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# EVALUATION OF IRON AND MANGANESE IN WATER FROM DELIBLATO SANDS AREA

*Jelena Popović-Djordjević[1], Goran Marković[2], Vibor Roje[3], Beka Sarić[4], Jelena Mutić[4]*

**Abstract:** Water is one of Nature's most valuable resources. The aim of this study was to evaluate the content of iron (Fe) and manganese (Mn) in nineteen water samples collected in the area of Deliblato Sands (southern Banat, Serbia). Concentrations of Fe and Mn were determined using Inductively coupled plasma – optical emission spectrometry (ICP-OES) analytical technic. In most studied samples concentrations of Fe and Mn were 5-10-fold higher than the maximum allowed concentrations (MAC - 50 µg/L) established by national regulations on the water quality for human use. The elevated concentrations of studied elements could be attributed to the geology of the terrain in the studied region.

**Key words**: Deliblato Sands, water quality, metals, ICP-OES analysis

## Introduction

Deliblato Sands is located in southern Banat of Vojvodina province, Serbia. It is a large sandy area covering ca. 300 km$^2$, positioned between the river Danube and the southwestern slopes of the Carpathian Mountains. The Deliblato Sands or popularly named 'European Sahara' is the largest sandy territory in Europe, formed by the retreate from the Pannonian Sea. It was formed durig the Ice Age from the layers of silico-carbon sand (Drakulić, 1969). The area is characterized by semi-arid continental climate with big annual temperature fluctuation (from -30 to +42 °C), sandy soil and absence of surface watercourses (IUCN 1998).

Deliblato Sands is a natural extraordinary feature in the European continent. The specific geomorphological phenomena are sand dunes formed by wind deposition. Deliblato Sands is one of the most important centers of biodiversity in Serbia. Due to its uniqueness, it was declared the special nature reserve and it is under protection of UNESCO (IUCN 1998; Vesić, 2017). Anthropogenic impacts are mostly manifested in the form of artificial afforestation in order to bind the drifting sand, plowing of the remaining steppes for agriculture purpose and intentional fires (Popović et al., 2012).

The quality of water is a basic precondition for a healthy and long-lasting life of people. Due to intensive environmental pollution or unfavorable geological and

[1] University of Belgrade, Faculty of Agriculture, Department of Food Technology and Biochemistry, Belgrade, Serbia (jelenadj@agrif.bg.ac.rs)
[2] University of Kragujevac, Faculty of Agronomy Čačak, Cara Dušana 34, Čačak, Serbia
[3] University of Zagreb, Faculty of Forestry and Wood Technology, Svetošimunska 23, Zagreb, Croatia
[4] University of Belgrade, Faculty of Chemistry, 12-16 Studentski trg, 11158 Belgrade, Serbia

geochemical characteristics, an increasing number of areas in the world have problems with providing healthy and quality water (Kostić et al, 2016a).

Iron, Fe, is one of the more abundant elements in the Environment where it is present in two oxidation states: II and III. Naturally, Fe enters water by rocks and soil weathering, while its anthropogenic release usually occurs in the context of coal and metal mining as well as metallurgical industries. In water, i.e. in water solutions, this element is predominantly present as Fe(III) in the form of hexaaqua complex ion, $[Fe(H_2O)]^{3+}$ (Bailey et al., 2002).

Manganese, Mn, is considered as an essential trace element. Anthropogenic input of Mn in the Environment is usually connected to industrial pollution and mine drainage. In natural water systems this element is present in the form of the oxidation state II (Bailey et al., 2002).

This work aimed to evaluate the quality of water at various locations in Deliblato Sands based on the content of iron and managanese.

## Material and methods

***Study area*** - Samples of water were collected in the area of Deliblato Sands (southern Banat, Vojvodina province, Serbia) during 2019-2020. A total of 19 samples (labeled as S1-S19) from different locations: Dolovo - **L1** (S1-S6, S11, S12, S16-S19), Mramorak - **L2** (S7-S10), Devojački bunar - **L3** (S13), Šušara - **L4** (S14) and Stara Palanka - **L5** (S15) within the study area were examined, Figure 1.

