



# Speciation of Manganese in Natural Waters Using Differential Pulse Stripping Voltammetry in Correlation with Physico-chemical Parameters

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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## **ABSTRACT**

To understand the bio-geochemical distribution, activities and environmental consequences of heavy metals, it is very important to know their physico-chemical form and the conditions under which the transformation from one form to another occurs. The bioavailability of heavy metals directly depends on the physico-chemical conditions of the environment, the concentration of anions and cations in water, the content of heavy metals as well as the ionic strength. Depending on the physico-chemical properties of water, metals are found in water as free ions or as complex compounds. Their change in the form in which metals occur is significantly influenced by pH, temperature, alkalinity, water hardness, organic matter, and biological activity. The total concentration of metal in water is only an indicator of pollution, and it is necessary to determine the form of the metal. Differential Pulse Anode Stripping Voltammetry with mercury electrode was used for determination of chemical speciation. Manganese belongs to the group of essential heavy metals if its concentration does not exceed the maximum allowed value.

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The aim of this work is to determine the available forms of manganese in the water of Modrac Lake in relation to the analyzed physico-chemical parameters. In addition to industrial applications, Modrac Lake is also used as an alternative source of drinking water, and it is a strategic resource for water supply of the region of north-eastern Bosnia.

*Keywords: Manganese; physico-chemical parameters; differential pulse stripping voltammetry.*

## 1. INTRODUCTION

Natural waters and their particulate matter form a complex heterogeneous electrolytic system which contains numerous inorganic and organic species distributed between the liquid and solid phases. Traces of metals entering natural waters become part of this system, and their distribution between the solid and liquid phases is controlled by few types of dynamic set of physico-chemical interactions and equilibria [1]. The problem of natural water quality is mainly caused of iron, manganese, hydrogen sulphide and hardness [2].

Heavy metals enter water systems from natural and anthropogenic sources [3,4,5]. In water, as sparingly soluble, carbonates, sulphides or sulphates residue at the bottom of water surfaces. Sediment pollution is different from water pollution, because due to its geogenic origin, heavy metals exist in sediment for much longer than in other parts of the biosphere [6]. When the adsorption capacity of the sediment is depleted, the concentration of metal ions in the water increases [7]. The mobility of heavy metals in water depends on a number of factors, and especially on the pH value of water, the present hydrated forms of Mn and Fe, the concentration of carbonates and phosphates and the content of organic matter. With increased acidity of the area and redox potential, some metals such as Cu and Pb are mobilized, and Mn and Fe hydroxides are mobilized under reducing conditions [8]. Manganese ingested can cause harmful effects on human health, and scientific researchers indicate that the intake of higher concentrations of manganese can damage the neurological system [9]. In addition, the presence of manganese in water in large quantities disrupts the organoleptic properties of water, causing an unpleasant taste of water, and is deposited on water pipes, which allows the growth and development of bacteria [10]. The prevalence of each species of manganese depends on the pH, redox potential (Eh) and temperature. Manganese is present in divalent form when the Eh value of surface waters range between 0.5

