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Anthropogenic influence on the degree of contamination by heavy metals of sediment river Spreča and selected tributaries

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ABSTRACT : *Metals are always naturally present in the aquatic environment, and their concentration is regulated by natural processes. Metal concentrations in aqueous systems depend on the rock composition and soil of the area in which they are located. Therefore, for each characteristic area, the natural level of heavy metals is determined individually and is valid for the given conditions. In the study of contaminated samples, determining the extent or degree of contamination with a particular heavy metal requires that the metal concentration in the contaminated sample be compared with the metal concentration in the uncontaminated, reference material. Contamination factor (CF) was used to assess the degree of heavy metal contamination of the sediment analyzed in this paper. A geochemical normalization approach was applied to estimate the extent of sediment contamination by heavy metals. According to the selected model, the degree of contamination is estimated, and taking into account when calculating the contamination factor (CF) that the sediment is of similar texture and mineral composition. The obtained values of contamination factor (CF) are shown graphically, individually for each analyzed metal. Based on the values of contamination factors, the impact of wastewater on river flows was assessed, as well as the impact of the inflow of one river onto another. The contamination factor was calculated individually for each of the analyzed metals. CF values range from high to moderate contamination.*

KEYWORDS: *heavy metals, contamination factor, geochemical normalization, sediment*

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I. INTRODUCTION

Metals are always naturally present in the aquatic environment, and their concentration is regulated by natural processes. Metal concentrations in aqueous systems depend on the rock composition and soil of the area in which they are located. Therefore, for each characteristic area, the natural level of heavy metals is determined individually and is valid for the given conditions. The range of natural concentrations of heavy metals ("background level") ranges from a few micrograms to 1 ng / L. Water pollution by heavy metals due to human activities (transport, agriculture, industry, municipal wastewater) is a serious environmental problem, because metals are not biodegradable and once introduced into the environment become permanently part of it. Thus, the concentrations of heavy metals are a very important parameter in assessing the state of natural water quality. In order to be able to determine the anthropogenic impact on a river water system, its natural composition must be known from the source to the mouth. In the study of contaminated samples, determining the extent or degree of contamination with a particular heavy metal requires that the metal concentration in the contaminated sample be compared with the metal concentration in the uncontaminated, reference material. Such material should be unpolluted or intact material comparable to the samples tested. In previous environmental studies, a method was used to compare the measured metal concentrations with the average metal values in sedimentary rocks [1] and the earth's crust [2] taken as a standard (Table 1). The main disadvantage of this method is that it does not take into account the natural variability of the geochemical composition, which would lead to certain abnormalities at the local level when determining the degree of pollution [3]. Recently, the aim is to establish reference values by comparing the concentration of the target metal, contaminated and uncontaminated sediments, similar or identical texture and mineral composition [4],[5]. In line with these efforts, the contamination factor was determined based on a comparison of heavy metal concentrations before and after inflow of certain wastewaters into the selected river (or before and after inflow of selected tributaries into the Spreča River).

Table 1.: Average values of concentrations of selected heavy metals in: (A) sedimentary rocks [1],[2] - "background level"

Metal	*A [ppm]*	*B [ppm]*
Cd	0,2	0,1
Cu	45	25
Co	30,74	24
Cr	203,51	126
Fe	47200	43200
Mn	1616,66	716
Ni	249,85	56
Pb	20	14,8
Zn	95	65

II. MATERIAL AND METHODS

Watercourses in the Tuzla Canton belong to the Spreča, Bosna and Tinja basins, with the Spreča basin being the most extensive. The hydrographic system of Spreča is located within the Spreča bay of the Dinaric direction of orientation with the basic direction southeast-northwest. The river Spreča is one of the longest rivers in our country. It springs below Velja Glava (619 m above sea level) near Zvornik and has a length of 115.7 km and a catchment area of 1945 km^2 [6],[7]. Selected sites for sampling are located in the upper basin of the river Spreča from the mouth of the Oskova to Lake Modrac, with associated watercourses Oskova, Litva and Gostelja, which due to the receipt of wastewater from coal mines (from surface mines and separation), wood industry and other wastewater do not meet the prescribed water quality and are classified in III-IV category of water quality according to the Regulation on water categorization of Bosnia and Herzegovina [8]. The Modrac reservoir is classified in category II water quality [8]. In accordance with the above, 11 sites were selected where in situ measurements were performed, followed by water and sediment sampling for laboratory analyzes. For each of the listed locations, the Garmin GPS device (MAGELLAN EXPLORIST 210) recorded the exact position and altitude (Table 2.).

