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CONTENT OF MAGNESIUM AND HEAVY METAL FRACTIONS IN SELECTED NATURAL FERTILISERS

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Abstract

Our objective has been to determine the total content of magnesium, iron, chromium and zinc, as well as the heavy metal fractions in selected natural fertilisers, such as swine and bovine manure and poultry litter from laying hens and broilers. The total content of the metals was determined by the ICP-AES method following dry mineralisation in a muffle furnace at 450°C and dissolving the ash in HCl (1:1). Fractions of Fe, Zn and Cr were isolated by the 3-step sequential fractionation method proposed by the Community Bureau of Reference (BCR). This study has shown that the analysed organic materials had different content of the determined metals. The largest amount of Mg was found in litter from laying hens and the largest amounts of Fe, Cr and Zn were in litter from broiler chickens. The smallest amount of Mg was found in swine manure, Fe and Cr were the least abundant in litter from laying hens, and the lowest Zn content was in bovine manure. The content of these four heavy metals was significantly differentiated by the origin of fertiliser. The exchangeable fraction F_1 had the smallest share in the total Fe content among all the fertilisers. As for chromium, this fraction made the smallest contribution to the total Cr content in litter from laying hens and broilers while the reducible fraction F_2 was the smallest part of the total content in both types of manure. Fraction F_1 of zinc was the smallest in the total content in swine and bovine manure and while the oxidisable fraction F_3 made up the smallest share in the total content of this metal in litter from broilers.

Keywords: natural fertilisers, magnesium, heavy metals, sequential analysis.

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INTRODUCTION

Soil is the basic element of an ecosystem, in which it is responsible for crop yields and their chemical composition. Fertile soil, with good structure, proper water and air conditions and abundant organic and mineral compounds, helps to ensure good crop quality. The amount of organic matter in Polish soils has been decreasing in recent years, which is due to the diminishing amounts of natural and organic fertilisers applied in plant cultivation as well as more intensive mineralisation, leading to a considerable reduction of the organic matter content. As well as being a reservoir of macro - and micronutrients for plants, organic compounds are vital for many processes in soil, such as enzymatic reactions and oxidation and reduction processes. Depletion of organic matter in soil leads to its gradual degradation. Low content of organic carbon in soil entails some disruptions of air and water relations, lower biological activity, worse buffer capacity and inferior soil fertility. Therefore, in order to maintain appropriate soil fertility, it is necessary to apply both mineral and organic fertilisers as well as natural and waste organic materials. The chemical composition of natural and organic fertilisers depends mainly on the animal species and age, rearing purpose, quality and quantity of bedding and fodder, water content and housing conditions (Pająk, Kowalik 2006, Bednarek et al. 2010). Apart from the main nutrients, such as nitrogen, phosphorus and potassium, natural fertilisers contain magnesium and micronutrients. Magnesium is a very important macronutrient because it is the main component of chlorophyll and therefore a crucial factor in the process of photosynthesis. Furthermore, magnesium affects energy conversion processes, synthesis of carbohydrates and proteins as well as the transport of assimilates. Its strong impact on the root system and the quality of cell walls determines plant resistance to diseases and infections (Pasternak et al. 2010, Grzebisz et al. 2010, Grzebisz 2011). The natural content of magnesium in Polish soils is low and additionally lowered by strong acidification and organic matter deficit (Sienkiewicz et al. 2009, Grzebisz et al. 2010). Zn and Fe are essential for proper plant metabolism, but can be toxic when present in excessive amounts. Zinc plays several roles: it is an active component of many enzymes, such as dehydrogenases, peptidases and phosphorylases; it takes part in the metabolism of carbohydrates and proteins; it regulates the formation of ribosomes and shares of different components on the cellular level and it enhances plant resistance to drought and diseases. Iron stimulates the synthesis of chlorophyll and participates in the transformation of nitrogen compounds and processes of oxidation and reduction (Wyszkowska et al. 2013). Thus far, chromium has not been shown to be indispensable to plant growth and development, but there have been reports on its regulatory effect on transformations of proteins and fats and its possible participation in enzymatic reactions. For plant nutrition and for the broadly understood environmental protection, these metal species present in soil and in fertilisers which can be directly absorbed by plants are important. Sequential extraction is the most common method used for the determination of different species and fractions of metals in samples taken in the natural environment (Quevauviller et al. 2003). There are many reports in the literature about different metal species in soils, but relatively few discuss the issue in the context of natural and organic fertilisers (Gondek 2006, Irshad et al. 2013).

