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EFFECT OF DIVERSIFIED FERTILIZATION ON HEAVY METAL CONTENTS IN MEADOW SWARD IN THE MOUNTAIN AREA

WPŁYW ZRÓŻNICOWNEGO NAWOŻENIA NA ZAWARTOŚĆ METALI CIĘŻKICH W RUNI ŁĄKOWEJ W REJONIE GÓRSKIM

Abstract: The research was conducted in 2005–2007 on a mountain meadow in Krynica. The experimental field was located at 640 m a.s.l. The experiment was set up on a brown soil with granulometric structure of loamy sand, pH_{KCl} 4.10 and comprised 6 treatments: the control, NPK, loose pen, loose pen + NP, tight pen and autumn loose pen. The mineral treatment was applied in the following doses: 120 N, 25 P and 50 K · ha^{-1}. Organic fertilization was applied as sheep penning. The penning was on two intensity levels: loose pen – 2 m^2 per sheep and tight pen – 1 m^2 per sheep. Each year the meadow was cut twice: in mid-June and at the beginning of September. The highest content of Ni, Cr and Pb was assessed on the treatment with autumn loose pen, Zn on NPK treatments and Cu on tight pen, whereas Cd on loose pen + NP. The second cut revealed higher contents of heavy metals than the first cut. The permissible limit of heavy metal contents for fodder plants was not exceeded in the meadow sward, whereas excessive amounts of cadmium were found only in plants on NPK treatment and loose fold supplemented with NP. The greatest deficiency of copper was found in the meadow sward. Irrespective of the experimental treatment, greater quantities of heavy metals were taken up with the first than the second cut yield, which was undoubtedly connected with greater plant biomass obtained on the first date of harvest.

Keywords: heavy metals, loose pen, tight pen, NPK, mountain meadow

In many countries grasslands play a crucial role in farm animal nutrition and cover a considerable part of their nutritional needs. Apart from organic component contents (proteins, carbohydrates) also minerals play an important role in the meadow sward quality assessment [1, 2]. According to many authors, food macroelement and trace element concentrations, including heavy metals determine the quality of fodder

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originating from these grasslands [3, 4]. The contents of heavy metals in feeds from grasslands depends on the individual species properties, habitat conditions, but also on fertilization [1, 4, 5]. Fertilization of meadows and pastures in mountain areas is conducted usually using sheep penning. Usually it proves the only way in which these grasslands can be fertilized, particularly if they are situated at higher altitude and have a considerable land slope. However, during the penning the sward may be partly damaged and its absorbability diminished. Therefore, if a great load of fertilizer components is left in a pen, its considerable amounts may remain unabsorbed by the vegetation and may be carried by seepage water leading to river water pollution. The investigations were conducted to assess the effect of diversified organic and mineral fertilization on heavy metal contents in a meadow sward.

Material and methods

The experiments were conducted in 2005–2007 on a mountain meadow in Krynica situated at the Experimental Unit of the Department of Grasslands, University of Agriculture in Krakow. The experimental field was located at the altitude of 640 m a.s.l. The experiment was set up on brown soil with granulometric structure of loamy sand, pH_{KCl} 4.10 and organic matter content 53 g · kg^{-1}. Moreover, the soil revealed low content of available phosphorus (12.3 mg · kg^{-1} d.m) and potassium (76.7 mg · kg^{-1} d.m.). The experiment comprised 6 treatments: the control, NPK, loose pen, loose pen + NP, tight pen and autumn loose pen. Mineral treatment was applied in the following doses: 120 N, 25 P and 50 K · ha^{-1}. Organic fertilization was conducted using sheep penning. The penning was on two intensity levels: loose pen – 2 m^2 per sheep and tight pen – 1 m^2 per sheep. The sheep stayed in the pens for two nights per 8 hours. Plant vegetation period lasted from 1 May until 30 September. Each year the meadow was cut twice: in mid-June and at the beginning of September. Monitoring of the temperature and rainfall was conducted during the experiment (Table 1). After harvest the plant material was dried at 65 ^oC in a forced air dryer, then crushed in a laboratory mill and subjected to chemical analysis. The contents of zinc, copper, nickel, chromium, lead and cadmium in the plant material were assessed using ICP-EAS method (inductively coupled plasma-atomic emission spectrometry) after dry mineralization and dissolving the ashes in HNO_3 (1:3). The obtained results were verified statistically using one-way ANOVA and Tukey test at significance level $\alpha < 0.05$ by means of Statistica 7 programme.

