0.85		0.78		
pH_{KCl}				–0.82	–0.85				–0.87		–0.87	–0.84
pH_{H_2O}				–0.81	–0.83				–0.86		–0.85	–0.82
Available P				0.81	0.83				0.86		0.81	0.82
Available Mg		0.77		0.86	0.83		0.81		0.91		0.86	0.85

* Total content in waste; ** Content of forms soluble in 1 mol $HCl \cdot dm^{-3}$.

Fe, Co and Al contents in bushgrass occurring in furnace ashes sections were most depended on the contents of bioavailable potassium, whereas Mn content in plants was most affected by ashes pH_{KCl}. On the other hand, Si and Al content in bushgrass growing in carbide lime section was determined by the presence of colloidal clay. The reaction of furnace ashes was negatively correlated with total content of aluminium in this waste. On the other hand, the reaction of carbide lime and the content of bioavailable phosphorus and magnesium to the highest degree affected the total content of Co and Al and their soluble forms in this waste. It was also found that the content of Si soluble in 1 mol HCl $\cdot$ dm^{-3} was negatively correlated with the pH but positively with bioavailable phosphorus and magnesium contents in carbide lime. The content of bioavailable Mg in carbide lime most affected Fe and Mn solubility in 1 mol HCl $\cdot$ dm^{-3}.

Previous investigations have shown that the element contents in plants and wastes may be determined by various physicochemical properties of wastes.

Discussion

Higher contents of Fe, Co, Mn, Al and Si in furnace ashes in comparison with carbide lime demonstrates that furnace ashes constitute a richer source of nutrients for plants. Total microelement content in incineration ashes is comparable with the contents in the ashes was found by Beresniewicz and Nowosielski [4]. Total content of cadmium and cobalt in the analyzed wastes does not basically differ from these elements contents in arable soils [13–14]. On the other hand, it was noted that in the investigated wastes iron and aluminium contents were much higher than in arable soil [15]. From among the analyzed elements manganese revealed the highest and cobalt the slightest solubility. Low solubility of cobalt in arable soils in relation to the total contents was also noted by Straczyk and Drobnica [14].

Furnace ashes constitute a rich source of elements, particularly such as: Fe, B or Si, which may be of crucial importance for plant fertilization [5]. High concentrations of microelements in furnace wastes may influence their excessive uptake by plants [4]. Small content of manganese in plants gathered from the landfills, as compared to the other elements, is justified by the fact that in alkaline environment this element passes into compounds unavailable to plants [16]. Small contents of manganese in plants growing on furnace ash and carbide lime landfills were caused by alkaline reaction of the substratum and presence of a great amount of lime. Research conducted by Maciak et al [17] corroborate the Authors' own investigations showing that in alkaline environment aluminium is intensely cumulated in plants, which on the other hand makes difficult the uptake of other elements, including phosphorus.

Microelement contents in the investigated plants were diversified. According to limit numbers suggested by Falkowski et al [12] and Gorlach [11], a high over-the-limit content of iron was registered, optimal content of cobalt but deficient content of manganese. The Author's own investigations revealed that cobalt contents in bushgrass collected from ash and carbide lime sections were much lower in comparison with plants gathered from incineration ash heap investigated by Andruszczak et al [16]. The research conducted by Macuda et al [18] revealed much bigger contents of cobalt in consumption plants cultivated in the vicinity of petroleum industrial wastes than in plants occurring on the analyzed landfills. On the other hands, investigations conducted by Curylo [19] showed that cobalt content in red fescue and meadow sward was comparable with its amount in plants growing on landfills. Iron content in the Author's own research was considerably bigger than in plants studied by Andruszczak et al [16]. Also Gora [20] found bigger contents of iron and aluminium in plants cultivated in furnace ashes.