The aim of this study was to determine the total content of magnesium, iron, chromium and zinc, as well as the heavy metal fractions in selected natural fertilisers: pig and cattle manure and poultry litter from laying hens and broilers.

MATERIAL AND METHODS

Swine (SM) and bovine (BM) manure and chicken manure from broilers [CM(B)] and layers [CM(L)], which originated from selected farms in the districts of Siedlece, Sokołów, Węgrów and Łosice, all located in the Province of Masovia (*województwo mazowickie*), were selected for the analyses. Samples of each type of natural fertilizers were collected at 10 stations in accordance with PN-R-04006:2000.

The research focused on magnesium, which is an indispensable plant nutrient, also regulating soil pH, and on the metals whose speciation is dependent on soil reaction.

The total content of Mg, Fe, Cr and Zn was determined with ICP-AES after the initial dry mineralization of each sample in a muffle furnace at 450°C and dissolving the ash in HCl (1:1) The fractions of heavy metals were determined with a 3-step method of sequential fractioning proposed by the Community Bureau of Reference – BCR (Rauret et al. 1999). A scheme of the procedure is given in Table 1. The content of zinc, iron and chromium in the examined organic waste materials was described with arithmetic means, standard deviations and variation coefficients. In order to determine the significance of differences between the average content of zinc, iron and chromium in the tested materials and individual fractions, a two-way analysis of

Table 1

A diagram of the BCR metal sequential extraction method

Fraction	Name fractions	Extraction reagents	pH
F_1	exchangeable and acid soluble	0.1M CH_3COOH	3.0
F_2	reducible	0.5M NH_2OH HCl	1.5
F_3	oxidizable	8.8M H_2O_2 + 1M CH_3COONH_4	2.0
F_4	residual	calculated as difference between total content and sum of three fractions separated previously	-

variance of the main effects and a Tukey test were performed. The Pearson's simple correlation coefficients between the content of these metals in waste organic materials were also calculated.

RESULTS AND DISCUSSION

The content of Mg in the analysed natural fertilisers was varied and depended on the origin of fertiliser (Table 2). The highest average amount of the macronutrient (8.311 g kg^{-1} DM) was found in poultry litter from laying hens (from 6.581 to 10.12) and the lowest one (3.337 g kg^{-1} DM) was determined in pig manure (from 2.251 to 4.483). This is probably caused by different composition of the fodders consumed by animals, the type and amount of bedding, but also by different methods of animal rearing and use. Similar findings have been observed by Maćkowiak, Żebrowski (2000) and Bednarek et al. (2010). Research on heavy metals in environmental samples (soil, organic and mineral fertilizers) is a complex issue, which involves serious difficulty for researchers due to the size of fractions that bind metals, their amorphous nature and, commonly, low concentrations of bound metals (Gondek, Filipek-Mazur 2003, Wang et al. 2003, Świetlik, Trojanowska 2009). The current study, and especially the analysis of variance and Tukey test, demonstrated that the examined materials contained various total quantities of Mg, Zn, Fe and Cr and diversified distribution (proportions) in the fractions identified with the BCR procedure (Tables 2, 3). The highest amount

Table 2

Descriptive statistics of Zn, Fe, Cr (mg kg^{-1} DM) and Mg (g kg^{-1} DM) total content in the analysed materials