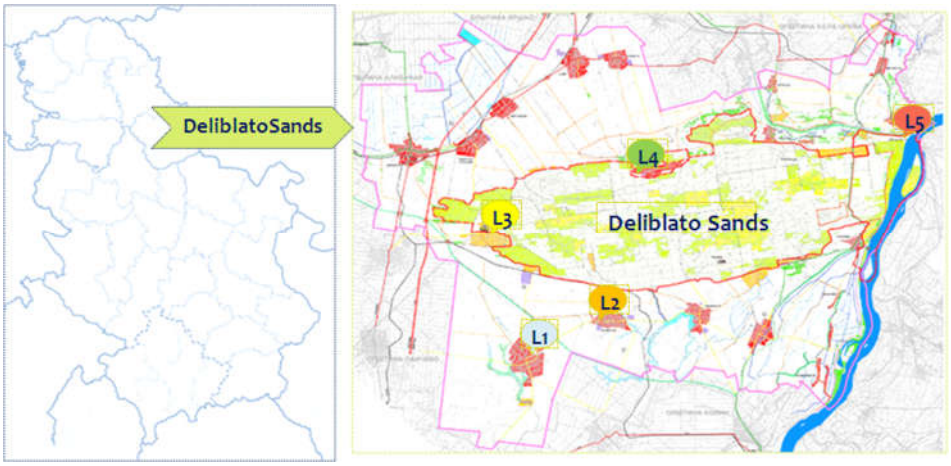


Figure 1. The geographical position of Deliblato Sands and sampling locations (L1-L5)*
*Slika 1. Geografski položaj Deliblatske peščare i lokacije uzorkovanja (L1-L5)*

**Deliblato Sands map adopted according to 'Prostorni plan područja posebne namene Specijalnog rezervata prirode Deliblatska peščara', 2006; available at: https://drive.google.com/file/d/1W7VFTs7WB9IAJuJfjJk9ENpv10G8Hd7Z/view

***Determination of Fe and Mn*** – Each water sample was taken in a 50 mL plastic bottle. Preservation of the samples was performed with 1 mL of 65 % nitric acid. The samples were stored in the refrigerator until the analysis. Sample preparation for metal recording was done in a microwave digestion system (ETHOS 1, Milestone, Italy), which is equipped with an HPR-1000/10S segmented rotor. The analytical technique of optical emission spectrometry with inductively coupled plasma, ICP-OES was used to determine the metal content. Thermo Scientific iCAP 6500 Duo ICP instrument (Thermo Fisher Scientific, Cambridge, UK) was used for the analysis (Kostić et al, 2016a).

***Statistical analysis*** **-** Microsoft Statistical Excel within the Data Analysis package was used for statistical processing of the obtained data. All results were presented as mean of triplicate measurements ± standard deviation. Student's t-test (comparative t-test) was used to determine whether the mean values obtained for manganese and iron differ significantly on the level of significance between the mean values at $p<0.05$.

## Results and discusion

The results obtained for the studied elements (iron and manganese) in water samples collected from the area of Deliblato Sands are shown in Table 1.

Table 1. Mass concentrations of iron and manganese in water samples at Deliblato Sands area

*Tabela 1. Masene koncentracije gvožđa i mangana u uzorcima vode na teritoriji Deliblatske peščare*

| Sample *Uzorak* | Fe (μg/dm$^3$) | Mn (μg/dm$^3$) | Sample *Uzorak* | Fe (μg/dm$^3$) | Mn (μg/dm$^3$) |
|---|---|---|---|---|---|
| S1 | 689.90±3.20* | 249.10±0.70 | S11 | 9.85±0.35 | 1.84±0.07 |
| S2 | 768.10±5.80 | 204.80±1,90 | S12 | 74.27±0.34 | 8.63±0.07 |
| S3 | 491,00±6.90 | 24.88±0.53 | S13 | 82.40±1.42 | 210.7±1.20 |
| S4 | 36.02±0.31 | 1.14±0.02 | S14 | 3.80±0.05 | 2.20±0.02 |
| S5 | 495.20±0.90 | 184.10±0.50 | S15 | 9.55±0.21 | 9,02±0,08 |
| S6 | 970.90±2.70 | 221.00±0.30 | S16 | 676.10±0.80 | 214.10±0.20 |
| S7 | 551.40±3.90 | 158.80±1.00 | S17 | 0.24±0.20 | 159.50±0.60 |
| S8 | 553.40±1.10 | 155.20±0.60 | S18 | 757.20±14.80 | 189.80±3.00 |
| S9 | 4.20±0.28 | 6.04±0.05 | S19 | 39.57±0.42 | 301.90±1.30 |
| S10 | 651.70±4.60 | 2155.00±11.00 | **MAC**** | 50 μg/dm$^3$ | 50 μg/dm$^3$ |

* The results are presented as mean ± standard deviation; ** Official Gazette, 1999.