and 1.0 V and manganese is largely soluble when pH value is close to 8.0. Keeping the Eh conditions and increasing the pH, manganese appears in the form of low-solubility oxides and hydroxides. Thus, an increased pH or Eh would be more favorable for the removal of manganese. As it is more stable in the reduced form than iron, manganese oxidation is more difficult, and simple aeration is generally insufficient for its removal. Additionally, it may be chelated by organic matter. Although this does not affect substantially the removal mechanisms, it can result in the formation of by-products when pre-disinfection is performed with chlorine compounds. The relevance of Mn is evidenced by the successive monitoring of water quality performed in Minas Gerais state (Brazil), which shows this metal to be the second most frequent parameter of violation for the streams of classes 1 and 2, for which the maximum allowable concentration of 0.10 mg L<sup>-1</sup> coincides with the provisions of the Brazilian Water Quality Standards [2]. Given the pH value and redox potential, manganese can occur in water in three oxidation states (Mn<sup>2+</sup>, Mn<sup>3+</sup>& Mn<sup>4+</sup>). Manganese in the oxidized form of MnO<sub>2</sub> in water occurs when the oxygen concentration in water is elevated and such a form of manganese is insoluble and its concentration in water is low. The most dominant form of manganese is Mn<sup>2+</sup> which is formed under reductive conditions, while the most unstable form is Mn<sup>3+</sup> [11]. Removal of manganese from water is carried out by oxidation when Mn<sup>2+</sup> is oxidized to Mn<sup>4+</sup> and precipitated in the form of manganese dioxide. In order to oxidize manganese, KMnO<sub>4</sub>, chlorine or chlorine-based preparations are dosed into the water [12]. The determination of heavy metals has great attention. Considering very low concentrations of manganese and iron in natural water samples, sensitive analytical techniques are required in order to detect them [13]. Various spectroscopic techniques are nowadays widely used for manganese determination; however, the electro-analytical techniques remain to be interesting alternatives due to their high sensitivity, easy procedures and low cost. Anodic stripping voltammetry (ASV) with mercury electrodes

has been employed for manganese determination in the eighties [14,15]. Due to the low solubility in mercury and quite a negative deposition potential of manganese, the cathodic stripping techniques using the accumulation of the analyte by oxidation of  $Mn^{2+}$  ions to  $MnO_2$  at non-mercury solid electrodes have been developed [15-18].

## 2. MATERIAL AND METHODS

Water samples for chemical analysis and analysis for manganese content were collected in sterile plastic bottles with a volume of 0.33 L. Three samples were taken from each locality.

The first sample was immediately acidified with concentrated  $HNO_3$  p.a., and was used for analysis of total heavy metals. The second sample taken for chemical analysis was preserved according to standard procedures, while the third sample was frozen at  $-40^\circ C$  and stored for further analysis for determination of chemical speciation. Water samples from the Modrac Lake accumulation were taken from four different localities over four seasons from a depth of 2.5 m.

Locality 1 – dam area of Modrac Lake

Locality 2 – the middle part of the Modrac Lake

Locality 3 – the mouth of the Turija River into Modrac Lake

Locality 4 – the mouth of the Spreča River into Modrac Lake

Analytical methods of spectrophotometry and volumetry were applied to determine the physico-chemical composition of the water in the Modrac Lake accumulation. An electrochemical method (differential pulse voltammetry) was used to determine the total concentration of magnesium in water samples. The use of electrochemical methods was performed using the method of standard addition which is a quantitative analysis technique used to minimize matrix effects that interfere with analyte measurement signals. This method is suitable for determining low concentrations of trace elements in small sample volumes. Differential pulse anodic and cathodic stripping voltammetry (DPASV and DPCSV) were used for chemical speciation. The analysis process using DPASV and DPCSV was performed in an electroanalytical cell with a volume of 10 ml with immersed three electrodes in the test sample. An electroanalytical cell, Princeton Applied Research model 303A, equipped a three-electrode system, as follows:

- Working electrodes, hanging mercury drop (HMDE)
- Reference electrodes, Ag/AgCl with constant potential and
- Auxiliary electrodes, Pt

During the experimental work, nitrogen was used as an inert gas of high purity, which was used to remove oxygen that can cause interference by reducing sensitivity and reproducibility.

In the preparation process of samples for chemical analysis as well as for analysis of manganese content, a standard solution of Mn with a concentration of 1 g/L was used, from which primary working solutions were prepared, then concentrated  $HNO_3$ , NaOH,  $KNO_3$  p.a. from which 0.1M  $KNO_3$  and 0.01M  $KNO_3$  were prepared. Glassware and used electroanalytical cells were kept in 6 M  $HNO_3$  for 24 h before use, after which they were rinsed with distilled water and dried in an oven. A potentiostat/galvanostat, PAR, model 303A, with Model 270/250 Research Electrochemistry Software, version 4.3 was used to determine the heavy metal content. Photometer and UV-VIS Spectrophotometer, Perkin Elmer Lambda 25 were used for chemical analysis. Chloride content was determined by the Moore method, and physico-chemical parameters such as temperature, pH value, dissolved oxygen, redox potential, conductivity, total salt content in the water were determined by direct measurement using HAANA multiparameters (pH, ISE, EC, DO & turbidity).