Material	Chicken manure (broilers) - CM(B)				Chicken manure (layers) - CM(L)			
Metal	Zn	Fe	Cr	Mg	Zn	Fe	Cr	Mg
Mean	328.0	3547.0	12.51	7.313	254.6	682.6	4.371	8.311
SD*	118.0	786.9	1.828	1.123	44.03	371.5	1.185	1.274
RSD**	35.97	22.18	14.62	15.36	17.29	54. 3	27.10	15.33
Min.	159.0	2156.2	9.823	5.122	210.6	349.9	2.164	6.581
Max.	438.4	4273.3	14.78	9.263	328.1	1396.7	6.485	10.12
Material	bovine manure – BM				swine manure – SM			
Metal	Zn	Fe	Cr	Mg	Zn	Fe	Cr	Mg
Mean	118.1	1342.0	9.542	4.652	196.9	961.8	4.864	3.337
SD	34.13	568.8	2.034	1. 68	31.30	188.0	0,703	0.793
RSD	28.89	42.39	21.31	25.11	15.90	19.54	14,46	23.78
Min.	86.62	812.6	6.251	3.332	165.6	745.2	3,861	2.251
Max.	182.6	2740.5	12.49	6.954	250.4	1316.2	6,043	4.483

* SD – standard deviation, ** RSD – relative standard deviation (%)

Table 3

Descriptive statistics of Zn, Fe, Cr (mg kg^{-1} DM) content in fraction of analysed materials

Metal	Zn					Fe					Cr				
Fraction	F_1	F_2	F_3	F_4	sum	F_1	F_2	F_3	F_4	sum	F_1	F_2	F_3	F_4	sum
Material	chicken manure (broilers)					chicken manure (broilers)					chicken manure (broilers)				
Mean	93.71	98.82	50.22	85.40	328.0	16.21	585.5	347.8	2597.6	3547.0	1.321	2.010	4.121	5.103	12.51
SD*	54.04	37.44	20.41	38.35	42.41	3.213	147.4	72.91	587.2	1062.3	0.211	0.224	0.645	1.120	1.701
RSD**	57.70	37.83	40.71	44.82	12.90	20.01	25.22	21.03	22.61	29.91	18.83	11.60	13.71	21.91	13.30
Min.	12.83	46.85	24.80	32.43		10.34	312.8	215.4	1542.8		1.023	1.622	3.314	3.543	
Max.	152.4	138.9	88.73	176.9		20.40	786.4	444.8	3152.7		1.811	2.331	5.021	6.713	
Mean for material	82.01					886.8					3.120				
SD for material	42.40					106.3					1.721				
RSD for material	51.72					119.8					53.10				
Material	chicken manure (layers)					chicken manure (layers)					chicken manure (layers)				
Mean	40.61	116.2	49.20	48.63	254.6	11.69	209.4	342.7	118.8	682.6	0.599	0.01	1.512	1.398	4.432
SD	9.301	24.90	7.732	20.54	3515	5.401	138.9	195.3	52.11	170.4	0.211	0.214	0.534	0.621	0.601
RSD	22.93	21.51	15.71	42.20	13.80	45.90	66.30	57.01	43.82	25.02	34.60	21.33	35.40	43.21	12.70
Min.	29.62	99.43	40.22	24.19		5.598	20.31	150.2	66.38		0.296	0.504	0.911	0. 32	
Max.	58.44	170.6	62.90	78.01		21.79	480.6	752.6	232.0		1.013	1.099	2.604	2.214	
Mean for material	63.71					170.6					1.132				
SD for material	35.10					170.4					0.601				
RSD for material	55.13					99.80					50.82				
Material	bovine manure					bovine manure					bovine manure				
Mean	1.911	8.589	63.70	43.91	118.1	50.89	371.3	213.8	706.0	1342.0	1.223	0.699	5.387	2.302	9.503
SD	0.603	2.411	19.81	13.02	28.10	17.70	70.91	273.2	267.7	308.4	0.399	0.211	1.141	0.734	2.010
RSD	32.30	28.30	31.02	29.53	23.82	34.93	19.12	127.8	37.90	23.01	32.02	30.90	20.40	32.30	20.70
Min.	1.121	5.201	46.74	28.39		32.60	285.3	80.31	414.4		0.798	0.402	3.611	1.499	
Max.	3.203	14.12	106.5	60.22		89.19	458.9	984.5	12722		2.023	1.033	7.014	4.011	
Mean for material	29.52					335.5					2.402				
SD for material	28.10					308.4					2.031				
RSD for material	95.23					91.1					82.70				
Material	swine manure					swine manure					swine manure				
Mean	1.811	12.80	62.21	120.0	196.9	35.11	306.8	122.3	497.7	961.8	1.112	0. 01	2.012	1.201	4.897
SD	0.401	3.696	23.20	19.24	49.61	8.498	53.90	34.21	121.6	192.0	0.201	0.112	0.403	0.197	0.601
RSD	21.39	28.91	37.29	16.00	25.20	24.20	17.61	28.02	24.41	20.01	14.70	19.50	21.30	17.51	11.90
Min.	1.203	8.123	39.81	77.39		23.92	208.6	82.64	353.0		0.899	0.431	1.601	0.921	
Max.	2.521	19.11	104.2	143.8		48.63	381.6	182.6	756.6		1.503	0.811	3.034	1.402	
Mean for material	49.20					240.4					1.203				
SD for material	49.63					192.0					0.610				
RSD for material	100.7					79.91					47.82				
Mean for fraction	34.50	59.12	56.31	74.50	224.4	28.41	368.3	256.6	980.0	1633,3	1.102	1.023	3.312	2.511	7.803
SD for fraction	46.32	54.03	19.20	39.21	158.7	18.73	175.6	191.5	1019.9	1405,6	0.413	0.601	1.733	1.699	4.421
RSD for fraction	134.3	91.30	34.12	52.63	312.4	65.70	47.70	74.61	104.1	292,0	34.20	60.80	53.54	69.20	217.6

