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Manganese release from peat soils

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A b s t r a c t. The paper demonstrated results about the investigations of Mn release phenomenon from peat soils into the soil solution. Laboratory experiment lasted 443 days, and was performed at 18ºC, under flooded conditions on three peatland samples (Moszne, Garbatówka and Orłowskie). The highest Mn concentration (0.07 mg kg^{-1}) was noted in Orłowskie peatland, whereas the lowest (0.022 mg kg^{-1}) in the soil taken from Garbatówka. It was indicated, that the ability of Mn release into the soil solution during incubation time decreased with the depth of the soil profiles (except of Moszne peatland, where maximum of Mn concentration at >50 cm was registered), and increased with drop of redox potential.

K e y w o r d s: manganese release, peatland, flooding, redox potential

INTRODUCTION

Manganese is the 12th most abundant element, within the Earth's crust. This metal can exist in different oxidation states, but the most widely occurring form are: soluble Mn (II) and insoluble Mn (IV) (Hardie *et al*., 2007). Manganese, an essential trace element, that is found in varying amounts in all tissues, is also an activator of a number of enzymes involved in the tricarboxylic acid cycle (Xue *et al*., 2001). Moreover, as a constituent containing superoxide dismutase, protects tissues from the toxic oxygen free radicals released in various enzyme reactions (Marschner, 1995; Paschke *et al*., 2005), and is used by plants to split H_2O during photosynthesis (Heal, 2001; Rezai and Farboodnia, 2008). However metals, such as Mn in soils and sediments are possible problems due to their importance as well as micronutrients (Paschke *et al*., 2005), as potential to become toxic pollutants (Boudissa *et al*., 2006; Rezai and Farboodnia, 2008; Stueben *et al*., 2004). The environmental Mn content ranged from 100 to 5000 μg g^{-1} in soils and from 0.0017 to 0.0050 mg l^{-1} in sea water (Ishibsashi *et al*., 2004). Phytotoxicity from Mn may occur in soils, containing low humus and acidic pH, where there is frequent flooding or prolonged containment of water. On the contrary, Mn deficiencies commonly occur in soils, that are alkaline or saline, calcareous, coarse textured or acid leached (Stueben *et al*., 2004). Due to the fact, thermodynamic consideration are useful for obtaining a general understanding of the potential reactions of manganese. Rampazzo *et al.* (1999) demonstrated the instability of Mn-oxides at low pH. Nevertheless, it is difficult to say if they are only leached into deeper horizons, or completely inhibited in their formation. An extensive summary of limiting stability relations for Mn in the light of presently available thermodynamic information is given by the pε-pH diagram (Fig. 1).

The chemistry of Mn is an important control on Mn mobilization and transport in the environment (Heal, 2001; Negra *et al*., 2005). Scheme of Mn transformation in the soil is presented in Fig. 2.

Both for economical and hygienic-environmental reasons, the understanding of the conditions favoring the Mn reduction in soil is very important (Atta *et al*., 1996). Many authors studied the distribution of different forms of Mn in a waterlogged soils (Atta *et al*., 1996; Hardie *et al*., 2007; Paschke *et al*., 2005). It has been shown, as a consequence of various biogeochemical studies, that plant roots can affect the species in which metals exist near rizosphere by altering the pH of this environment (Boudissa *et al*., 2006; Stueben *et al*., 2004). High Mn levels in soil may lead to plant nutrient imbalances, especially in relation to other divalent cations, such as Mn^{2+} and Ca^{2+} (Marschner, 1995; Paschke *et al*., 2005). In fact, one of the first symptoms associated with Mn toxicity is related to both Ca and Mg deficiencies (Marschner, 1995).

