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Iron and nickel fractions in selected organic materials

Frakcje żelaza i niklu w wybranych materiałach organicznych

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Abstract

The objective of this study was to determine the basic physical and chemical parameters and the total content of Fe and Ni as well as their proportion in the fractions sequenced with Bureau of Reference (BCR) procedure in the selected organic materials used as soil fertilisers: bovine manure and chicken manure from broilers and layers. The highest content of dry matter, organic carbon and total nitrogen was found in the chicken layer manure. All examined materials had a comparable, C:N ratio (10–11:1). The highest amount of iron and nickel was found in the chicken broiler manure, whereas the lowest was in the chicken layer manure. The distribution of tested metals in the fractions sequenced with BCR procedure was differentiated. In the bovine manure and chicken broiler manure, the highest amount of iron was sequenced in the residual fraction, whereas in the chicken layer manure it was in the oxidative fraction. The oxidative fraction constituted the highest proportion in the total nickel content in the bovine manure and chicken layer manure, whereas in the chicken broiler manure it was the reducible fraction.

Streszczenie

Celem badan było oznaczenie podstawowych właściwości fizyko-chemicznych oraz zawartości ogólnych Fe i Ni i ich udziału we frakcjach wydzielonych według procedury BCR w wybranych materiałach organicznych stosowanych do nawożenia gleb – oborniku bydlęcym, kurzeńcu (pomiocie) pochodzącym od niosek i brojlerów. Największą zawartość suchej masy, $C_{org.}$ i $N_{cał.}$ stwierdzono w pomiocie pochodzącym od niosek. Wszystkie analizowane materiały miały zbliżony, w granicach 10-11 : 1 stosunek C : N. Największą ilość żelaza i niklu znaczono w kurzeńcu od brojlerów, a najmniejszą w kurzeńcu od niosek. Rozmieszczenie badanych metali we frakcjach wydzielonych według procedury BCR było zróżnicowane. W oborniku i pomiocie od brojlerów najwięcej żelaza wydzielono we frakcji rezydualnej, a w pomiocie od niosek we frakcji utlenialnej. W oborniku i kurzeńcu od niosek największy udział w zawartości ogólnej niklu stanowiła frakcja utlenialna a w kurzeńcu od brojlerów frakcja redukowalna.

1. INTRODUCTION

The content of heavy metals in organic fertilisers and organic waste materials allows their applicability for natural purposes (such as agriculture) to be determined [Kalembasa et al. 2007a,b, Kuziemska, Kalembasa 2011]. However, the total content of these metals does not provide a reliable indicator of their bioavailability from the substances introduced into the soil. Such an evaluation can be performed by assessing the proportion of metals in mobile and non-mobile fractions [Szumska (Wilk), Gworek 2009, Tessier et al. 1979, Jaremko, Kalembasa 2011]. To this end, sequential analysis is widely applied and permits the identification of compound groups to which a given metal is bound [Gondek 2006, Ignatowicz et al. 2011]. The scope of speciation analysis includes not only a qualitative speciation of elements but also a determination of the content of specific forms in a solution [Szumska (Wilk), Gworek 2009, Zhou et al. 1998]. Based on the sequentially analysed forms of elements in conjunction with modern statistical methods, it is possible to determine a variety of factors such as bioavailability, accumulation, migration, toxicity, solubility and sorption. Iron and nickel are categorised as essential elements for plants and animals. In plants, iron is a component of photosynthetic enzymes and a catalyst in the biosynthesis of chlorophyll, whereas in animals it is incorporated in haemoglobin and is a coenzyme involved in the synthesis of ATO. The indispensable role of nickel in the functioning of organisms was only discovered in the 1970s. This element is a component of urease and plays a key role in the process of microbiological binding of molecular nitrogen. The content of these elements in soil and plants requires careful monitoring since their potentially dangerous levels may be attained in plant-based animal diets without inducing noticeable symptoms in plants [Symanowicz, Kalembasa 2009].