Manganese (Mn) and iron (Fe) concentrations in most samples exceeded the maximum allowable values (MAC) for these elements (50μg/dm$^3$) set by the national regulations (Official Gazette, 1999). Concentration of Fe was over MAC value in the samples S1-S3, S5-S8, S10, S12, S13, S16, and S18. When it comes to Mn, its content was elevated in the samples S1, S2, S5-S8, S13, and S15-S19, Figure 2. It was observed that there was a value of Mn (2155.00 μg/dm$^3$) exceeding the reasonable range (outlier) in the sample S10. Results obtained for Fe and Mn in the location **L1** were in line with the results of our previous study conducted in Dolovo (Kostić et al, 2016b). Mn is associated with Fe in igneous rocks (Kostić et al, 2016a). In that respect ,water in natural sources could be more or less loaded with these elements that can be toxic if present in concentrations above MAC (Kostić et al, 2016a; Trišović et al, 2021). The potential risk for human health regarding the elevated concentration of iron and manganese was observed in our previous study (Kostić et al, 2016a,b).

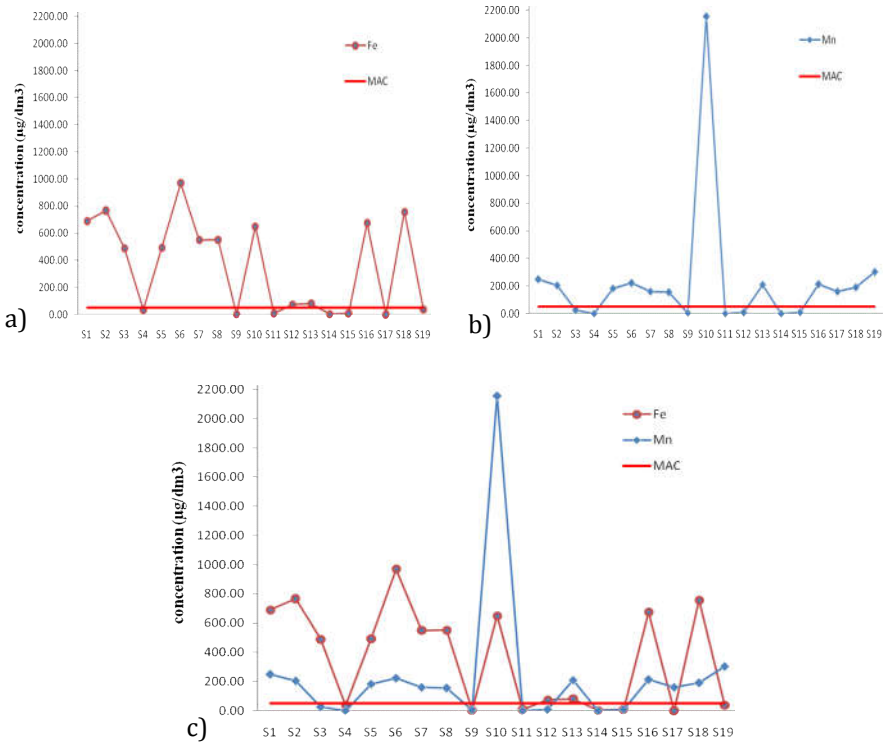


Figure 2. The differences in content between a) iron b) manganese, and c) iron and manganese in water samples from Deliblato Sands area

*Slika 2. Razlike u sadržaju a) mangana b) gvožđa, i c) mangana i gvožđa između uzoraka vode na području Deliblatske peščare*

A comparative t-test was performed to determine whether the mean values obtained for manganese and iron differ significantly. According to our data set $t_{calculated} < t_{critical}$ (1.13 <2.10) there was no statistically significant difference in the results of manganese and iron.

Table 2 shows the correlation coefficients of the elements whose concentrations were determined. The correlation coefficient can have values from 0 to 1. Manganese and iron are not correlated with each other, which may indicate their different anthropogenic origins or different content according to the type of water.

Table 2. Correlation coefficients of elements in the studied water samples
*Tabela 2. Koeficijenti korelacije elemenata u proučavanim uzorcima vode*

| | **Mn** | **Fe** |
|---|---|---|
| **Mn** | 1 | |
| **Fe** | 0,319 | 1 |

## Conclusion

Based on the obtained results and statistical comparisons, it could be noticed that the concentrations of manganese and iron in water in the study area are quite high. The geological composition of the terrain could offer a possible explanation. In order to evalute the mineral content and water quality in the studied area, it is necessary to focus further work on other macro- and trace elements as well as other parameters of water quality.