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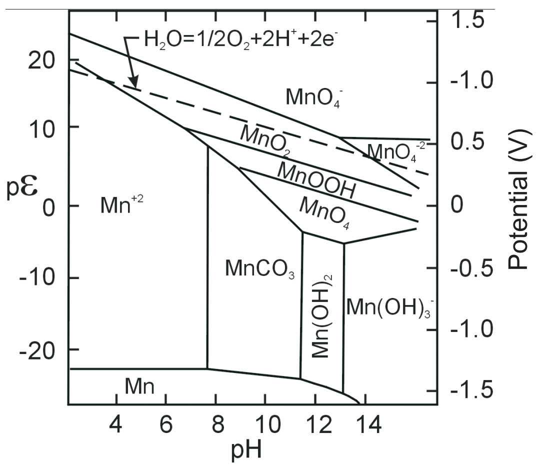

Fig. 1. pε-pH diagram for Mn. C_T = 2 $10^{-3}M$, activity of soluble metals ion species, 10^{-5} *M*.

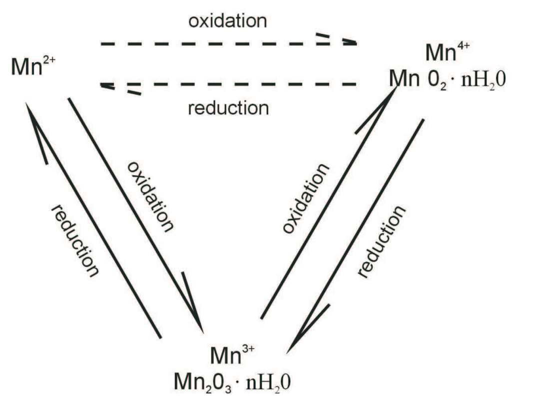

Fig. 2. Scheme of Mn transformation in the soil environment.

Human practices have raised Mn content and availability in many soils. Mine tailings and metal smelters increase soil Mn concentration with subsequent effects on vegetation structure and composition (Boudissa *et al*., 2006; Paschke *et al*., 2005). Long-term and heavy dose applications of sewage-sludge, or other organic amendments to agricultural soils and soil anaerobic conditions or poor drainage may also lead to an increase in the Mn content (Paschke *et al*., 2005).

Peatlands ecosystems are composed with peat deposits and residues of plants, thus have as well high humidity as high level of groundwater and therefore anaerobic conditions. The Mn content in wetlands is governed by a complex and dynamic exchange at the sediment-water interface. Therefore, the retention capacity of wetlands depends on the relative importance of Mn precipitation on the surface of the sediments over the release of these metal (Goulet and Pick, 2001).

The purpose of the current study was to determine the Mn concentration and its release ability during 443 days of laboratory incubation under flooding conditions.

MATERIALS AND METHODS

The soil materials used for laboratory experiment were taken from different depths (0-20, 30-50, >50 cm) of Moszne (1), Orłowskie (2) and Garbatówka (3) peatlands, situated in the Łęczyńsko-Włodawskie Lake District, SE part of Poland. Moszne peatland is overgrowed with as well of dwarf forest as rushes. High capacity of humid substances is a cause of pH level maintained at the range 3-4. Orłowskie peatland is an area, which is periodically flooded during the year. Nowadays, is deteriorated, dried and developed as a meadow, with an alkaline pH. Garbatówka is a type of low peatland, supplied with ground water, rich in organic amendments. Similarly to 2nd place, currently is developed as a meadow and characterized of alkaline pH. The main features of the peat soil materials are presented in Table 1.

Peat soil samples (1 kg) were placed in hermetic closed, plastic containers, flooded with water to obtain a full water saturated conditions, and incubated at 18ºC. Three platinum electrodes were installed, in order to make possible the measurement of redox potential (Eh). An agar bridge closing electric circuit between reference and measuring electrode, located in the soil and ceramic filter with outlet pipe, in order to taken soil solution were installed (Fig. 3).

Particular elements of measurement set, were installed on the same depth in the peat soil of each samples (20 cm from the bottom of container). Water sample (15 ml) for analysis of Mn content were taken in 7th days intervals. Every time, after taking liquid sample, the same volume (15 ml) of distilled water was filled up in the containers. Laboratory experiment lasted 443 days.

Mn concentration in tested extracts were determined by AAS technique (GFAAS method) with use Z-8200 Hitachi Spectrophotometer (Japan). Each samples were replicated three times. Analysis were performed with total sample volume of 20 μl, at λ = 279.6 nm. Mn content in peat soil samples are expressed as a mg kg^{-1} FW of peat.