* SD – standard deviation, ** RSD – relative standard deviation (%)

of all the analysed metals was detected in chicken (broiler) manure, namely Zn – 328.0, Fe – 3547.0, Cr – 12.51 mg kg^{-1} DM. The lowest average concentration of Zn was found in bovine manure (118.1 mg kg^{-1} DM) and the lowest amounts of Fe and Cr were found in chicken (layer) manure (682.6 mg kg^{-1} DM and 4.371 mg kg^{-1} DM, respectively).

In nearly all the analysed organic materials, except for chicken (layer) manure, the highest amount of iron was extracted in the residual fraction F_4, which is non-absorbable to plants, while the lowest one was in the exchangeable fraction F_1, which is directly absorbable to plants, and these observations are consistent with some previous studies (Kalembasa et al. 2007, Kuziemska, Kalembasa 2011).

The distribution of iron in the determined fractions within the analysed fertilizers can be arranged in the following order:

– swine and bovine manure: $F_4 > F_2 > F_3 > F_1$;
– chicken manure (layers): $F_3 > F_2 > F_4 > F_1$;
– chicken manure (broilers): $F_4 > F_2 > F_3 > F_1$.

In both types of manure, chromium in the organic fraction F_3 and bound to sulphides constituted the highest proportion in the total content, whereas the smallest proportion was in the reducible fraction F_2. In chicken manure, both from layers and broilers, the highest amount of the metal was detected in the residual fraction F_4, while the lowest was in the exchangeable fraction F_1.

The proportions of chromium in the fractions according to the BCR procedure can be presented in the following arrangement:

– swine and bovine manure: $F_3 > F_4 > F_1 > F_2$;
– chicken manure (layers and broilers): $F_4 > F_3 > F_2 > F_1$.

