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INFLUENCE OF SECONDARY TRANSFORMATION INDEX OF PEAT-MUCK SOILS ON THE CONTENT OF SELECTED METALS

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A b s t r a c t. The main aim of the study was the determination of the content of selected metal ions in soils originating from Polesie Lubelskie and Biebrza River Region, as well as an attempt at relating the results obtained to the degree of secondary transformation of studied soils. All the soils belonged to peat-muck soils and differed from each other in their secondary transformation index. The study included analyses of the content of potassium, calcium, magnesium and manganese with the use of absorption atomic spectroscopy for the determination of the concentration of those metals. At the next stage of the study, relationships between the secondary transformation index of peat-muck soils and selected metal contents were examined. Weak linear relationships were found for the secondary transformation index and the content of calcium, manganese and potassium. A more complex situation was observed for the relation of magnesium ions. The lack of a straight-line trend could be explained in this case by the effect of chemical processes occurring in particular classes of mucks transformation on magnesium ion binding.

K e y w o r d s: peat-muck soil, Polesie Lubelskie, Biebrza River

INTRODUCTION

The peatlands of Polesie Lubelskie Region as well as those situated in the region of Biebrza River belong to one of the most valuable natural resources of Poland. Apart from their high tourism values, these areas are also the habitat of unique fauna and flora. Peatlands are also a large reservoir of organic matter that is responsible for sorption properties, structure of soils and microbial activity. However, peats still undergo various continuing transformations related both to natural processes and, in particular, to inappropriate water economy (offhand land reclamation treatments) (Gawlik and Harkot 2000). The main goal of land reclamation processes of peats and bogs is the accretion of wetlands. Most of the peatlands in Poland have been drained and subjected to agricultural use. Processes of such kind cause acceleration of peat mass transformation to mucks (Inisheva and Dement'eva 1998, Matyka-Sarzyńska and Sokołowska 2004). Changes in peat evolution under melioration processes are mostly characterised by mineralisation and secondary humification. The above processes lead to changes in the morphological, chemical, biological and physical properties of peat soils. One of the indicators which could describe the changes in peat mass could be the water holding capacity index proposed by Gawlik (1992, 2000). This parameter characterises the secondary transformation processes taking place in soils. Earlier studies showed that the water holding capacity index stays in relations with some physical and chemical parameters of organic soils such as humification index, specific surface area, surface charge or amount of amino acids (Matyka-Sarzyńska and Sokołowska 2004, Sokołowska *et al.* 2011). In connection with the above, this parameter should also display relationships with the content of mineral components of peat-muck soils because in the course of their transformation their mineral composition is also dynamically changed. The process of secondary transformation of soil is connected with chemical and physical changes of organic matter, especially humic substances (Kyzioł 2002). Humic and fulvic acids and their functional acidic groups, such as the carboxylic and phenolic, are the main factors responsible for binding metal cations and, consequently, for their state and concentration in soils (Lux 1993).

Investigations of mineral management of soils originating from peats (for example mucks) are very important because this can make it possible to use these soils in agriculture and to increase their productivity potential. On the other hand, knowledge about the mineral status of non-degraded peatlands can also contribute to better protection of such areas.

In consequence, there is necessity to conduct monitoring of status of organic soils environment, especially in relation with metal ion content.

In connection with the above, the main aim of the study was investigation of the content of selected metal ions: potassium, calcium, magnesium and manganese in peat-muck soils of Polesie Lubelskie and Biebrza River Region, as well as an attempt at relating the results obtained to the varied degree of secondary transformation of studied soils.

MATERIAL AND METHOD

The studies were conducted on eight peat-muck soil samples. The samples were collected at depth of 5-20 cm from sites located in a low moor area of the Wieprz-Krzna Canal (Polesie Lubelskie) and Biebrza river in Poland. The degree of transformation of the peat-muck soils was characterised by the value of water holding capacity (W_1) determined according to the Gawlik method (Gawlik 1992). The procedure of method was as follows:

The soil material, after careful mixing by hand and removing live plant roots, was divided into two parts. The first one (sub-sample A) was soaked for 7 days, put into a special sieve and centrifuged at 1000 g for one hour. Then it was weighed, oven-dried at 105^{o}C and reweighed. The same procedure was applied to the second part (to sub-sample B) but, in this case, it was air-dried at room temperature before soaking and subsequently dried to remove all water (at 105^{o}C). Differentiation between the water holding capacity of peat materials was expressed with the help of the W_1 index calculated from the following formula:

$$W_1 = b/a \quad (1)$$

where *a* is the centrifugal-moisture equivalent of sub-sample A (in grams of water per 100 g of absolutely dry soil) and *b* is the centrifugal moisture equivalent of sub-sample B (in grams of water per 100 g of absolutely dry soil). Exemplary classification of muck formations formed from peats is presented in Table 1.