## 3. RESULTS AND DISCUSSION

In the first phase of the experimental work, the physico-chemical composition of the water was determined through the seasons for all the mentioned localities. The results of these analyzes are presented in the Tables 1 to 4.

### 3.1 Results of Water Samples Analysis for Free/labile Metal Ion and Metal Ion Bounded to Organic Complexes

In the first phase, after performed chemical analysis, the concentration of metal that was bounded to a labile organic complex at different localities depending on the season was determined. Water samples stored at  $-40^\circ C$  were first defrosted, then filtered through 0.45  $\mu m$  porous filter paper to remove colloidal particles present in the water. After filtration, the water samples were acidified with HCl to pH 2 and irradiated in a UV sterilizer

"SPECTROLINKER XL-1500 UV CROSS LINKER" of 100 W for three hours. By the process of radiation, metals that have been bounded to an organic complex with organic matter present in water are released. In this way were determined an inert form of the metal which is the least toxic (metal which was bounded to stable complexes).

The Table 5 provides the results calculated for the free/labile metal ions bounded to organic complexes obtained by the DPSV method using the stated deposition potentials.

The inorganic speciation of the analyzed samples on the manganese content in water was performed using the VISUAL MINTEQ program taking into account the temperature, pH value and chemical composition of the water. The

results are presented in Tables 7, 8. Two seasons were selected to show the results where the greatest difference was observed.

An increased amount of manganese the form of  $Mn^{2+}$  were noticeable in the spring and summer period when the water temperatures were quite high. There was a decrease in redox potential and pH value, and the concentration of dissolved oxygen was much lower compared to winter-autumn period. Under these conditions, faster oxidation of manganese from reducing sediments occurs, which increases the concentration of  $Mn^{2+}$  in water, and thus the toxicity. From the Fig. 1 it can be seen that almost all manganese is in the form of the free ion  $Mn^{2+}$  in the summer. By increasing the pH value, i.e. by creating oxidation conditions, manganese turns into an insoluble metal form of oxide or oxyhydrate.

**Table 1. Physico-chemical parameters - autumn period**

Physico-chemical parameters	LOCALITY			
	1	2	3	4
Temperature [°C]	6.78	6.26	4.63	4.66
pH – value	7.91	8.26	8.44	8.59
Dissolved oxygen [mg/L]	4.55	4.78	7.73	5.9
Oxydo-reduction potential	84.1	230	46.6	55.7
Pressure [kPa]	96.53	96.37	96.33	95.32
Conductivity [ $\mu$ S/cm]	410	424	428	465
Total dissolved solid [ppm]	205	212	214	233
Sulfates [mg/L]	62	130.1	83	199
Phosphates [mg/L]	1.1	1.55	1.3	3.5
Chlorides [mg/L]	14	11	11	9
Organic matter [mg/L]	33.1	44.4	30.8	27.9
Ionic strength [mol/L]	0.047	0.028	0.049	0.029

**Table 2. Physico-chemical parameters - winter period**

Physico-chemical parameters	Locality			
	1	2	3	4
Temperature [°C]	7.08	7.59	8.45	7.5
pH – value	8.01	8.25	8.22	8
Dissolved oxygen [mg/L]	0.2	0.57	1.17	0.5
Oxydo-reduction potential	256.4	121.7	146.5	140
Pressure [kPa]	98.46	98.39	98.4	99.2
Conductivity [ $\mu$ S/cm]	325	322	339	400
Total dissolved solid [ppm]	163	161	170	160
Sulfates [mg/L]	282.2	146.85	137.71	84.85
Phosphates [mg/L]	1.089	1.180	0.907	3.00
Chlorides [mg/L]	31.49	16.99	13.99	18.99
Organic matter [mg/L]	41.09	22.75	43.46	17.7
Ionic strength [mol/L]	0.053	0.0303	0.054	0.044