Table 1

Monitoring of the weather factors in 2005–2007

Climatic factor	Temperature [^oC]			Rainfalls [mm]		
	2005	2006	2007	2005	2006	2007
Mean I–XII	5.6	6.1	7.4	1250	996.9	930.5
Mean IV–IX	12.4	13.0	13.4	732.6	610.3	504.6
Range	–6–16.7	–8.2–18.6	–2.4–17.1	24.6–199.5	19.9–164.3	25.8–212

Results and discussion

Among the determined heavy metals are elements which belong to microelements necessary for proper growth and development of plants (Zn, Cu and Ni) and animals (Cr), whose optimal contents in the sward should fulfill the nutritional requirements of these organisms. The other metals (Pb and Cd) are not necessary and even small amounts may have a toxic effect on living organisms [6]. In the presented research the assessment of heavy metal contents in meadow sward was based on its potential utilization for fodder according to limit values of heavy metals in plants as stated by various authors: Falkowski [7], Gorlach [8], Curyło et al [9], Kabata-Pendias et al [10] and the Regulation of the Minister of Agriculture and Rural Development of 23 January, 2007 on the admissible contents of undesired substances in fodders [11]. The permissible contents of heavy metals in fodder material have been determined as follows: < 100 mg Zn; < 10 mg Cu; < 10 mg Cr; < 10 mg Ni; < 0.5 mg Cd; < 10 mg Pb · kg^{-1} d.m. The contents of the above-mentioned heavy metals in the analyzed plant material were diversified depending on the kind of applied fertilization and date of harvest, however the greatest changeability was demonstrated for Pb, then for Cd > Cr > > Zn > Ni > Cu (Tables 2 and 3). In comparison with other metals the sward contained the greatest quantities of Zn, while levels of the other metals were as follows: Cu > Ni > > Pb > Cr >Cd.

Table 2

Contents of zinc, copper and nickel in meadow sward (2005–2007)

Treatment	Zinc		Copper		Nickiel	
	I cut	II cut	I cut	II cut	I cut	II cut
	[mg · kg^{-1} d.m.]					
Control	39.13[a]	60.68	5.85	6.74	1.60[ab]	1.88
NPK	42.38[ab]	67.37	5.36	6.81	1.49[ab]	1.82
Loose pen	54.53[bc]	57.53	6.23	6.38	1.65[b]	1.68
Loose pen + NP	57.22[c]	59.17	6.63	6.66	1.57[ab]	1.75
Tight pen	42.80[ab]	60.90	5.38	7.17	1.00[a]	1.65
Autumn loose pen	38.18[a]	55.88	4.87	6.38	2.19[b]	2.09
$LSD_{0.05}$	18.32	n.s.	n.s.	n.s.	0.89	n.s.
Standard deviation	9.74		0.70		0.30	
V%	18.4		11.2		17.9	

Homogeneous groups according to the Tukey test, $\alpha < 0.05$; n.s. – not significant.

Mean content of Zn ranged from 38.18 to 67.90 mg · kg^{-1} d.m. The highest zinc concentration was noted on the loose pen + NP (I cut) and on NPK (II cut), whereas irrespectively of the harvest date, the lowest amount was found on autumn loose pen, but no significant differences in this metal content were registered in II cut under the influence of diversified fertilization (Table 2). Analysis of the harvest date revealed 24 % higher content of zinc in the meadow sward harvested in the second cut. As found

by Falkowski et al [7] good quality feed should contain between 30 and 50 mg Zn · kg^{-1} d.m., so 2 % of samples collected for the three year period of research revealed its deficit, 60 % had optimal content, whereas excessive quantities of zinc were assessed in 40 % of the samples. On the other hand, numerous authors reported frequent zinc deficits in meadow sward [12–14]. Zinc absorbability in plants is affected by soil pH, Ca:Zn and Fe:Zn ratios, the contents of phosphorus, magnesium, nitrogen and copper in soil and by fertilization [15].