Table 1. Classification of muck formations formed from proper peats and weakly silted peats (Gawlik 2000)

W_1	Classes	Stage of transformation
0.36-0.45	I	Initially secondary transformed
0.46-0.60	II	Weakly secondary transformed
0.61-0.75	III	Medium secondary transformed
0.76-0.90	IV	Strongly secondary transformed
>0.90	V	Completely degraded

Total concentration of magnesium, potassium, calcium and manganese was investigated in studied samples. Concentration measurements were made after soil mineralisation using microwave oven and with the application of absorption atomic spectroscopy (AAS).

Afterwards, relationships between metals content and secondary transformation index (meaning water holding capacity W_1) were calculated and determination indexes were found using Microsoft Excel software.

RESULTS AND DISCUSSION

Measurements of water holding capacity index W_1 showed that studied peat-muck soil samples differed from each other in terms of secondary transformation stage (Tab. 1). Sample No. 1 (W_1 = 0.44) belonged to initially secondary transformed. Samples No. 2 (W_1 = 0.48) and 3 (W_1 = 0.6) belonged to the 2nd group of soils (weakly secondary transformed). Samples No. 4-8 (respectively: W_1= 0.61, 0.65, 0.71, 0.72 and 0.74) were described by the 3rd class of water holding capacity index which means medium secondary transformed samples.

Table 2. Water holding capacity of studied peat-muck soils

No	1	2	3	4	5	6	7	8
W_1	0.44	0.48	0.6	0.61	0.65	0.71	0.72	0.74
Class	I	II	II	III	III	III	III	III

The content of potassium in the studied peat-muck soils varied from 0.04 to 0.14 g kg^{-1} of dry mass. The highest amount of potassium was measured for samples with the lowest value of W_1 index (especially for samples from classes I and II). In general, potassium content decreased with secondary transformation increase. The relationship between potassium concentration and W_1 parameter could be expressed by a straight line trend with determination index R^2 = 0.67 (Fig. 1).

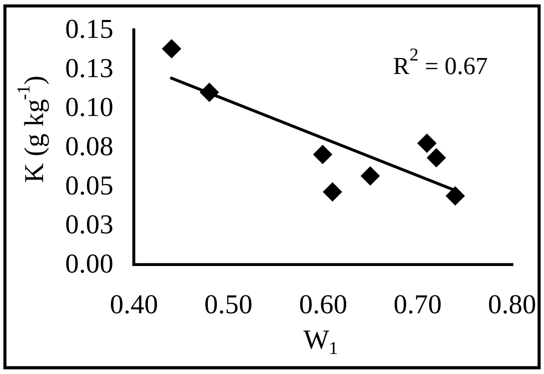

Fig. 1. Total concentration of potassium (g kg^{-1}) in peat-muck soils in relation to secondary transformation index (W_1)

A weak negative dependence was also found for manganese content and W_1 index. The determination index (R^2) was only 0.46 (Fig. 2). The concentration of manganese ranged from 0.07 to 0.32 g kg^{-1} of dry mass.

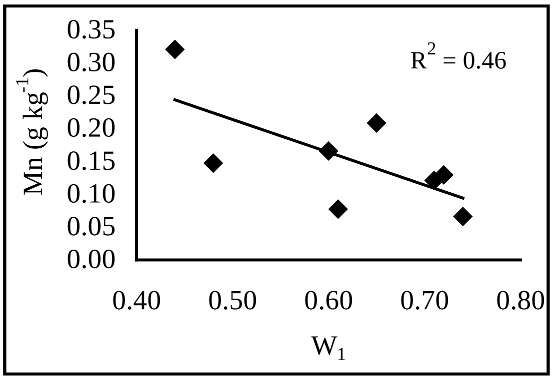

Fig. 2. Total concentration of manganese (g kg^{-1}) in peat-muck soils in relation to secondary transformation index (W_1)

Measurements of calcium showed concentration from 10.84 to 27.80 g kg^{-1} of dry mass. A positive correlation was found for the content of this element and W_1 index. The determination index of linear dependence R^2 was equal to 0.54 (Fig. 3).