**Table 3. Physico-chemical parameters - summer period**

Physico-chemical parameters	Locality			
	1	2	3	4
Temperature [°C]	30.0	30.23	30.41	29.54
pH – value	8.1	8.11	8.2	7.18
Dissolved oxygen [mg/L]	0.3	0.38	0.4	0.16
Oxydo-reduction potential	123.6	121.7	122	154.6
Pressure [kPa]	97.49	97.43	97.41	97.59
Conductivity [ $\mu$ S/cm]	359	363	360	970
Total dissolved solid [ppm]	179	181	180	170
Sulfates [mg/L]	61.71	127.71	273	81.7
Phosphates [mg/L]	1.134	1.61	1.31	3.63
Chlorides [mg/L]	14.99	11.49	11.5	8.99
Organic matter [mg/L]	35.08	47.412	31.608	38.44
Ionic strength [mol/L]	0.0275	0.0318	0.028	0.0432

**Table 4. Physico-chemical parameters - spring period**

Physico-chemical parameters	Locality			
	1	2	3	4
Temperature [°C]	24.78	23.59	23.65	23
pH – value	8.08	8.25	8.05	7.8
Dissolved oxygen [mg/L]	0.38	1.5	1.1	0.9
Oxydo-reduction potential	217.5	175.8	146.6	160
Pressure [kPa]	97.34	97.37	97.26	97
Conductivity [ $\mu$ S/cm]	385	369	381	400
Total dissolved solid [ppm]	192	185	190	160
Sulfates [mg/L]	69.85	85	51	241
Phosphates [mg/L]	1.49	1.92	1.47	1.88
Chlorides [mg/L]	13.9	9.49	14.99	16.99
Organic matter [mg/L]	23.706	20.54	26.23	8.21
Ionic strength [mol/L]	0.0169	0.0215	0.0245	0.0455

**Table 5. Deposition potential of Mn**

Metal	Initial potential (mV)	Final potential (mV)
Mn	-1.65	-1.25

**Table 6. Physico-chemical parameters - spring period**

Locality	Spring (mg/l)		Summer (mg/l)		Autumn (mg/l)		Winter (mg/l)	
	*b.r.	**a.r.	*b.r.	**a.r.	*b.r.	**a.r.	*b.r.	**a.r.
1	$42 \cdot 10^{-3}$	$33 \cdot 10^{-2}$	$95 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$70 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$7.8 \cdot 10^{-3}$	$19 \cdot 10^{-3}$
2	$3 \cdot 10^{-4}$	$47 \cdot 10^{-3}$	$36 \cdot 10^{-3}$	$45 \cdot 10^{-3}$	$6.9 \cdot 10^{-3}$	$80 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$46 \cdot 10^{-3}$
3	$5 \cdot 10^{-4}$	$12 \cdot 10^{-2}$	$38 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$44 \cdot 10^{-3}$	$27 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$38 \cdot 10^{-3}$
4	$24 \cdot 10^{-3}$	$24 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$16 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$23 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	$88 \cdot 10^{-3}$

\*b.r. – before radiation, \*\*a.r. – after radiation

**Table 7. Chemical form of Mn, summer period**

Locality	Chemical form					
	Mn <sup>2+</sup>		MnSO <sub>4(aq)</sub>		MnHPO <sub>4(aq)</sub>	
	mol/l	%	mol/l	%	mol/l	%
1	$1.54 \cdot 10^{-6}$	89.3	$1.314 \cdot 10^{-7}$	7.59	$4.62 \cdot 10^{-8}$	2.67
2	$6.458 \cdot 10^{-7}$	94.2	$3.9 \cdot 10^{-8}$	5.97	$9.7 \cdot 10^{-9}$	1.48
3	$6.5 \cdot 10^{-7}$	94.1	$9.2 \cdot 10^{-9}$	4.17	$2.89 \cdot 10^{-8}$	1.33
4	$1.37 \cdot 10^{-7}$	75.7	$3.8 \cdot 10^{-8}$	20.9	$5.94 \cdot 10^{-9}$	3.26