Furthermore, determination of the total organic carbon by Tiurin method as well as pH and Eh measurements with pIONeer 65 apparatus (Radiometer Analytical S.A.), equipped to combined electrode cartrode (pHC 5977), were performed. Statistical analysis (One-way ANOVA test) were made by Statgraphics 3.0 software.

T a b l e 1. Main characteristics of investigated peat soil samples

Peat soil	Depth (cm)	$C_{org.}$ (%)	pH	Eh (mV)	Water content (%)
	0-20	31.58	3.6	764	198
Moszne (1)	30-50	27.75	3.5	757	491
	>50	26.56	4.4	541	692
	0-20	35.56	6.3	627	283
Orłowskie (2)	30-50	35.35	6.7	549	481
	>50	32.98	6.5	506	568
	0-20	27.60	7.4	589	592
Garbatówka (3)	30-50	34.92	7.0	523	556
	>50	35.30	6.8	527	624

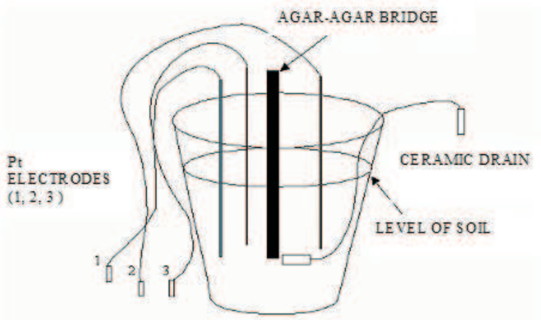

Fig. 3. Scheme of measurement set (Stępniewska and Szafranek, 2004).

RESULTS AND DISCUSSION

As a consequence of ANOVA test it was found that tested peatlands significantly differ (p<0.001) among each other, taking into account quantity of organic carbon. The highest amount of $C_{org.}$ (35.5%) in 2nd place (0-20, 30-50 cm) was found (p > 0.05), meanwhile significant (2%) drop of C content in subsoil (>50 cm) was noted and described by R= -0.90***. Lower level of $C_{org.}$ (31.5%) were noted at Moszne peatland (0-20 cm), whereas the lowest values were observed, as follows: 27.75 and 26.56%, in the depth of 30-50 and >50 cm, respectively (R= -0.95***). In the case of Garbatówka the maximum content of $C_{org.}$ (35.3%) in the subsoil >50 cm was estimated, whereas surface layer (0-20 cm) contained only 27.6% C_{org}. Due to this fact, a positive correlation was indicated between $C_{org.}$ and peat soils depth (R=0.89***).

At each peat soil samples incubated under flooded conditions, a release of Mn into the soil solution were registered. The obtained results are presented in Fig. 4.

Till to 70th day of incubation, concentration of Mn in 1st place samples, fluctuated between 0.04-0.09 mg kg^{-1}, after that drop of Mn content to the level of *ca* 0.01 mg kg^{-1} was observed (Fig. 4a). Final Mn concentration at mentioned above peatland did not exceed the value of 0.01 mg kg^{-1}.

Fluctuations of Mn concentration in the surface layer of 2nd place during 300 days of incubation, changed of *ca* 0.05 to 0.09 mg kg^{-1}, then dropped down significantly (p<0.001) to the value of 0.012 mg kg^{-1} and persisted on that level to the end of the experiment (Fig. 4b). In different cases (30-50, >50 cm): the highest concentration of Mn *ca* 0.07 mg kg^{-1} through the first 70 days were observed. Afterwards noted values were much lower and oscillated between 0.08 to 0.018 mg kg^{-1}.

In the case of 3rd place, the highest Mn concentration (between 0.04-0.06 mg kg^{-1}) during the first 75th days, at each of analyzed depth were observed. At surface layer (0-20 cm) the strongest Mn fluctuations between 0.05 and 0.024 mg kg^{-1} were noted till to 300 days of experiment, whereas at deeper part of investigated peat soil profile Mn content remained at the level not exceeding 0.01 mg kg^{-1}, what was similar to 1st place. An average concentrations of Mn dis- played decreasing tendency with growth of the depth of soil profiles (Table 2).