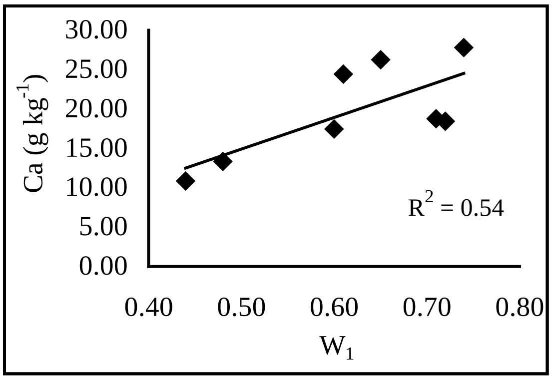

Fig. 3. Total concentration of calcium (g kg^{-1}) in peat-muck soils in relation to secondary transformation index (W_1)

No linear correlation was found for magnesium concentration and the W_1 parameter. This relationship was probably more complex (Fig. 4). A nonlinear, quadratic trend was found, but the R^2 index was low (0.45).

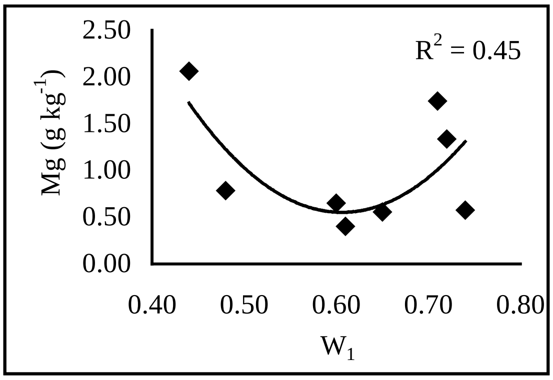

Fig. 4. Total concentration of magnesium (g kg^{-1}) in peat-muck soils in relation to secondary transformation index (W_1)

One way of explanation of such behaviour could be different mechanisms of magnesium binding depending on the stage of secondary transformation of soil, chemical differences in humus substances and the ratio of fulvic to humic acids. If only classes I and II of secondary transformation stage were considered, magnesium content decreased with W_1 increase. Concentration of this element increased at W_1 increase if samples from class III only were considered. In general, this assumption needs further detailed studies. However, some earlier investigations related to the dependence of different W_1 parameters of peat-muck soils and surface charge of samples confirmed the presence of linear regression: negative and positive in two groups of soils divided in terms of secondary transformation stage. As in the above situation: the first group related to the initially and weakly transformed class and the second to the medium and strongly degraded class (Sokołowska *et al.* 2005).

Our investigations showed that the amount of potassium was very low in the studied samples. The most degraded peat-muck soils contained the lowest concentration of potassium. This tendency was also confirmed by others researches (Niedźwiedzki *et al*., 2009). The above trend results probably from the formation of well-soluble ionic compounds of potassium with carboxylic groups of humic acids. All humates of monovalent metals (group I of periodic table) are well soluble and show great mobility in soil. Therefore, the amount of potassium could undergo a reduction in soils with higher degree of degradation. The relationship displayed in Figure 1 could also result from the fact that potassium is a chemical element which can be easily displaced by other cations like, for example, calcium or magnesium. Such a mechanism is highly probable because, according to literature, deficiency of this cation in organic soils is commonly known (Sigua *et al.* 2006, Piaścik and Łachacz 2001, Brandyk *et al.* 2008).

Calcium belongs among elements displaying high affinity to humic acids. Calcium humates are compounds that are not well-soluble. Increase of calcium concentrations at increase of secondary transformation degree could result from increased HA/FA ratio, because due to transformation of "younger" compounds like lignins, fulvic acids are transformed to elder compounds like humic acids (Kovaleva and Kovalev 2009). It could be favourable for forming not well-soluble bonds with calcium ions and, in consequence, for the concentration of higher amounts of this element in soil.

Manganese displays great mobility in organic soils and weak affinity to humic acids in comparison to other multivalent metals like aluminium or iron. For this reason manganese ions can be easily replaced by others and its concentration in soil can undergo a decrease. High mobility of manganese is additionally conditioned by pH. In acidic organic soils, this element is present in the form Mn^{2+}, therefore its amount in soil could be low. An exception to this could be the surface layer of soil, where oxidising processes take place and manganese can have higher local concentrations (Kalembasa *et al.* 2008).