Table 2.: Positions of sites with altitudes

Locality	Geographic latitude	Longitude	Altitude
1	44°22'49.86"	18°40'06.34"	309.40 m
2	44°24'59.64"	18°39'46.37"	268.60 m
3	44°27'09.07"	18°38'28.79"	241.90 m
4	44°27'49.63"	18°37'10.79"	253.40 m
5	44°28'09.90"	18°37'53.90"	207.26 m
6	44°24'11.48"	18°33'45.16"	360.70 m
7	44°24'31.87"	18°31'49.50"	352.50 m
8	44°24'44.92"	18°32'26.26"	369.10 m
9	44°25'01.81"	18°33'36.36"	331.60 m
10	44°28'46.19"	18°32'51.99"	193.24 m
11	44°27'58.46"	18°35'32.24"	199.34 m

The sampling sites are numbered 1 to 11 on a situation map taken from Google Earth, with a brief description as follows:

Site 1 - sediment sample from the Gostelja riverbed above the inflow of wastewater from RMU Đurđevik;
Site 2 - sediment sample from the Gostelja riverbed after inflow of wastewater from RMU Đurđevik;
Site 3 - sediment sample from the Oskova riverbed after the mouth of the Gostelja in Oskovo;
Site 4 - sediment sample from the Spreča riverbed after the Oskova estuary;
Site 5 - sediment sample from the Spreča riverbed before the Oskova estuary;
Site 6 - sediment sample from the Oskova riverbed before the mouth of Lithuania, and above the tailings with minimal anthropogenic activity;
Site 7 - sediment sample from the bed of the Litva river before the confluence of the river Draganje;
Site 8 - sediment sample from the Litva riverbed above the inflow of wastewater from RMU Banovići;

Site 9 - sediment sample from the Litva riverbed after the inflow of wastewater from RMU Banovići;
Site 10 - sediment sample from the river Spreča just before flowing into Lake Modrac;
Site 11 - sediment sample from the Spreča riverbed after the Oskova estuary (between site 4 and site 10).

To determine the content of Zn and Cd in the sediment, flame atomic absorption spectrophotometry AAS was applied on the Atomic Absorption Spectrometer type AANALIST 200, Perkin Elmer, USA, using standard solutions for the tested elements of the same company. Determination of Cu, Ni, Pb, Fe and Mn content in the sediment was performed on an optical emission spectrophotometer, which works on the principle of induction coupled plasma - type ICP - OES OPTIMA 2100 DV, manufactured by Perkin-Elmer USA using standard solutions for the tested elements of the same company. The results for the metal content were calculated on the dry mass of sediment.

III. RESULTS AND DISCUSSION

Contamination factor (CF) was used to assess the degree of heavy metal contamination of the sediment analyzed in this paper. A geochemical normalization approach was applied to estimate the extent of sediment contamination by heavy metals. The geochemically normalized contamination factor is calculated according to the following formula [9]:

$$KF = \frac{(C)_{metal}}{(C)_{background}}$$

Where C_{metal} is the total metal concentration in the sample and $C_{background}$ represents the average background values of the metal in the sediment ("background level"). In this paper, it was not possible to take one of the samples for the so-called "background level" because the concentrations of the investigated metals in the upper part of the flow (above the anthropogenic influence) of Gostelja, Litva and Oskova differ significantly in the sediments. The assessment was performed by comparing the concentration of heavy metals in the sediment sampled before and after the inflow of wastewater into selected watercourses, where it is important that the sediment is from the same watercourse, to be similar in texture and mineral composition. Several categories of ranking systems are used to indicate the degree of anthropogenic contamination. The value of contamination factor (KF) could be found in any of the levels of contamination (Table 3) [10],[11].