An initial Mn concentration reached the highest value (0.09 mg kg^{-1}) in 1st place, whereas at other samples: Orłowskie and Garbatówka remained at similar level: 0.061 and 0.052 mg kg^{-1}, respectively. Final Mn content came to 0.0171 mg kg^{-1} in 2nd place (0-20 cm), whilst in Moszne and Garbatówka dropped as follows to: 0.0066 and 0.0077 mg kg^{-1}. Mn concentration reached its maximum at different time of incubation. In the upper layers (0-20 cm) the highest Mn content after 1st, 65th and 239th days of experiment were registered, in Moszne, Garbatówka and Orłowskie, respectively. At deeper layer (30-50 cm) maximum of Mn concentration between 38-51st days of incubation was observed, whereas in the subsoil (>50 cm) maximum of Mn appeared

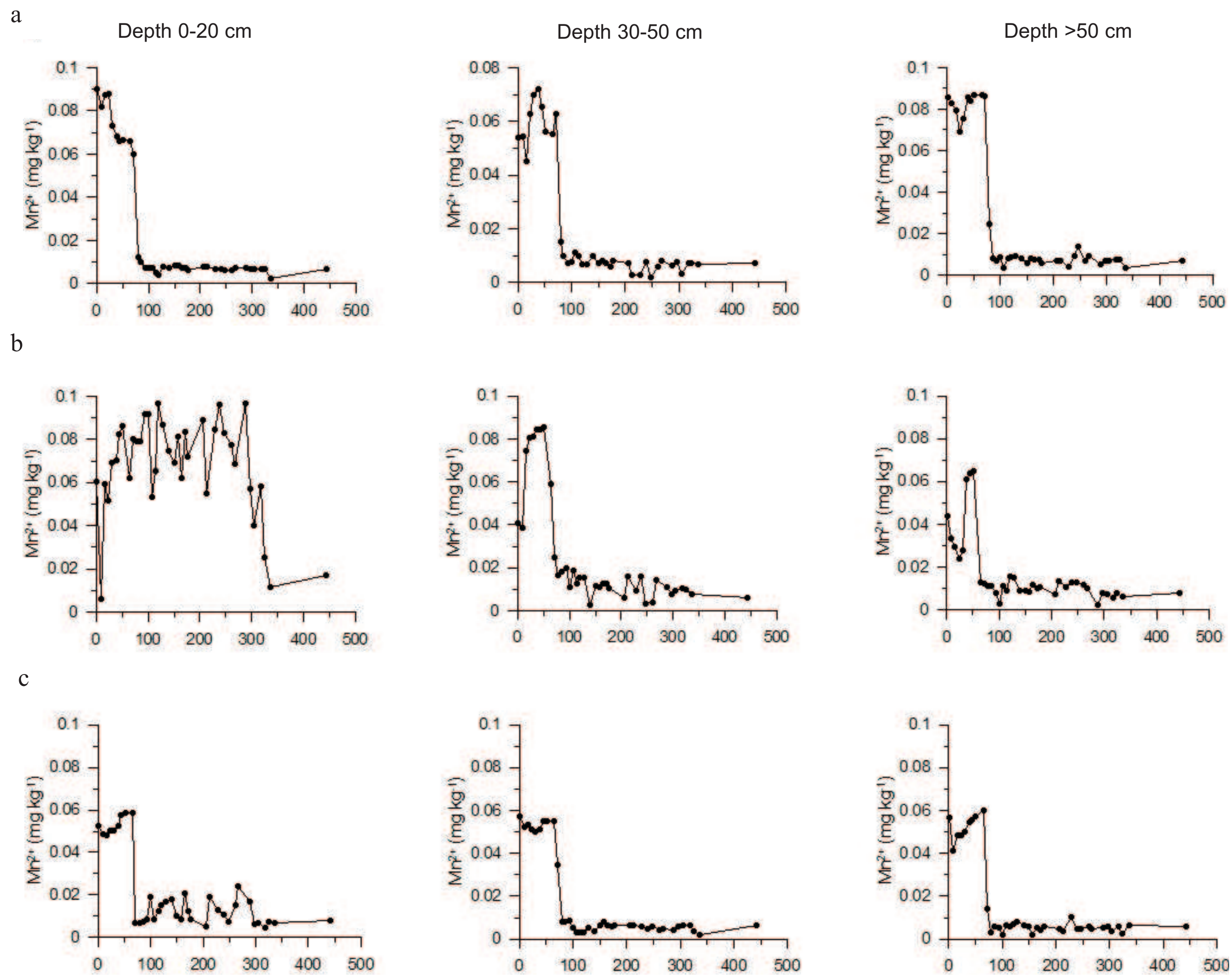

Fig. 4. Changes of Mn concentration during incubation time at different depth of: a – Moszne, b – Orłowskie, and c – Garbatówka peatlands.