Conclusions

1. Furnace ashes contain more Fe, Co, Mn, Si and Al than carbide lime.
2. Bushgrass occurring on furnace ashes revealed higher contents of Fe, Co and Al, whereas Si content was smaller in comparison with carbide lime.
3. Above the norm content of Fe was registered in bushgrass occurring on ashes, close to optimal in the plants from carbide lime section and close to optimal in the plants originating from carbide lime section. Mean content of Mn in plants growing on ashes and carbide lime was below the optimal values. Co content in bushgrass occurring on ashes was on the optimal level, whereas on carbide lime it was deficient.
4. Due to high content of microelements (Fe, Co and Mn) in the incineration ashes and carbide lime they are suggested for use for reclamation measures on post-industrial areas.
5. In case the wastes are not used for reclamation measures, the landfills where the analyzed wastes are deposited should be protected against dusting and migration of elements. Prior to biological turfing of the landfills, a deficient chemistry of ashes and carbide lime should be improved, among other through supplying the nutrients which these wastes lack.

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Abstrakt: Zdeponowane na składowiskach popioły paleniskowe i wapno pokarbidowe mogą stanowić cenny surowiec m.in. w biologicznej rekultywacji terenów poprzemysłowych. Ich wykorzystanie w środowisku wymaga oceny przydatności pod względem zawartości nie tylko metali ciężkich, ale także innych składników, w tym mikroelementów. Popioły pochodzące ze spalania węgla kamiennego stanowią bogate źródło mikroelementów, zwłaszcza Fe, B, Mn i Co, mających bardzo duże znaczenie w prawidłowym wzroście. Jednakże bardzo duże zawartości mikroelementów w odpadach paleniskowych mogą powodować nadmierne ich pobieranie przez rośliny, co w konsekwencji prowadzi do ich obumierania. Aczkolwiek duże nagromadzenie mikroelementów w roślinach nie zawsze jest toksyczne dla samych roślin, ale może spowodować groźne następstwa chorobowe u ludzi lub zwierząt spożywających te rośliny.

Zawartość wybranych pierwiastków w trzcinniku piaskowym zebranym ze składowisk odpadów paleniskowych i wapna pokarbidowego była zróżnicowana i wahała się w zakresie: 49,70–1800,0 mg Fe; 0,01–1,17 mg Co; 7,33–146,0 mg Mn; 17,20–120,0 mg Si oraz 8,68–1500,0 mg Al $\cdot$ kg^{-1} s.m. Większe zawartości żelaza, kobaltu, manganu i glinu stwierdzono w roślinności zebranej ze składowisk popiołów paleniskowych, a mniejsze z kwatery wapna pokarbidowego. Optymalna zawartość mikroelementów w roślinach przeznaczonych na paszę wynosi: 40–70 mg Fe; 0,3–1,0 mg Co i 40–60 mg Mn $\cdot$ kg^{-1} s.m. Wyceniając rośliny według tego kryterium, stwierdzono ponadnormatywną zawartość żelaza w próbkach zebranych ze składowiska popiołów paleniskowych nieczynnej kwatery. Natomiast zawartość żelaza w roślinności zebranej ze składowiska wapna pokarbidowego mieściła się w granicach wartości optymalnej. Optymalną zawartość kobaltu stwierdzono w roślinności zebranej z nieczynnej kwatery popiołów paleniskowych, a niedoborową z kwatery czynnej popiołów paleniskowych oraz wapna pokarbidowego. W badaniach własnych stwierdzono niedoborową zawartość manganu (< 40 mg $\cdot$ kg^{-1}) w 13 próbkach pobranych z czaszy składowisk popiołów paleniskowych i wapna pokarbidowego. Tylko w 6 próbkach roślin zawartość manganu przekraczała wartość optymalną. Zawartość manganu w roślinności zebranej z półek składowisk mieściła się poniżej wartości optymalnej. Małą zawartość manganu w roślinności pobranej ze składowisk, w porównaniu z innymi mikroelementami, można uzasadnić tym, że w środowisku alkalicznym pierwiastek ten tworzy połączenia, z których jest trudno dostępny dla roślin.

Słowa kluczowe: trzcinnik piaskowy (*Calamagrostis epigejos* L.), składowiska, popioły paleniskowe, wapno pokarbidowe, Fe, Co, Mn, Al, Si