Table 3.: Anthropogenic contamination ranking system based on CF values (Sabo et al. 2013, Nasr et al. 2006)

Value of KF contamination factor	Description of the degree of contamination
$KF < 1$	Low level of contamination
$1 \leq KF < 3$	Moderate level of contamination
$3 \leq KF \leq 6$	High level of contamination
$KF > 6$	Very high contamination

According to the selected model of estimation of the degree of contamination, and taking into account when calculating the contamination factor (CF) that the sediment is of similar texture and mineral composition, the obtained CF values are shown graphically, individually for each metal. Based on the values of contamination factors, the impact of wastewater on river flows was assessed, as well as the impact of the inflow of one river into another. The contamination factor was calculated individually for each metal in all four seasons as follows:

- 2:01 - impact of wastewater from RMU Đurđevik on the watercourse of the river Gostelja;
- 3:01 - impact of the Gostelja river flowing into the Oskova river;
- 4:05 - the impact of the Oskova River flowing into the Spreča River;
- 7:06 - the impact of wastewater collected from Banovići on the watercourse of the Litva river;
- 8:06 - impact of wastewater from RMU Banovići on the watercourse of the river Litva;
- 9:06 - the impact of wastewater collected in the Litva river watercourse on the Oskova river watercourse.
- 10:05 - the impact of the Oskova river flowing into the Spreča river, at a greater distance from the Oskova estuary;
- 11:05 - the impact of the Oskova River flowing into the Spreča River, just before it flows into Lake Modrac;

Assessment of anthropogenic impact in terms of sediment pollution by heavy metals was done for selected metals: copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni), lead (Pb), manganese (Mn) and iron (Fe). The values of contamination factors for copper range from 0.44 to 5.75, and it can be observed that a high degree of contamination is expressed after the confluence of the Oskova River with the Spreča River, CF = 5.75 (Figure 1). It is certainly encouraging that this level of contamination decreases along the course of the river Spreča and at the confluence with Modrac is 2.8-5.35, depending on the season. This fact confirms the extraordinary power of self-purification of watercourses, although it is still a moderate to high contamination. Variations in the degree of contamination can also be observed depending on the season, the amount of wastewater, water flow, the amount of precipitation and physico-chemical changes in the water-sediment system. Moderate to high degree of contamination is observed after the inflow of wastewater from RMU Đurđevik to the watercourse of the river Gostelja (1.07-1.44) and wastewater from RMU Banovići to the watercourse of the river Litva and the river Oskova (1.09-3.28).