between 51 and 65th days of experiment. Stępniewska *et al.* (2006) found that also phosphorus release from peat soils demonstrated analogical for manganese trend of its reduction with soil depth, as they noted the highest P-PO_4^{3-} release in the soil surface (0-20 cm) layers.

Redox potential (Eh) is the aeration parameter characterizing the intensity of soil redox transformations (Włodarczyk *et al.*, 2003). A well-oxidized soil has a redox potential range up to +400 to +700 mV (Stępniewska *et al.*, 2006). Flooded soils may reach redox potential values lower than –300 mV, as the consequence of O_2 absence and the activity of facultative and obligate anaerobic bacteria. The correlations between Mn concentration and redox potential (Eh) values are presented in Fig. 5. As a result of analysing Fig. 5 it is possible to state, that values of Eh during laboratory study ranged from –150 to –250 mV and were well-favoured for Mn release into the soil solution. Moreover, minus values of redox potential testify as well an acidic pH, in which activity of Mn ions displayed an increasing trend, as reduction of oxidized Mn form. Correlation coefficients (R^2), describing mentioned above dependences reached values from 0.12 to 0.55 (Fig. 5). Presented results reported, that amount of Mn is significantly dependent (p<0.05) from water-air conditions. Only at surface and subsurface layers of 3rd place the level of Mn increase independently from Eh value. Meanwhile, at subsoil (>50 cm) process of Mn precipitation with its loss was noted.

Simultaneously, with a decrease in Eh the solubility of phosphorus compounds changes, which is caused by the transformation of such element as iron, manganese and the changes in pH value (Stępniewska and Szafranek, 2004). According to Wu *et al.* (2001) highly possible explanation includes the fact, that dissolved Mn was directly supported by the reduction and dissolution of particulate matter in the