Cu content in the analyzed meadow sward ranged from 4.87 to 7.7 mg · kg^{-1} d.m. (Table 2). On all treatments II cut was characterized by on average a 14 % greater content of Cu in comparison with I cut (Table 2). the smallest amounts of this element, similarly as for zinc were detected in the meadow sward of loose autumn pen. On the other hand the sward in loose pen + NP (I cut) and in tight pen (II cut) revealed the highest copper contents. Optimal copper concentrations in feeds are between 7 and 10 mg · kg^{-1} d.m. [7], therefore it may be said that a majority of the sward samples, ca 75 % revealed its deficiency. As has been found by various authors, copper deficiencies in feeds from grasslands are a common phenomenon in Poland [2, 13, 16]. Copper phytoavailability depends on the soil pH, contents of organic matter, phosphorus, manganese and iron in soil, and on plant biological properties [1, 15, 16].

The highest mean content of nickel in both cuts was found in the sward on autumn loose pen and the lowest on tight pen. Its contents ranged from 1.00 to 2.09 mg · kg^{-1} d.m. (Table 2). As in the case of zinc and copper, on a majority of treatments II cut was characterized by on average 17 % bigger content of this metal than cut I. A reverse dependency was demonstrated only on autumn loose pen. Irrespective of the kind of fertilization and harvest date, nickel content in the harvested plants was low (below 10 mg · kg^{-1} d.m.) allowing for the sward utilization for animal feed.

Depending on the kind of fertilization used and harvest date, chromium content ranged from 0.50 to 1.74 · kg^{-1} d.m. (Table 3). Both in I and II cut the greatest amounts of chromium were registered on autumn loose pen, whereas the smallest in the control sward (Table 3). Therefore all kinds of applied fertilization caused a 12–53 % increase in this metal content in the meadow sward (I cut) in comparison with the treatment without fertilization and 19–67 % increase (II cut) in comparison with the control. On the other hand, the analysis of harvest date revealed on average 36 % greater content of zinc in the meadow sward harvested in II cut than in I cut. The exception was only the sward harvested from loose pen where I cut revealed 19 % higher chromium content than II cut. Like in the case of nickel, low chromium content allows to use the analyzed meadow sward for animal feed.

Lead and cadmium are counted to the heavy metals posing special hazards to feed quality. Lead content ranged from 0.43 to 1.92 mg · kg^{-1} d.m. Irrespective of the harvest date, the greatest lead content was registered on autumn loose pen and the smallest on tight pen (I cut) and on the control (II cut) (Table 3). On all treatments II cut showed on average 49 % greater lead content in comparison with I cut. Assuming the standard lead content between 0.1 and 1.0 mg · kg^{-1} d.m. stated by Gorlach [8] as safe for feeds, it was found that over the three year period of investigations 30 % of sward samples revealed excessive amounts of this metal. On the other hand, assessment of the sward

according to the criteria stated by the Minister of Agriculture and Rural Development of 23 January 2007 on admissible contents of undesired substances in feeds [11] revealed that it met the requirements concerning lead content for good quality feeds.

Table 3

Contents of chromium, lead and cadmium in meadow sward (2005–2007)

Treatment	Chromium		Lead		Cadmium	
	I cut	II cut	I cut	II cut	I cut	II cut
	[mg · kg^{-1} d.m.]					
Control	0.50	0.57^{a}	0.51	0.76^{a}	0.38^{b}	0.54
NPK	0.57	1.02^{abc}	0.50	1.27^{abc}	0.36^{ab}	0.75
Loose pen	0.87	0.70^{ab}	0.68	0.93^{a}	0.49^{c}	0.57
Loose pen + NP	0.56	0.82^{ab}	0.57	1.01^{ab}	0.41^{bc}	1.18
Tight pen	0.59	1.28^{bc}	0.43	1.57^{bc}	0.27^{a}	0.53
Autumn loose pen	1.06	1.74^{c}	0.84	1.92^{a}	0.36^{ab}	0.59
$LSD_{0.05}$	n.s.	0.92	n.s.	0.91	0.12	n.s.
Standard deviation	0.37		0.46		0.24	
V%	43.2		50.7		45.2	

Homogeneous groups according to the Tukey test, $\alpha < 0.05$; n.s. – not significant.