Different relationships were found for zinc. In swine manure, zinc was found in the highest proportion in the residual fraction (F_4). In bovine manure and in chicken (layers and broilers) manure, the highest proportion of zinc was found in the organic fraction (F_3) and the reducible fraction (F_2), respectively. In both types of manure and in chicken (layers) manure, the lowest amount of zinc was extracted in the exchangeable fraction F_1, whereas in chicken (broilers) manure, the organic fraction F_3 was characterised by the lowest amount of zinc.

The distribution of zinc in the individual fractions in the analysed materials is arranged in the following order:

– swine manure: $F_4 > F_3 > F_2 > F_1$;
– bovine manure: $F_3 > F_4 > F_2 > F_1$;
– chicken manure (layers): $F_2 > F_3 > F_4 > F_1$;
– chicken manure (broilers): $F_2 > F_1 > F_4 > F_3$.

The analysis of variance and the Tukey test demonstrated significant differences between the average concentrations of zinc, iron and chromium in the examined materials. The significance of differences is presented in Tables 4 and 5.

Table 4

Significant differences between the content of Zn, Fe and Cr (mg kg^{-1} DM) in the analysed materials

Metal	Zn				Fe				Cr			
Material	CM(B)	CM(L)	BM	SM	CM(B)	CM(L)	BM	SM	CM(B)	CM(L)	BM	SM
CM(B)	-	n.i.	**	**	-	**	**	**	-	**	**	**
CM(L)	n.i.	-	**	n.i.	**	-	n.i.	n.i.	**	-	**	n.i.
BM	**	**	-	n.i.	**	n.i.	-	n.i.	**	n.i.	-	**
SM	**	n.i.	n.i.	-	**	n.i.	n.i.	-	**	n.i.	**	-

** – differences significant at $\alpha < 0.01$
n.i. – differences insignificant

Table 5

Significant differences between the content of Zn, Fe and Cr (mg kg^{-1} DM) in particular fractions

Metal	Zn				Fe				Cr			
Fraction	F_1	F_2	F_3	F_4	F_1	F_2	F_3	F_4	F_1	F_2	F_3	F_4
F_1	-	**	**	**	-	**	n.i.	**	-	n.i.	**	**
F_2	**	-	n.i.	n.i.	**	-	n.i.	**	n.i.	-	**	**
F_3	**	n.i.	-	n.i.	n.i.	n.i.	-	**	**	**	-	**
F_4	**	n.i.	n.i.	-	**	**	**	-	**	**	**	-

** – differences significant at $\alpha < 0.01$
n.i. – differences insignificant

The correlation analysis showed a significant relationship between the content of Mg, Zn, Cr and Fe in the fertilisers, which is demonstrated by high values of the Pearson's linear coefficients (Table 6). The highly significant relationship between the content of Zn and Mg (r = 0.48 **) and between Fe and Cr (r = 0.77 **) is particularly noteworthy.

Recapitulating, the chemical analyses and the statistical calculations demonstrated that the analysed natural fertilisers, pig and cattle manure and poultry litter from laying hens and broilers, differed in terms of the total content of the metals as well as the distribution of Fe, Zn and Cr in the frac-

Table 6

Values of the Pearson's correlation coefficients between the content of Zn, Fe, Cr and Mg in the analysed materials

Metal	Zn	Fe	Cr	Mg
Zn	-	0.41*	0.29	0.48**
Fe	0.41*	-	0.77**	0.17
Cr	0.29	0.77**	-	0.10
Mg	0.48**	0.17	0.10	-

* – differences significant at $\alpha < 0.05$
** – differences significant at $\alpha < 0.01$

tions isolated in accordance with the BCR procedure, in which our report concides with the findings of Bednarek et al. (2010). The highest content of Mg was found in litter from laying hens, while the other metals were present in the highest amounts in broiler litter. This variation may be due to the different method of feeding and use of animals from which the analysed organic materials originated. In order to verify this hypothesis, our research should be extended to cover feed analyses. All the analysed fertilisers contained relatively little of the heavy metals in the exchangeable fraction, and therefore they are not a potential source of contamination for plants.