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## References

Bailey, R. A., Clark, H.M., Ferris, J.P., Krause, S., Strong, R. L. (2002). Chemistry of the Environment, 2nd ed., Academic Press, San Diego, pp. 347-354, 383-388., 389.

Drakulic, M. (1969). Interactions of lambda vir and of uv-irradiated t $ sub 1$ bacteriophage during mixed infection, Columbia Univ., New York. Radiological Research Lab. (No. NYO-2740-6).

IUCN (1998). The proposal for the protecton of the Natural Reserve Deliblato Sands as Special Nature Reserve. Institute for Nature Conservation of Serbia, Novi Sad, pp.154

Vesić, M. (2017). Weekend tourism and unplanned construction in Deliblato Sands. Zbornik radova-Geografski fakultet Univerziteta u Beogradu, (65-1a), 419-432.

Popović, Z., Smiljanić, M., Matić, R., Kostić, M., Nikić, P., Bojović, S. (2012). Phytotherapeutical plants from the Deliblato Sands (Serbia): Traditional pharmacopoeia and implications for conservation.

Kostić, A. Ž., Pantelić, N. Đ., Kaluđerović, L. M., Jonaš, J. P., Dojčinović, B. P., Popović-Djordjević, J.B. (2016a). Physicochemical properties of waters in southern Banat (Serbia); potential leaching of some trace elements from ground and human health risk. Exposure and Health, 8(2), 227-238.

Kostić A., Lačnjevac Č., Pantelić N., Popović–Đorđević J. (2016b). Procena potencijalnog zdravstvenog rizika usled prisustva makro- i mikroelemenata u pijaćoj vodi sa područja Dolova (opština Pančevo). X Naučno savetovanje po pozivu–Održivi razvoj raničevskog okruga i energetskog kompleksa Kostolac, Kostolac, Srbija. Zbornik radova str. 91–94.

Official Gazzete (1998/1999). Regulation on hygienic quality of drinking water 42/98 and 44/99 (*In Serbian*).

Trišović, T., Rafailović, L., Li, W., Grgur, B., Trišović, Z. (2021). Sistem za prečlšćavanje pijaće vode sa povećanom tvrdoćom i koncentracijom amonijaka, gvožđa, mangana, XXVI Savetovanje o biotehnologiji, 12 - 13. март 2021, Zbornik radova, 357-362.

## ODREĐIVANJE GVOŽĐA I MANGANA U VODI SA PODRUČJA DELIBLATSKE PEŠČARE

*Jelena Popović-Djordjević[1], Goran Marković[2], Vibor Roje[3], Beka Sarić[4], Jelena Mutić[4]*

### Izvod

Voda je jedan od najvrednijih resursa prirode. Cilj ovog istraživanja bio je da se odredi sadržaj gvožđa (Fe) i mangana (Mn) u uzorcima vode prikupljenim na području Deliblatske peščare (južni Banat, Srbija). Koncentracije Fe i Mn određene su analitičkom tehnikom induktivno spregnute plazme – optička emisiona spektrometrija (*eng*. ICP-OES). U većini proučavanih uzoraka koncentracije Fe i Mn bile su iznad maksimalno dozvoljenih koncentracija (MDK - 50 μg/L) utvrđenih nacionalnim propisima o kvalitetu vode za ljudsku upotrebu. Vrednosti sadržaja Fe i Mn u pojedinim uzorcima bile su 5-10 puta veće od MDK vrednosti. Povišene koncentracije proučavanih elemenata mogu se pripisati geologiji terena u ispitivanom području.

**Ključne reči**: Deliblatska peščara, kvalitet vode, metali, ICP-OES analiza

[1]Univerzitet u Beogradu, Poljoprivredni fakultet, Odsek za prehrambenu tehnologiju i biohemiju, Nemanjina 6, Beograd-Zemun, Srbija (jelenadj@agrif.bg.ac.rs)
[2] Univerzitet u Kragujevcu, Agronomski fakultet u Čačku, Cara Dušana 34, Čačak, Srbija
[3] Sveučilište u Zagrebu, Fakultet šumarstva i drvne tehnologije, Svetošimunska 23, Zagreb, Hrvatska
[4] Univerzitet u Beogradu, Hemijski fakultet, Studentski trg 12-16, 11000 Beograd