Cadmium content in the analyzed meadow sward fell within the 0.27–1.18 mg · kg^{-1} d.m. range depending on treatment and harvest date (Table 3). The highest cadmium content in meadow sward was registered on loose pen (I cut) and on loose pen + NP (II cut), the lowest on tight pen, irrespective of the harvest date, but in I cut the differences in this metal content affected by diversified fertilization were statistically significant. On all treatments II cut was characterized by on average 42 % greater cadmium content in comparison with I cut (Table 3). According to the norms stated above, cadmium content below 0.5 mg · kg^{-1} d.m. does not limit use of the analyzed plants for fodder. Therefore 70 % of the sward samples had optimal cadmium content, whereas its excess was found in 30 %.

Table 4

Values of correlation coefficients between heavy metal contents in meadow sward

Element	Zinc	Copper	Nickiel	Chromium	Lead
Copper	0.44***				
Nickiel	0.33**	–0.18			
Chromium	0.33**	–0.07	0.59***		
Lead	0.46***	0.15	0.50***	0.84***	
Cadmium	0.33**	0.12	0.25*	0.09	0.14

Significant: * $r \leq 0.05$, ** $r \leq 0.01$, *** $r \leq 0.001$

The interrelations of heavy metal contents in the sward fluctuated widely, which evidences changing quality of fodder obtained during the vegetation period (Table 4).

The research demonstrated significantly positive correlation between zinc content and the levels of copper and lead ($r \leq 0.001$) but also the levels of nickel, chromium and cadmium ($r \leq 0.01$). Nickel content was also apparently positively correlated with chromium and lead concentrations ($r \leq 0.001$). the same positive correlation was noted for chromium level and lead content ($r \leq 0.001$).

Heavy metal uptake per area unit is a resultant of the crop yield and their contents in the plant mass. Aggregate uptake of zinc by the meadow sward fluctuated during the three-year period of experiments from 214.52–369.05 g; uptake of copper 27.98–42.41 g; nickel 6.32–11.92 g; chromium 2.42–7.12; lead 2.78–6.49 g and cadmium 1.32 to 3.70 g · ha^{-1} (Table 5).

Table 5

Heavy metal uptake by meadow sward (2005–2007)

Treatment	Zinc	Copper	Nickiel	Chromium	Lead	Cadmium
	[g · ha^{-1}]					
Control	214.52	29.32	7.64	2.42	2.78	1.93
NPK	337.71	39.65	10.69	4.76	4.87	3.20
Loose pen	267.68	31.39	7.62	3.94	3.61	2.48
Loose pen + NP	369.05	42.41	9.78	3.81	4.27	3.70
Tight pen	263.04	34.67	6.32	4.25	4.25	1.92
Autumn loose pen	221.78	27.98	11.92	7.12	6.49	2.15
Standard deviation	62.24	5.79	2.14	1.55	1.26	0.73
V%	22	17	24	35	29	29

From among the analyzed heavy metals zinc was taken up with the sward yield in the greatest quantities, whereas cadmium in the smallest. Irrespective of the treatment higher uptake of the metals with I cut yield was noted than with II cut, which was undoubtedly connected with greater plant biomass obtained at the first harvest date. The increase was 42 % for zinc, 46 % for copper, 52 % for nickel, 39 % for chromium, 13 % for lead and 20 % for cadmium. Zinc uptake by meadow sward fertilized by loose penning supplemented by NP was the greatest. In comparison with the control treatment the increase was 42 %. The smallest quantity of zinc was taken up with control plant yield. Copper uptake by the sward was little diversified as evidenced by the lowest variation coefficient (V % = 17). Like in the case of zinc, the highest copper uptake was revealed on loose pen + NP. In comparison with the control the increase was 31 %. The smallest quantities of copper were removed with the meadow sward yield on autumn loose pen (Table 5). The greatest nickel uptake was noted on autumn loose pen and the smallest on tight pen (Table 5). Chromium uptake by the meadow sward on the analyzed treatments was the most diversified (V = 35 %). Like in the case of nickel, fertilization using autumn loose penning most influenced an increase in chromium uptake, which reached 66 % more than on the control. Non-fertilized plants absorbed the least quantities of chromium. The relationships were similar for lead uptake. The