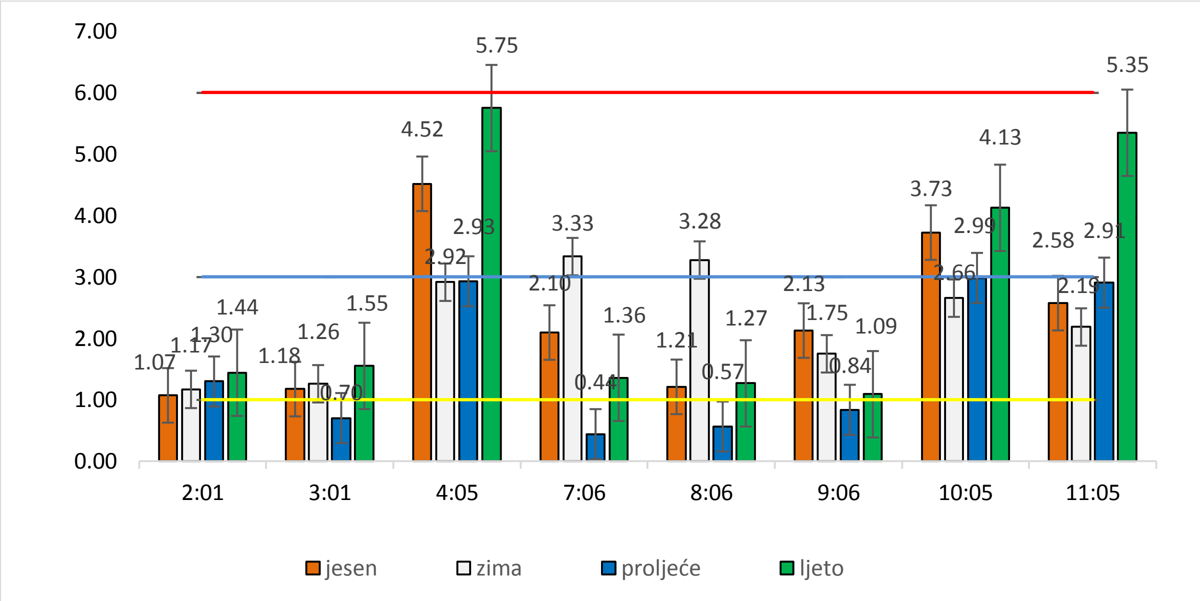

Figure 1. Graphical representation of contamination factors for Cu in sediment

Based on the values of zinc contamination factors ranging from 0.63–2.92, it is clear that this is a mild to moderate contamination of sediment with zinc (Figure 2). The most significant impact is on the Litva river watercourse with associated wastewater on the Litva river watercourse. As for the watercourse of the river Spreča, the most significant impact is the inflow of Oskova with its associated wastewater, and this is most pronounced in the summer (2,3-2,81).

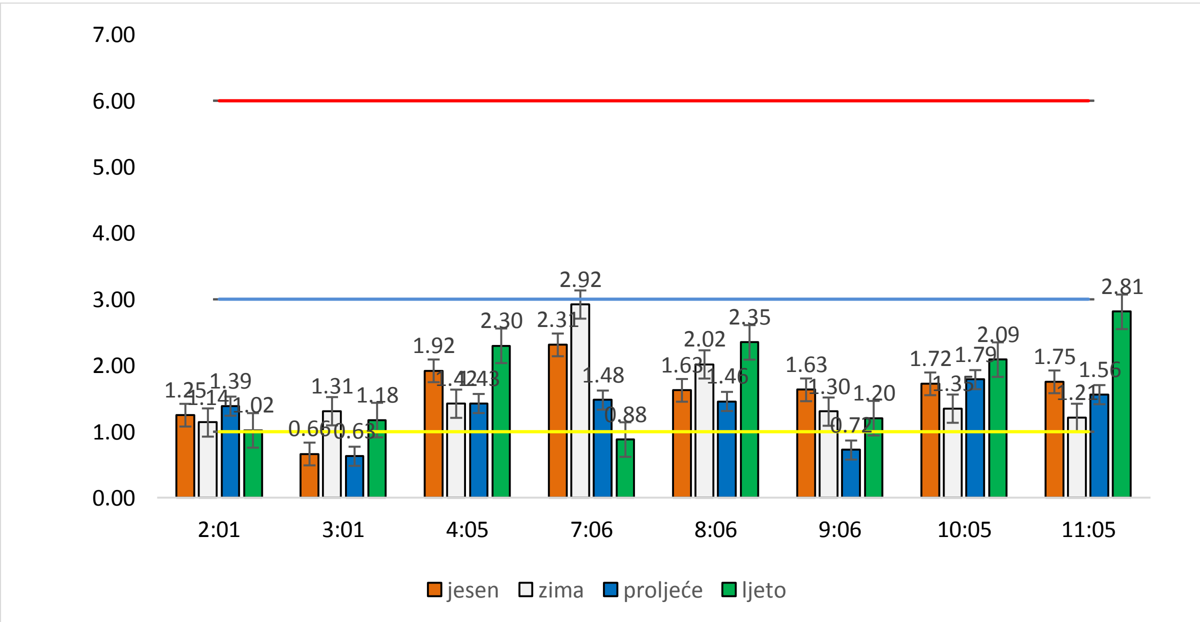

Figure 2. Graphical representation of the contamination factor for Zn in the sediment

According to the calculated CF values for cadmium (Figure 3), it is a moderate to high sediment contamination in some parts. It is clear that the most pronounced impact is on the Litva river watercourse with associated wastewater on the Oskova river watercourse (4.61), while the impact of RMU wastewater on the Gostelje (3.06) and Litva river watercourses cannot be ignored (3.39).) and Oskove (2.22). The ultimate impact of all these watercourses is moderate contamination of the Spreča river sediment (2.55) and the confluence with Lake Modrac (1.68).