Table 8. Chemical form of Mn, winter period

Locality	Chemical form					
	Mn <sup>2+</sup>		MnSO <sub>4(aq)</sub>		MnHPO <sub>4(aq)</sub>	
	mol/l	%	mol/l	%	mol/l	%
1	1.15 · 10 <sup>-7</sup>	81.3	2.49 · 10 <sup>-8</sup>	17.5	1.47 · 10 <sup>-9</sup>	1.03
2	8.3 · 10 <sup>-8</sup>	93.4	5 · 10 <sup>-9</sup>	5.7	6.7 · 10 <sup>-10</sup>	0.7
3	8.6 · 10 <sup>-8</sup>	95.4	3.6 · 10 <sup>-9</sup>	4	3.9 · 10 <sup>-10</sup>	0.4
4	8.7 · 10 <sup>-10</sup>	96.3	2.5 · 10 <sup>-11</sup>	2.7	7.9 · 10 <sup>-12</sup>	0.87

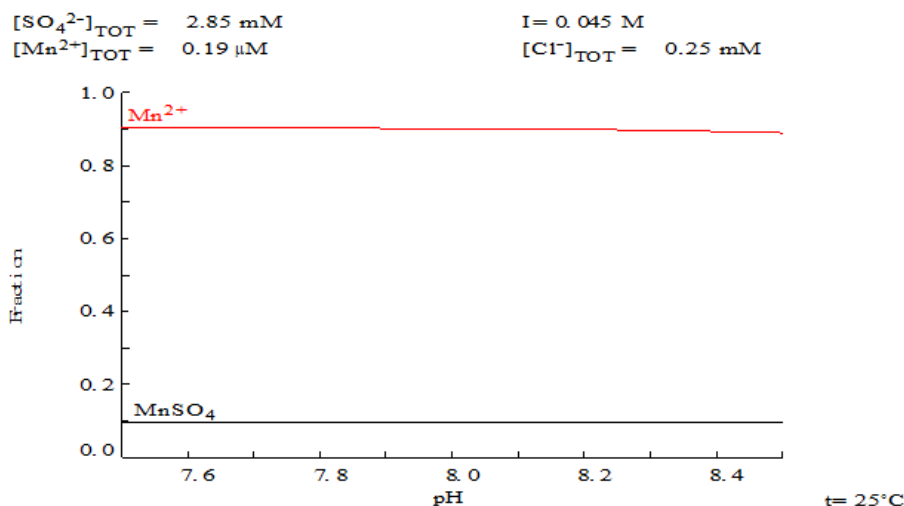


Fig. 1. Dominant labile forms of manganese in the summer period

#### 4. CONCLUSION

1. The distribution of manganese traces in four different localities through four seasons was monitored by applying an electrochemical method, differential pulse stripping voltammetry. The method proved to be very selective for determining the content of very low concentrations in the water.
2. Testing the metals mobility in the water/sediment system by changing the physico-chemical conditions, enables a better understanding of the environmental risk assessment and understanding of the distribution process from the sediment.
3. The obtained analysis results for manganese are important for the revitalization of the Modrac Lake accumulation. They clearly indicate the certain presence of metals and provide information on the sediment quality.
4. Inorganic speciation has determined that the highest metals concentrations are in the labile form for manganese in the spring and summer due to lower redox conditions

compared to autumn and winter, which results in the release of this metal from the sediment and increase its concentration in water.

5. The composition or concentration of labile forms of metals is controlled by pH value, the type of ligand to which the metal binds and the ionic strength. Increased ionic strength in the summer is the result of the excretion of higher concentrations of contaminants in the Modrac Lake accumulation.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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