In our studies the amount of manganese decreased with increase of secondary transformation degree. This could result from the transformation of humus substances during secondary transformation processes. According to literature (Szajdak *et al.* 2007), increase of secondary transformation degree causes a decrease of nitrogen and organic carbon levels in ground waters, which results from the fact that under secondary transformation processes organic matter is changed from hydrophilic to hydrophobic (Sokołowska *et al.* 2005). These changes are a consequence of humus substances transformation. This process goes towards the formation of humic acids that complex with manganese ions only weakly. As a result, the amount of manganese in soil can decrease.

Magnesium concentration was quite high in the studied samples. However, it changed in different ways for samples representing different classes of secondary transformation. Interpretation of the relationship from Figure 4 could be carried out in two groups. In the group of initially and weakly transformed soils, the amount of magnesium decreased with increase of secondary transformation degree. This situation could take place due to the chemical properties of humus compounds typical for the initial stages of secondary transformation. Low degrees of secondary transformation might be the evidence of the superiority of young compounds like fulvic acids. They are well soluble, also in the form of salts with metal ions. In the case of soils with the initial transformation stage, magnesium concentration could also be dependent on calcium amount (calcium and magnesium ions have similar chemical properties, mainly due to identical valence and origin from group II of the periodic table) as well as on the amount of carboxylic functional groups and the rate of chemical transformations that are fast on this level. Peat-muck samples with more advanced transformation stage are characterised by higher content of humic acids, i.e. compounds with higher particle mass, higher degree of condensation of aromatic rings and high amounts of carboxylic and phenolic groups. Humic acids, opposite to fulvic acids, contribute to the concentration of bigger amounts of multivalent metals in soil (Leita *et al.* 1999), therefore their increasing amount with increasing transformation degree could be the reason for higher metal sorption, including magnesium sorption. In consequence, the relationships presented in Figure 4 (part for samples weakly transformed) could have a positive trend.

CONCLUSIONS

1. The results of our studies showed high variability of concentration of investigated metals in studied peat-muck soil samples. In the case of manganese, potassium and calcium, it could be noticed that weak linear relationships between metal concentration and secondary transformation index (expressed as water holding capacity index) occurred.

2. Increase in the value of W_1 parameter positively corresponded with increase in the concentration of calcium ions. Negative correlation was found for potassium ions (R^2 = 0.67). A weaker positive relationship was also observed between the secondary transformation index and the content of manganese ions. No similar, simple relationship was found for the concentration of magnesium ions in the studied samples.

3. Studies on the concentration of selected metal ions in peat-muck soils indicate a significant influence of the mucking processes and the humification stage on the mobility of magnesium, potassium and manganese ions. This information can find an extensive application in rational mineral treatments of organic soils, in improvement of soils; such studies can also be useful in the protection of non-degraded peat areas.

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WPŁYW STOPNIA WTÓRNYCH PRZEOBRAŻEŃ GLEB TORFOWO-MURSZOWYCH NA ZAWARTOŚĆ WYBRANYCH METALI

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S t r e s z c z e n i e . Głównym celem pracy było zbadanie zawartości wybranych metali w glebach torfowo-murszowych pochodzących z Polesia Lubelskiego i Doliny Biebrzy, jak również próba odniesienia uzyskanych wyników do stopnia przeobrażeń wtórnych poszczególnych gleb. Badania obejmowały analizy potasu, wapnia, magnezu i manganu. W celu oznaczenia wyżej wymienionych pierwiastków wykorzystano metodę absorpcyjnej spektrometrii atomowej W kolejnym etapie badań wyznaczone zostały zależności pomiędzy zmierzonymi zawartościami metali, a stopniem przeobrażeń wtórnych gleb, mierzonym jako współczynnik pojemności wodnej. Wyniki wykazały istnienie słabych liniowych korelacji pomiędzy jonami potasu, wapnia i manganu, a stopniem przeobrażeń wtórnych. Bardziej złożoną zależność zaobserwowano dla jonów magnezu. Brak prostoliniowego trendu mógł być w tym przypadku tłumaczony silnym wpływem na wiązanie jonów magnezu, chemicznych zmian występujących w poszczególnych klasach wtórnej transformacji utworu glebowego.

S ł o w a k l u c z o w e : gleba torfowo-murszowa, Polesie Lubelskie, Biebrza