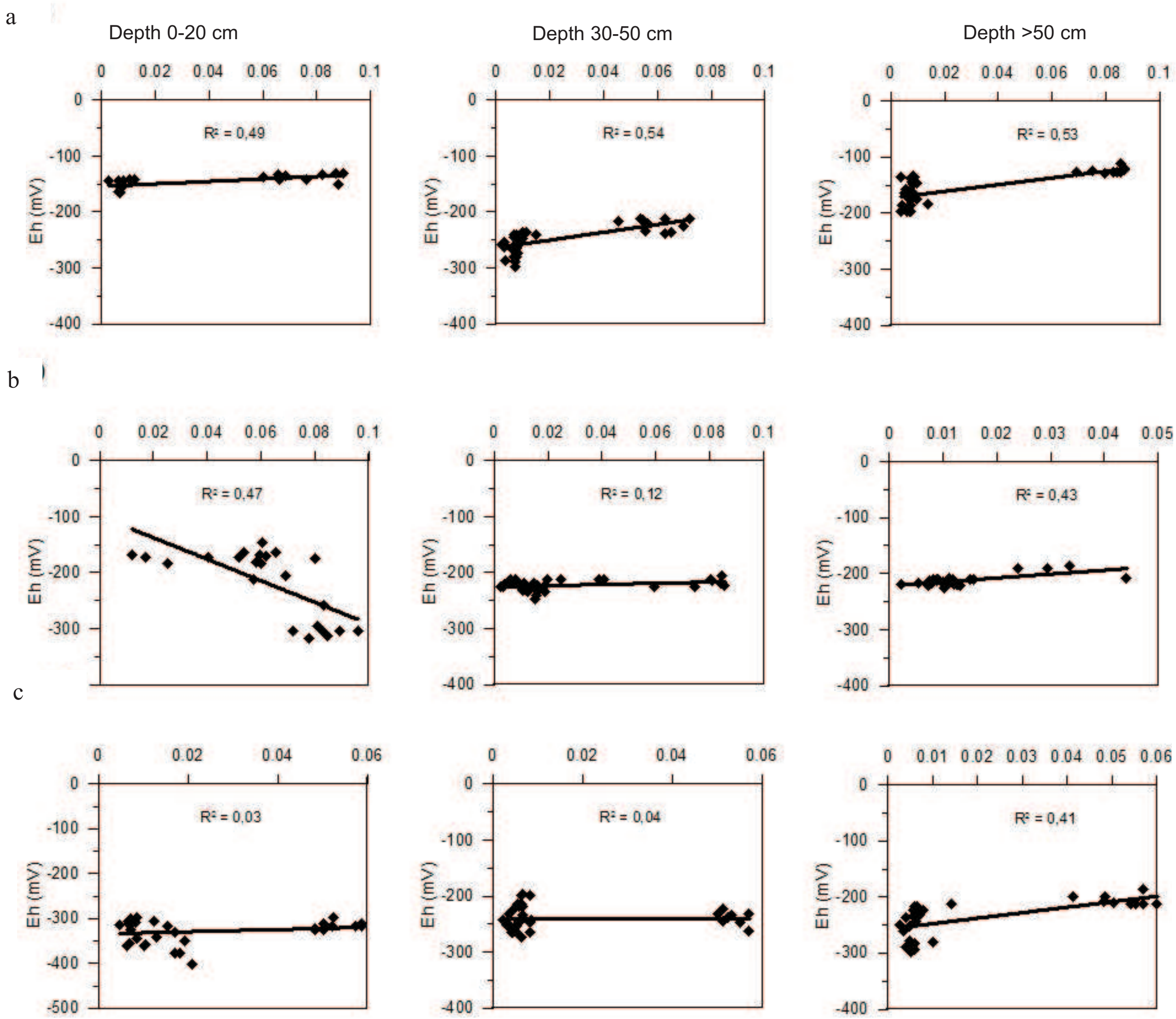

Fig. 5. Relationship between Mn content and Eh value at different depth of: a – Moszne, b – Orłowskie, c – Garbatówka.

T a b l e 2. Differences in Mn content during incubation period (443 days)

Peatland	Depth (cm)	Mn initial content (mg kg^{-1})	Mn final content (mg kg^{-1})	Mn max. content/ day of incubation
Moszne (1)	0-20	0.0901	0.0066	0.0901/ 1
	30-50	0.0539	0.0072	0.0720/ 38
	>50	0.0855	0.0071	0.0871/ 65
Orłowskie (2)	0-20	0.0606	0.0171	0.0959/ 239
	30-50	0.0407	0.0059	0.0855/ 51
	>50	0.0440	0.0080	0.0647/ 51
Garbatówka (3)	0-20	0.0525	0.0077	0.0588/ 65
	30-50	0.0571	0.0063	0.0571/ 1; 51
	>50	0.0569	0.0058	0.0601/ 65

sediments, as suggested by much higher concentrations of dissolved Mn near the interface. Our observations are also supported by the results of Stępniewska *et al*. (2006), who indicated that similar as for Mn also an aactivating of phosphates occurred in clearly negative oxidoreducing conditions at Eh <100 mV and intensified with deepening anaerobiosis.

Other author observed, that dissolved Mn concentrations markedly increased with both time (from July to September), and with depth in the bottom water (Goulet and Pick, 2001; Heyden and New, 2004; Wood and Shelley, 1999). It was confirmed, that Mn content increased from 0.001mg l^{-1} in winter, to 0.047 mg l^{-1} in summer (Wu *et al*., 2001). In addition in summer time, dissolved Mn concentration, just above the sediment surface were higher, than those in the pore water, showing that Mn reductions and dissolution occurred earlier (in a shallower layer), than in winter (Wu *et al*., 2001).

CONCLUSIONS

1. Mn was released at each depth of peat soil, however in the surface layers (0-20 cm) reached the maximum values.

2. Mn release decreased with the depth of the soil profile (except of Moszne peatland, where maximum of Mn in subsoil was stated).