greatest amounts of lead were removed with plants fertilized with autumn loose pen, where the increase in comparison with the control reached 57 %. The largest quantities of cadmium were taken up with the sward yield on NPK treatment, whereas the smallest on tight pen and on the control (Table 5).

Animal excrements are valuable organic fertilizer which plays an important role not only supplying necessary nutrients in plant and animal nutrition, but also in shaping soil fertility [17, 18]. According to Kasperczyk et al [19], organic fertilizers are a supplement of mineral fertilizers used on grasslands because they contain vital trace elements, which generally mineral fertilizers lack. A positive effect of applied organic fertilization was also revealed in the presented research since heavy metal contents in the meadow sward given in Tables 2 and 3 evidence that the permissible border for plants designed for animal feeds was not exceeded. Only in the case of cadmium plants on NPK treatments and loose pen supplemented with NP revealed its over the norm contents. Additionally it was found that a majority of the analyzed trace elements showed the optimal contents in the meadow sward, and only copper deficit was assessed in 75 % of samples.

Conclusions

1. Among the fertilizer treatments the highest contents of Ni, Cr and Pb were assessed on the treatment with autumn loose pen, Zn on NPK treatments, Cu on the treatment with tight pen, whereas Cd on treatments with loose pen + NP.

2. The second cut revealed on average: higher contents of heavy metals (24 % Zn; 14 % Cu; 17 % Ni; 36 % Cr; 49 % Pb and 42 % Cd) than the first cut.

3. The experiments revealed that the permissible limit of heavy metal contents in plants destined for animal feeds was not exceeded. Only in case of Cd the plants from NPK treatment and loose pen supplemented with NP revealed its over the norm content.

4. Among the analyzed metals the greatest deficiency in the meadow sward was registered for copper.

5. The greatest uptake of zinc and copper was found on the treatment with loose pen supplemented with NP, absorption of nickel, chromium and lead on the treatment with autumn loose pen and cadmium under the influence of NPK.

6. Irrespective of the experimental treatment, greater uptake of metals with I than II cut was found, which was undoubtedly connected with greater plant biomass obtained at the first harvest date.

References

[1] Falkowski M., Kozłowski S. and Kukułka J.: Właściwości chemiczne roślin łąkowych. Wyd. AR, Poznań 2001.
[2] Trąba Cz. and Wolański P.: Annales UMCS, Sec. E, 2004, **59**(3), 1319–1326.
[3] Wiśniowska-Kielian B. and Paździorko A.: Annales UMCS, Sec. E, 2004, **59**(3), 1371–1379.
[4] Kopeć M. and Gondek K.: Acta Agrophys., 2004, **4**(1), 51–58.
[5] Warda M. and Ćwintal B.: Zesz. Probl. Post. Nauk. Rol., 2000, **471**, 841–846.
[6] Preś J. and Kinal S.: Zesz. Probl. Post. Nauk. Rol., 1996, **434**, 1043–1061.
[7] Falkowski M., Kukułka I. and Kozłowski S.: Zesz. Probl. Post. Nauk. Rol., 1996, **442**, 41–49.

