MANGANESE FRACTIONATION ANALYSIS IN SPECIFIC SOIL AND SEDIMENT SAMPLES

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Abstract: Manganese has been determined in soil- and sediment samples taken from selected regions with high manganese concentrations anthropogenic and/or geogenic. The total content of manganese in chosen sediment- and soil samples has been determined applying FAAS after microwave digestion and the manganese fractions after sequential extraction procedures using galvanostatic stripping chronopotentiometry. The highest content of manganese has been determined in sediment from Hôrka (6243.6 ± 56.2 mg kg^{-1}), while the lowest value has been obtained in the sediment from Kráľová (278.6 ± 3.9 mg kg^{-1}). Using a modified Tessier's procedure it was found, that manganese in sediments from Kráľová is associated mainly with the carbonate fraction (>50%), while in sediments from Lozorno and Hôrka it is associated primarily with the Mn and Fe oxide fraction (80% and 42% respectively).

Key words: manganese, galvanostatic stripping chronopotentiometry, fractionation analysis

1. Introduction

Manganese is an essential micronutrient for all organisms, playing an important role in tissue and bone formation, in reproductive functions and in carbohydrate and lipid metabolisms (ANJOS *et al.*, 2007), but at higher levels it can be toxic. In man, chronic manganese poisoning affects the central nervous system, with symptoms resembling those of Parkinson's disease. Manganese toxicity is a serious constraint to crop cultivation since manganese is taken-up by plants and can easily be passed into the food chain (KHOO *et al.*, 1996; BANKS *et al.*, 2005; PEARSON and GREENWAY, 2005). Therefore, the determination of manganese in several matrices samples is very important for some areas, such as environmental chemistry and food control (LEMOS *et al.*, 2008).

Measurement of total metal concentrations is useful to evaluate the heavy metal burden but their mobility depends strongly on their specific chemical forms or ways of binding. However, the determination of specific chemical species or binding forms is as a rule very complex and often hardly possible. For this reason, sequential extraction procedures are commonly applied because they provide information about the fractionation of metals in the different lattices of the solid sample which is a good compromise to give information on environmental contamination risk (MARGUÍ *et al.*, 2004).

For manganese determination highly sensitive methods are required. Various techniques have been used for the determination of trace manganese in biological and environmental samples, such as spectrophotometry and atomic absorption spectrometry. However the electronalytical techniques such as stripping analysis, which incorporate a preconcentration step, e.g. stripping voltammetry and stripping chronopotentiometry are the most used in trace metal determination in complex samples. These techniques have been shown to be suitable, versatile and rapid for multicomponent analysis, having good selectivity and adequate sensitivity (TOWN and LEEUWEN, 2001; FILIPE *et al.*, 2003).

2. Materials and methods

2.1 Samples

Soils and sediments analyzed in this study were collected - from regions with high concentrations of anthropogenic and/or geogenic manganese - at five sampling sites: Kráľová (N 48°12'35"; E 17°48'02"), Lozorno (N 48°32'83"; E 17°05'85"), Kišovce (N 49°01'18"; E 20°37'95"), Primovce (N 49°01'18"; E 20°37'95") and Hôrka (N 49°01'18"; E 20°39'06"). Soil samples were taken from top layer (horizon A; 0-15 cm) and subsurface substrate (35-45 cm). The samples were air-dried, homogenized, screened through a 0.3 mm sieve, and stored for subsequent analysis.

2.2 Mineralization

Soil and sediment samples (0.25 g) have been transferred into PTFE digestion vessels and digested with 2 ml of conc. HCl and 5 ml of conc. HNO_3 in a microwave oven Multiwave MW 3000 (Anton Paar GmbH, Austria) according to the following working conditions: 210°C; 30 min; 40 bars. The acid solution was diluted to 25 ml and the metal content was determined by FAAS using the atomic absorption spectrometer Varian Spectraa-200 (Varian Inc., Australia).

2.3 Sequential extraction procedure

The sequential extractions have been performed using the modified Tessier's procedure on 1 g of soil and sediment samples. The relevant procedure is described in Table 1.

Table 1. Sequential extraction procedure.