CONCLUSIONS

1. The total content of Mg, Fe, Zn and Cr in the natural fertilisers under study and the content of heavy metals in the fractions isolated in accordance with the BCR procedure were differentiated by the fertiliser origin.

2. The largest amount of magnesium was found in litter from laying hens while the other metals were present in the highest amounts in broiler litter.

3. The content of Fe, Zn and Cr in the exchangeable fraction F_1 was relatively low in all the analysed natural fertilisers.

REFERENCES

Bednarek W., Tkaczyk P., Dresler S. 2010. *The content of dry matter and macroelements in natural fertilizers from the Lublin region*. Acta Agroph., 16(1): 5-13.

Gondek K. 2006. *The content of various forms of heavy metals in sewage sludge and composts*. Acta Agroph., 8(4): 25-838. (in Polish)

Gondek K., Filipek-Mazur B. 2003. *The binding of heavy metals by humus in soils exposed to communication pollutants*. Acta Agroph., 2(4): 759-770. (in Polish)

Grzebisz W. 2011. *Magnesium – food and human health*. J. Elem., 16(2): 299-323. DOI: 10.5601/jelem.2011.16.2.13

Grzebisz W., Przygocka-Cyna K., Szczepaniak W., Diatta J.B., Potarzycki J. 2010. *Magnesium as a nutritional tool of nitrogen efficient management - plant production and environment*. J. Elem., 15(4): 771-788.

Irshad M., Malik A. M., Shaukat S., Mushtag S., Ashraf M. 2013. *Characterization of heavy metals in livestock manure*. Pol. J. Environ. Stud.,22(4): 1257-1262.

Kalembasa S., Kuziemska B., Godlewska A. 2007. *Sequential analysis of selected heavy metals in organic wastes*. Pol. J. Environ. Stud., 16, A :757-762.

Kuziemska B., Kalembasa S. 2011. *Effects of liming and sewage sludge addition to the distribution of fractions of selected heavy metals in soil contaminated with nickel*. Ochr. **Środ**. Zas. Nat., 50: 9-19.

Maćkowiak C., **Żebrowski** J. 2000. *The chemical composition of manure in Poland*. Fertilizers Fertilization, 4: 119-130.

Pająk J., Kowalik B. 2006. *The impact of nutrition and animal welfare system on the quantity and composition of manure from cattle*. Fertilizers Fertilization, 4: 20-35.

Pasternak K., Kocot J., Horecka A. 2010. *Biochemistry of magnesium*. J. Elem., 15(3): 601-616.

PN-R-04006. 2000: *Organic fertilizers - Sampling and sample preparation manure and compost.*

Quevauviller P., Booc Review. 2003. *Methodologies for soil and sediment fractionation studies*. Sci. Total Environ., 303: 263-264.

Rauret G., Lopez-Sanchez J.F., Sahuquillo A., Rugio R., Davidson C., Ure A., Quevauculler Ph. 1999. *Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials*. J. Environ. Monit., 1: 57-61.

Sienkiewicz S., Krzebietke S., Wojnowska T., Żarczyński P., Omilian M. 2009. *Effect of long-term differentiated fertilization with farmyard manure and mineral fertilizers on the content of available forms of P, K and Mg in soil*. J. Elem., 14(4): 779-786.

Świetlik R., Trojanowska M. 2009. *Chemical fractionation methods used in environmental studies*. Monit. Środ. Przyr., 9: 29-36. (in Polish)

Wang Q., Cui Y., Liu X., Dong Y., Christie P. 2003. *Soil contamination and plant uptake of heavy metals at polluted sites in China*. Environ. Sci. Health, Part A, 38: 823-838.

Wyszkowska J., Borowik A., Kucharski M., Kucharski J. 2013. *Effect of cadmium, copper and zinc on plants, soil microorganisms and soil enzymes*. J. Elem., 18(4): 769-796. DOI: 10.5601/jelem.2013.18.4.455