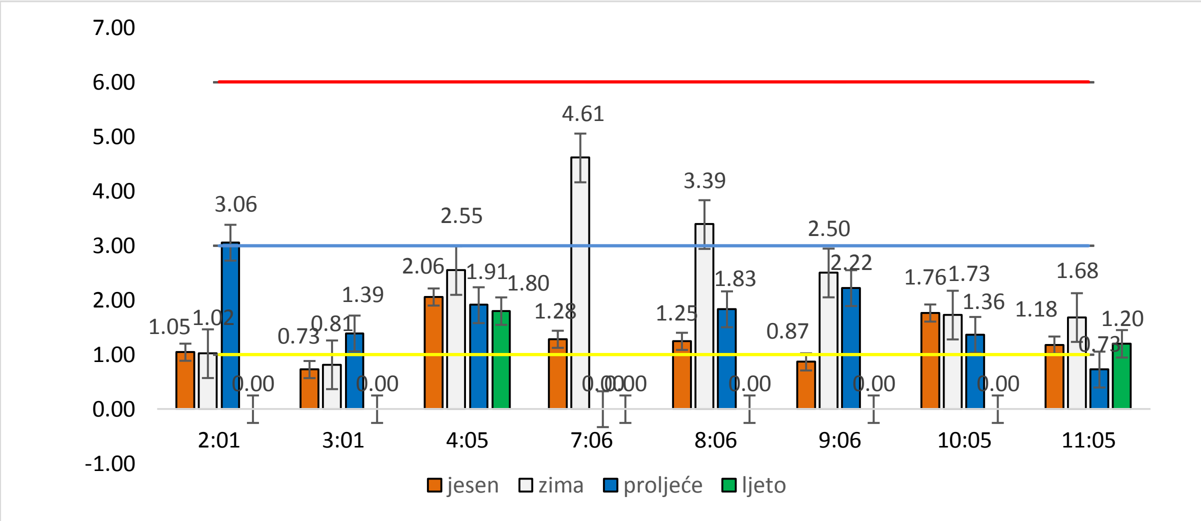

Figure 3. Graphic representation of Cd contamination factors in sediment

The characteristic presence of nickel in the watercourses into which the mine wastewater flows is confirmed by the obtained CF values in this paper (Figure 4). It can be clearly concluded that this is a moderate (0.97-2.93) and high contamination (4.33-5.04), with the most pronounced impact of wastewater from RMU Đurđevik on the watercourse of the river Gostelja (3.1) as the pouring of Gostelja in Oskova (4.33) and Oskove in Spreča (5.04).