Extracted fraction	***Procedure***
F1- Exchangeable	1.0 g sample; 8 ml 1 M $MgCl_2$ (pH=7), 1 h agitation; room temperature, centrifugation 4000 RPM, 5 min; rinsing of solid residue with 3 ml deionized H_2O; centrifugation 4000 RPM, 5 min
F2- Bound to carbonates	solid residue from step 1; 8 ml 1 M NaOAc (pH=5), 5 h agitation; room temperature, centrifugation 4000 RPM, 5 min; rinsing of solid residue with 3 ml deionized H_2O; centrifugation 4000 RPM, 5 min
F3- Bound to Fe-Mn oxides/Reducible	solid residue from step 2; 8 ml 0.1 M $NH_2OH.HCl$ (pH=2), 16 h agitation; room temperature, centrifugation 4000 RPM, 5 min; rinsing of solid residue with 3 ml deionized H_2O; centrifugation 4000 RPM, 5 min
F4- Oxidisable	solid residue from step 2; 8 ml 30% H_2O_2, 5 h agitation; room temperature, centrifugation 4000 RPM, 5 min; rinsing of solid residue with 3 ml deionized H_2O; centrifugation 4000 RPM, 5 min

2.4 Galvanostatic stripping chronopotentiometry (SCP)

The amount of Mn in obtained fractions after evaporation and dissolving in electrolyte has been determined by galvanostatic stripping chronopotentiometry using the flow-through system EcaFlow model GLP 150 (Istran Ltd., Slovakia).

For the determination, stripping chronopotentiometry on a macroporous electrode has been applied. At suitable positive potential Mn(II) is deposited from a slightly acidic solution on the electrode surface as a hydrate oxide:

$$Mn(H_2O)_x^{2+} \rightarrow Mn(H_2O)_{x-3}(OH)_3 + 3H^+ + e^-$$

In the next step the deposit is stripped applying a constant negative current. During this step the signal (chronopotentiogram) is recorded and the concentration of Mn in the sample is evaluated.

The compact flow-through electrochemical cell EcaCell 104, Ag/AgCl reference electrode and carbon porous working electrode E-104 has been used. Basic (carrier) electrolyt solution of 0.1 mol dm^{-3} Na_2SO_4 + 0.01 mol dm^{-3} NaH_2PO_4 and reagent solution of 0.1 mol dm^{-3} HCl has been used. Standard solutions 50 µg dm^{-3}, 100 µg dm^{-3} and 200 µg dm^{-3} Mn(II) were prepared from certified reference material (Merck). Deionised water (conductivity of 0.054 µS cm^{-1}) has been used for all solutions. In all experiments analytical grade reagents were used. Table 2 shows the applied experimental parameters for Mn determination using SCP.

Table 2. Experimental conditions for the determination of Mn (www.istran.sk).

Deposition potential	1100 mV
Deposition time	60 s
Initial potential	1100 mV
Final potential	500 mV
Dissolution current	-25 µA
Time of stabilization	10 s
Max. time of stripping	120 s
Regeneration potential	400 mV
Time of regeneration	10 s
Volume of sample	1 ml
„Standby“ potential	650 mV

3. Results and discussion

The total Mn concentrations and the manganese fractions obtained by the chosen sequential extraction procedures are shown in Tables 3-5.

Samples from Kráľová contain anthropogenic manganese markedly derived from waste dump of a former nickel smelter in Sereď. Manganese in sediments has been found only in carbonate fraction. This is caused evidently by higher pH values of the water reaching 8.2.

Manganese in soil samples from the same site has been bound to Fe-Mn oxides in higher proportion, while significant differences of its abundance in different soil horizons have not been observed.

The total Mn concentrations of investigated soil samples show similar values as well. Our results show for manganese concentrations in soils - in comparison with the ones in sediments - higher values. We assume that for soils floods may act as a not negligible source of Mn. In the same time by lower pH values caused by acid rains the soluble Mn species reach the deeper soil horizons.

Table 3. Concentrations of Mn in samples of stream sediments after modified Tessier's extraction procedure.