The objective of this study was to determine the total content and fractions of iron (Fe) and nickel (Ni) in the selected organic materials used for soil fertilisation: bovine manure and chicken manure originating from layers and broilers.

2. MATERIALS AND METHODS

The experiment was carried out with bovine manure and chicken manure originating from layers and broilers from selected large-scale farms and small-scale operations located in Siedleckie County (the six samples from same subjects). The samples were collected in accordance with the standard PN-R-04006: 2000.

The following parameters were determined in the organic materials: dry matter content with a drying–weighing method, the total nitrogen content with an elementary analysis on a CHN analyser with a thermal conductivity detector (IDC) Series II (Perkin-Elmer) and organic carbon content with the oxidation-titration method. The ICP–AES method was used to measure the total content of Fe and Ni following "dry" mineralisation in a muffle furnace at 450°C and dissolving crude ash in HCl (1:1). The fractions of heavy metals were determined with a three-stage method of sequential fractioning proposed by the Community Bureau of Reference (BCR) [Rauret et al. 1999], which is presented in Table 1. The evaluation of the content of metals with the sequential method was verified with a mass balance that yielded a degree of conformity of approximately 90%.

3. RESULTS AND DISCUSSION

It was found that the examined organic materials, i.e. bovine manure and chicken manure originating from layers and broilers, differed in their content of dry matter, total carbon and total nitrogen (Table 2). The highest content of dry matter, i.e. 86.47%, total C – 326.5 and total N – 33.8 g•kg^{-1} DM was determined in the chicken layer manure. All examined materials had a comparable C:N ratio that approximated 10–11:1. Similar findings were reported by Bednarek et al. [2010]. The C:N ratio in the soil fertilised with natural and organic fertilisers is within the 8–15:1 range and most commonly oscillates around 12:1.

The total content and proportion of iron in the fraction sequenced with BCR procedure in the examined organic materials are presented in Table 3. The highest concentration of this metal was found in the chicken broiler manure, whereas this value was almost 1.5 times lower in the bovine manure and nearly eight times lower in the chicken layer manure. Regardless of the origin of natural fertilisers, the smallest amount of this metal was sequenced in the F1 (exchangeable) fraction, which indicates its limited availability to plants. This fraction constituted 1.14% (in relation to its total content) in the bovine manure, 1.60% in the chicken layer manure and only 0.38% in the chicken broiler manure. The highest amount of iron was sequenced in the F4 (residual) fraction in the bovine manure and chicken broiler manure and in the F3 (oxidative) fraction in the chicken layer manure, which may be explained with different feeding technologies. In the chicken manure that originated from layers, a substantial amount of iron was sequenced in the F2 fraction (35.39% of the total content) that might be potentially available to plants. The distribution of iron in the particular fractions in the examined organic materials can be arranged in the following orders of decreasing values:

Bovine manure: $F_4 > F_3 > F_2 > F_1$
Chicken manure (broilers): $F_4 > F_2 > F_3 > F_1$
Chicken manure (layers): $F_3 > F_2 > F_4 > F_1$

The total content of nickel and its distribution in the fractions sequenced with BCR procedure in the examined organic fertilisers is presented in Table 4. The highest concentration of this metal was detected in the chicken broiler manure, i.e. 9.49 mg•kg^{-1} DM, whereas the lowest content, i.e. 2.81 mg•kg^{-1} DM, was found in the chicken layer manure. These results are consistent with the findings recorded in previous studies [Kalembasa et al. 2007a].

In the bovine manure and chicken layer manure, the highest amount of nickel was sequenced in the F3 (oxidative) fraction, which indicates that this metal is included in organic compounds. Ignatowicz et al. [2011] investigated the distribution of nickel in sludge and showed that the highest amount of this metal was bound to the F3 fraction similarly to our studies. In the chicken broiler manure, the highest proportion of nickel was sequenced in the F2 (reducible) fraction that is potentially available to plants. The bovine manure and chicken layer manure contained the smallest amount of this metal in F4 (residual) fraction, whereas in the chicken broiler manure – in the F1 (exchangeable) fraction.