[8] Gorlach E.: Zesz. Nauk. AR w Krakowie 262, Ser. Sesja Nauk., 1991, **34**(1), 13–22.
[9] Curyło T., Gorlach E. and Grzywnowicz I.: Rocz. Glebozn, 1985, **19**(36), (2), 85–99.
[10] Kabata-Pendias A., Motowicka-Terelak T., Piotrowska M., Terelak H. and Witek T.: Wyd. IUNG, Puławy 1993, seria **P(53),** 20 p.
[11] Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi z dnia 23 stycznia 2007 w sprawie dopuszczalnych zawartości substancji niepożądanych w paszach, Dz. U. 2007, nr 20, poz. 119.
[12] Trąba C.: Zesz. Probl. Post. Nauk Rol., 1996, **434**, 401–405.
[13] Woźniak L. and Trąba C.: Zesz. Nauk. AR w Krakowie, 1998, 330, Sesja Nauk. **54**, 37–43.
[14] Trąba C. and Wolański P.: Zesz. Probl. Post. Nauk. Rol., 2000, **471**, 811–817.
[15] Kabata-Pendis A. and Pendias H.: Biogeochemia pierwiastków śladowych. Wyd. Nauk. PWN, Warszawa 1999, pp. 398.
[16] Ostrowska B.: Wiad. Inst. Melior. Użyt. Zielon., 1997, **19**(2), 93–103.
[17] Antonkiewicz J., Radkowski A. and Jasiewicz Cz.: Zesz. Probl. Post. Nauk Rol., 2003, **494**, 17–26.
[18] Jankowska-Huflejt H.: *Nawozy organiczne pochodzenia zwierzęcego w renowacji i nawożeniu użytków zielonych – sposoby ich składowania i stosowania*. Mat. Konf. "Produkcja i wykorzystane pasz z użytków zielnych w rolnictwie integrowanym na ternie górskich i podgórskich", Muszyna 25–27 XI 1997. Wyd. IMUZ, Falenty 1998, 41–50.
[19] Kasperczyk M., Radkowski A. and Kacorzyk P.: Pam. Puławski, 2001, **125**, 37–42.

WPŁYW ZRÓŻNICOWNEGO NAWOŻENIA NA ZAWARTOŚĆ METALI CIĘŻKICH W RUNI ŁĄKOWEJ W REJONIE GÓRSKIM

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Abstrakt: Badania prowadzono w latach 2005–2007 na łące górskiej w Krynicy. Pole doświadczalne znajdowało się na wysokości 640 m n.p.m. Doświadczenie założono na glebie brunatnej o składzie granulometrycznym piasku gliniastego, pH_{KCl} 4,10. Doświadczenie obejmowało 6 obiektów doświadczalnych: obiekt kontrolny, NPK, koszar luźny, koszar luźny + NP, koszar ciasny i koszar luźny jesienny. Na obiekcie z nawożeniem mineralnym zastosowano nawożenie w następującej dawce: 120 N, 25 P i 50 K kg · ha^{-1}. Nawożenie organiczne przeprowadzono za pomocą koszarzenia, przy udziale owiec. Koszarzenie obejmowało dwa poziomy intensywności: koszar luźny – 2 m^2 na owcę, koszar ciasny – 1 m^2 na owcę. Łąkę corocznie koszono 2-krotnie w połowie czerwca i na początku września. Największą zawartość Ni, Cr i Pb stwierdzono w obiekcie z koszarem luźnym jesiennym, Zn w obiektach z NPK, Cu w obiekcie z koszarem ciasnym, natomiast Cd w obiektach z koszarem luźnym + NP. Pokos drugi charakteryzował się większą zawartością metali ciężkich niż pokos pierwszy. W runi łąkowej nie została przekroczona dopuszczalna granica zawartości metali ciężkich przewidziana dla roślin wykorzystywanych na paszę. Jedynie w przypadku kadmu rośliny w obiektach nawożonych NPK i koszarem luźnym uzupełnionym NP wykazywały ponadnormatywne jego zawartości. Największy niedobór w runi łąkowej wykazano w przypadku miedzi. Niezależnie od obiektu doświadczalnego większy wynos metali stwierdzono wraz plonem I pokosu niż II, co niewątpliwe było związane z większą biomasą roślin uzyskanych w pierwszym terminie zbioru.

Słowa kluczowe: metale ciężkie, koszar luźny, koszar ciasny, NPK, łąka górska