Sample	Concentration of Mn ± SD in fractions [mg kg^{-1}]				Total concentration of Mn ± SD [mg kg^{-1}]
	F1	F2	F3	F4	
Kráľová	-	141.4 ± 2.9	-	-	278.6 ± 3.9
Lozorno	-	48.2 ± 3.6	645.8 ± 22.1	-	779.9 ± 10.9
Hôrka	-	594.9 ± 2.1	2586.8 ± 56.1	219.5 ± 0.2	6243.6 ± 56.2
Kišovce	-	209.9 ± 12.8	50.3 ± 6.7	2.4 ±0 .8	617.3 ± 13.6
Primovce	-	969.1 ± 5.2	516.6 ± 11.3	45.2 ± 0.4	3219.8 ± 61.2

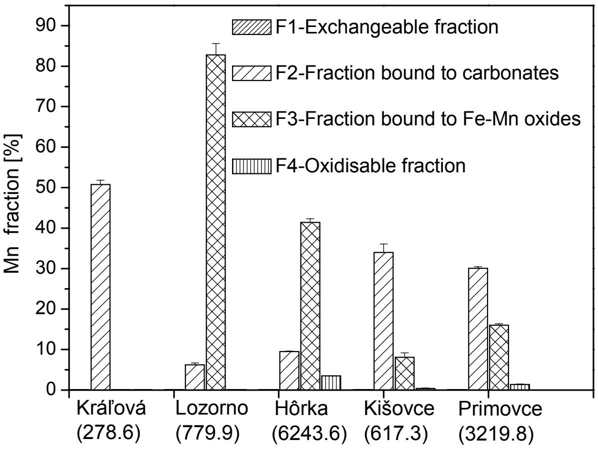

Fig. 1. Percentual abundance of Mn in particular fractions using modified Tessier's extraction procedure in sediment samples (data under the graph represent total manganese concentrations [mg kg^{-1}] determined by FAAS).

Table 4. Concentrations of Mn in soil samples taken from horizon A after modified Tessier's extraction procedure.

Sample	Concentration of Mn ± SD in fractions [mg kg^{-1}]				Total concentration of Mn ± SD [mg kg^{-1}]
	F1	F2	F3	F4	
Kráľová	-	101.2 ± 4.0	145.9 ± 1.8	14.7 ± 0.6	733.2 ± 10.9
Lozorno	-	27.4 ± 0.9	471.6 ± 3.3	-	590.1 ± 7.08
Kišovce	-	145.4 ± 9.2	309.6 ± 5.4	85.7 ± 27.9	1339.7 ± 26.8
Primovce	-	498.9 ± 6.4	620.9 ± 23.9	167.6 ± 4.1	2426.6 ± 16.9

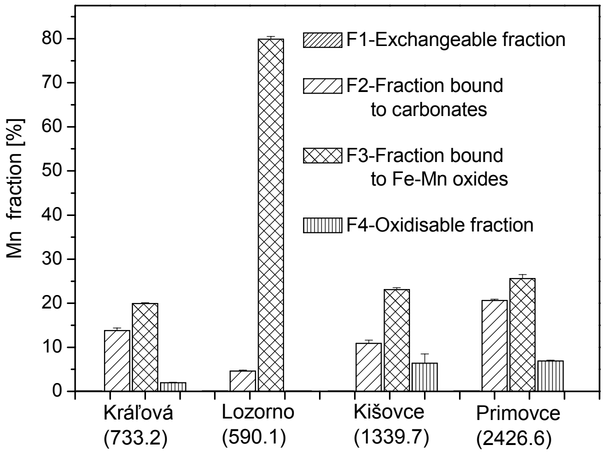

Fig. 2. Percentual abundance of Mn in particular fractions of the modified Tessier's extraction procedure in soil samples taken from horizon A (data under the graph represent total manganese concentrations [mg kg^{-1}] determined by FAAS).

Table 5. Concentrations of Mn in soil samples taken from subsurface substrate after modified Tessier's extraction procedure.

Sample	**Concentration of Mn ± SD in fractions [mg kg^{-1}]**				**Total concentration of Mn±SD [mg kg^{-1}]**
	F1	**F2**	**F3**	**F4**	
Kráľová	-	79.9 ± 5.4	198.3 ± 6.1	32.3 ± 0.6	757.7±12.1
Lozorno	-	4.5 ± 0.4	343.2 ± 5.3	-	446.6±15.2
Kišovce	-	81.8 ± 6.6	65.5 ± 1.2	8.9 ± 0.5	488.1±8.3
Primovce	-	298.9 ± 32.3	952.8 ± 126.6	248.3 ± 15.2	2620.8±28.8