The distribution of nickel in the fractions sequenced with the BCR procedure in the examined natural fertilisers can be arranged in the following order of decreasing values:

Bovine manure: $F_3 > F_2 > F_1 > F_4$
Laying hen droppings: $F_3 > F_1 > F_2 > F_4$
Broiler droppings: $F_2 > F_3 > F_4 > F_1$

In summary, it was found that the examined fertilisers: bovine manure and chicken (broilers and layers) manure differed in the total content of Fe and Ni as well as in their distribution in the particular fractions. The highest amount of both metals was detected in the chicken broiler manure and the smallest concentration was in the chicken layer manure, which is associated with feeding and rearing technologies. Both types of chicken manure may be a good source of nitrogen and organic matter (comparable to bovine manure) as well as Fe and Ni to plants with an on-going monitoring of their content in soil.

4. CONCLUSIONS

1. The highest amount of both metals was detected in the chicken broiler manure, whereas the lowest was in the chicken layer manure.
2. In the bovine manure and chicken broiler manure, the highest amount of iron was sequenced in the residual fraction. In the chicken layer manure, the oxidative fraction contained the highest concentration of this metal.
3. The oxidative fraction constituted the highest proportion of the total nickel content in the bovine manure and chicken layer manure. In the case of chicken broiler manure, it was the reducible fraction.

Table 1. A diagram of the Bureau of Reference (BCR) sequential extraction method [Rauret et al. 1999]

No.	Name fractions	Extraction reagents	pH
F_1	Exchangeable and acid soluble	0.1 M CH_3COOH	3.0
F_2	Reducible	0.5 M $NH_2OH \cdot HCl$	1.5
F_3	Oxidisable	8.8 M H_2O_2 + 1 M CH_3COONH_4	2.0
F_4	Residual	Calculated as difference between total content and sum three previously separated fractions	–

Table 2. Selected physical and chemical parameters of the examined organic materials

Parameters	Organic materials		
	Manure	Laying hen droppings	Broiler droppings
DM (%)	20.76	86.47	28.4
$C_{org.}$ (g•kg^{-1} DM)	303.2	326.5	204.4
N_t (g•kg^{-1} DM)	26.9	33.8	18.4
C:N	11.3:1	9.7:1	11.1:1

Table 3. Content of Fe in the fractions sequenced with Bureau of Reference (BCR) procedure [mg•kg^{-1} DM] and their proportion in the total content (%) in the examined organic materials

Fraction	Organic materials					
	Manure		Laying hen droppings		Broiler droppings	
	Content (mg•kg^{-1} DM)	%	Content (mg•kg^{-1} DM)	%	Content (mg•kg^{-1} DM)	%
F1	31.81	1.14	8.71	1.60	15.96	0.38
F2	444.35	15.93	192.54	35.39	620.58	14.66
F3	942.72	33.79	258.79	47.57	444.75	10.50
F4	1371.21	49.14	83.99	15.44	3152.77	74.46
Sum	2790.09	100	544.03	100	4234.06	100

Table 4. Content of Ni in the fractions sequenced with Bureau of Reference (BCR) procedure (mg•kg^{-1} DM) and their proportion in the total content (%) in the examined organic materials

Fraction	Organic materials					
	Manure		Laying hen droppings		Broiler droppings	
	Content (mg•kg^{-1} DM)	%	Content (mg•kg^{-1} DM)	%	Content (mg•kg^{-1} DM)	%
F1	0.92	13.07	0.95	33.81	1.73	18.23
F2	1.81	25.71	0.48	17.08	3.71	39.10
F3	3.64	51.70	1.04	37.01	2.24	23.60
F4	0.67	9.52	0.34	12.10	1.81	19.07
Sum	7.04	100	2.81	100	9.49	100

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