3. The highest concentration of Mn in Orłowskie (0.07 mg kg^{-1}), whereas the lowest in Garbatówka (0.022 mg kg^{1}) was indicated.

4. Decrease of redox potential (Eh) was a cause of increase the Mn release into the soil solution, what was confirmed by negative linear correlations.

5. Generally total amount of Mn was indirectly dependent from water-air conditions occurred in the soil environment.

REFERENCES

Atta S.K., Mohammed S.A., Van Cleemput O., and Zayed A., 1996. Transformation of iron and manganese under controlled Eh, Eh-pH conditions and addition of organic matter. Soil Tech., 9, 223-237.

Boudissa S.M., Lambert J., Müller C., Kennedy G., Gareau L., and Zayed J., 2006. Manganese concentration in the soil and air in the vicinity of a closed manganese alloy production plant. Sci. Tot. Environ., 361, 67-72.

Goulet R.R. and Pick F.R., 2001. Changes in dissolved and total Fe and Mn in a young constructed wetland: Implications for retention performance. Ecol. Eng., 17, 373-384.

Hardie A.M., Heal K.V., and Lilly A., 2007. The influence of pedology and changes in soil moisture status on manganese release from upland catchments: soil core laboratory experiments. Water Air Soil Poll., 182, 369-382.

Heal K.V., 2001. Manganese and land-use in upland catchments in Scotland. Sci. Tot. Environ., 265, 169-179.

Heyden C.J. and New M.G., 2004. Sediment chemistry: a history of mine contaminant remediation and an assessment of processes and pollution potential. J. Geochem. Expl., 82, 35-37.

Ishibashi Y., Matsuo H., Baba Y., Nagafuchi Y., and Imato T., 2004. Association of manganese effluent with the application of fertilizer and manure on tea field. Water Res., 38, 2381-2826.

Marschner H., 1995. Mineral Nutrition of Higher Plants. Academic Press, London, UK.

Negra C., Ross D.C., and Lanzirotti A., 2005. Oxidizing behavior of soil manganese. Soil Sci. Soc. Am. J., 69, 87-95.

Paschke M.W., Valdecantos A., and Redente E., 2005. Manganese toxicity thresholds for restoration grass species. Environ. Poll., 135, 313-322.

Rampazzo N., Schwertmann U., Blum W.E.H., and Mentler A., 1999. Effect of soil acidification on the formation of Fe-, Al-, and Mn-oxides and the stability of soil aggregates. Int. Agrophysics, 13, 283-293.

Rezai K. and Farboodnia T., 2008. The response of pea plant to manganese toxicity in solution culture. Agric. J., 3(3), 248-251.

Stępniewska Z., Borkowska A., and Kotowska U., 2006. Phosphorus release from peat soils under flooded conditions of the Łęczyńsko-Włodawskie Lake District. Int. Agrophysics, 20, 237-243.

Stępniewska Z. and Szafranek A., 2004. Changes of phosphate level in some peats being transformed in different degree. Environ. Prot. Eng., 4, 121-126.

Stueben B.L., Cantrelle B., Sneddon J., and Beck J.N., 2004. Manganese K-edge XANES studies of Mn speciation in Lac des Allemandes as a function of depth. Microchem. J., 76, 113-120.

Włodarczyk T., Stępniewska Z., and Brzezińska M., 2003. Denitrification, organic matter and redox potential transformations in Cambisols. Int. Agrophysics, 17, 219-227.

Wood T.S. and Shelley M.L., 1999. A dynamic model of bioavailability of metals in constructed wetland sediments. Ecol. Eng., 12, 231-252.

Wu F.C., Wan G.J., Huang R.G., Pu Y., and Cai Y.R., 2001. Geochemical processes of iron and manganese in a seasonally stratified lake affected by coal-mining drainage in China. Limnology, 2, 55-62.

Xue S.G., Chen Y.X., Reeves R.D., Baker A.J.M., Lin Q., and Fernando D.R., 2001. Manganese uptake and accumulation by the hyper accumulator plant *Phytolacca acinosa Roxb*. (*Phytolaccaceae*). Environ. Poll., 131, 393-399.