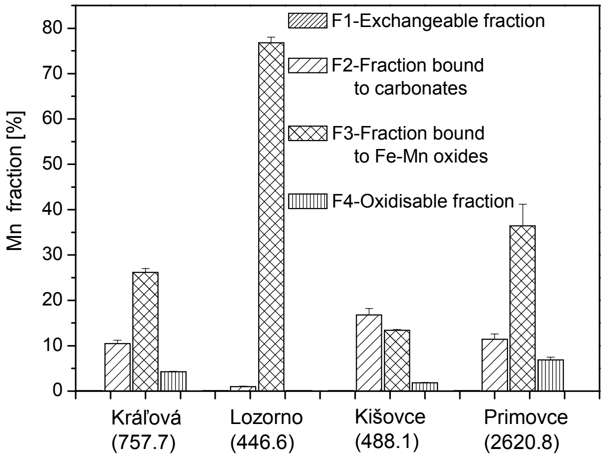

Fig. 3. Percentual abundance of Mn in particular fractions of the modified Tessier's extraction procedure in soil samples taken from subsurface substrate (data under the graph represent total manganese concentrations [mg kg^{-1}] determined by FAAS).

Acidic soils are typical for Zahorie region. This is evidently caused by chemically inactive soil constituents. Both, iron and manganese as well, are at oxidizing conditions in higher oxidation states and so they are present in precipitated chemical forms. In such conditions major proportions of iron and manganese in sediments as well as in investigated soil horizons are bound to Fe and Mn oxides.

The highest contents of total manganese have been measured in samples taken from Hôrka, Kišovce and Primovce. This region is known as one with high geogenic manganese concentrations. At lower pH values the carbonate system consists of hydrogen carbonates predominantly and manganese is in such conditions soluble.

According to our observation sediments near Hôrka contain extremely high manganese concentrations. This fact is avowedly caused by former mining activity. We found that manganese is in this region predominantly bound to Mn-Fe oxides caused apparently by oxidation of manganese originated from mining activity.

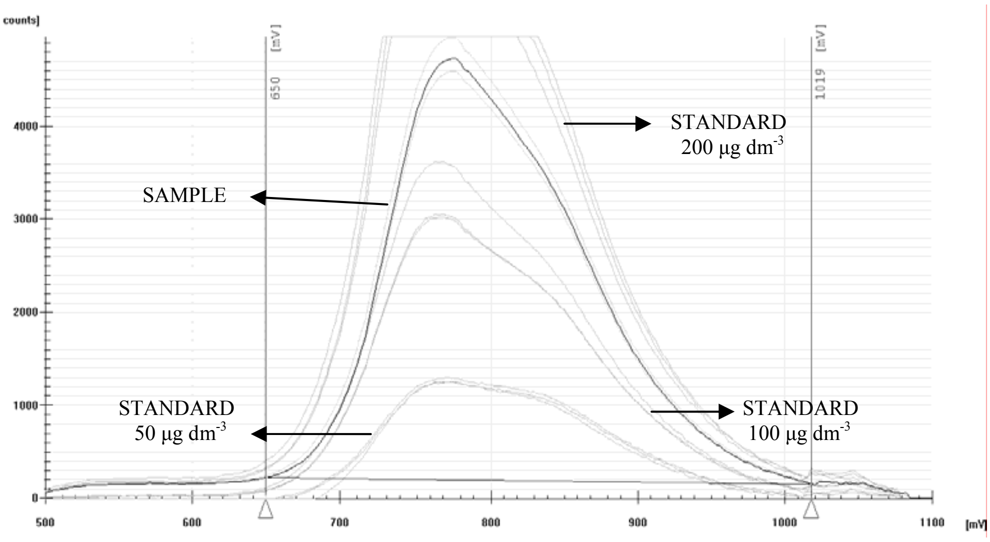

Fig. 4. Typical chronopotentiograms obtained by manganese determination using SCP.

4. Conclusions

Results of fractionation experiments prove that the type of manganese coupling to the sediment- and soil matrix is strongly affected by factors connected to geological bedrock as well as to relevant pH values. In regions with low pH values the carbonate system consists mostly from hydrogen carbonates and at such conditions manganese is soluble. For this reason manganese in sediments from Lozorno and Hôrka is present in fraction bound to Fe-Mn oxides, namely 80% and 42% respectively.

In regions with higher pH values the solubility of carbonates is low. Manganese in sediment from Kráľová is bound to carbonates, namely >50%.

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