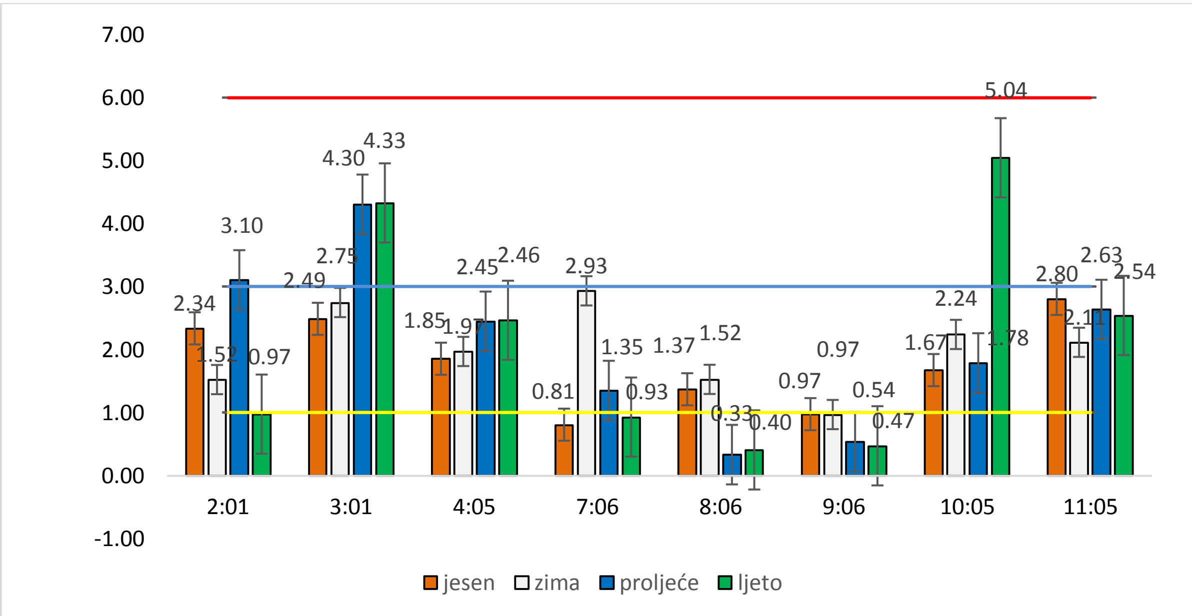

Figure 4. Graphical representation of contamination factors for Ni in sediment

Lead contamination of lead sediment is moderate to high, which is confirmed by the values of CF for lead shown in Figure 5. The most pronounced impact of wastewater from RMU Đurđevik on the watercourse of the river Gostelja (3.25), wastewater of various effluents (sewage, car wash, etc.) from Banovići to the watercourse of the river Litva (4.84) and wastewater from the RMU Banovići watercourses of the river Litva and Oskova (3.28).

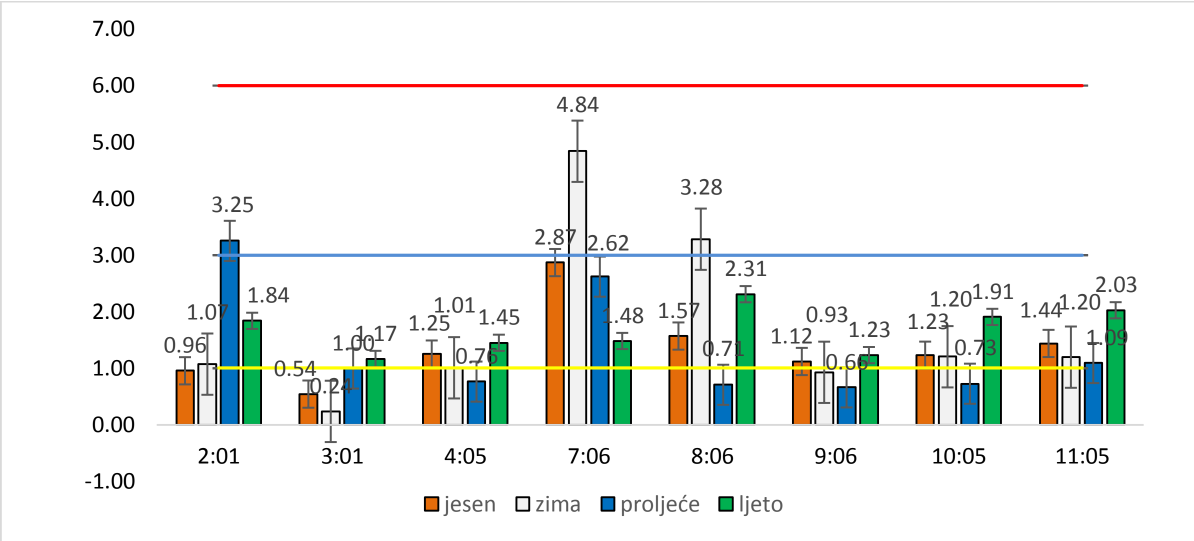

Figure 5. Graphical representation of contamination factors for Pb in sediment

Figure 6 graphically shows the values of manganese contamination factors where it can be seen that there is very little to moderate contamination of the sediment with manganese (0.07-3.07).

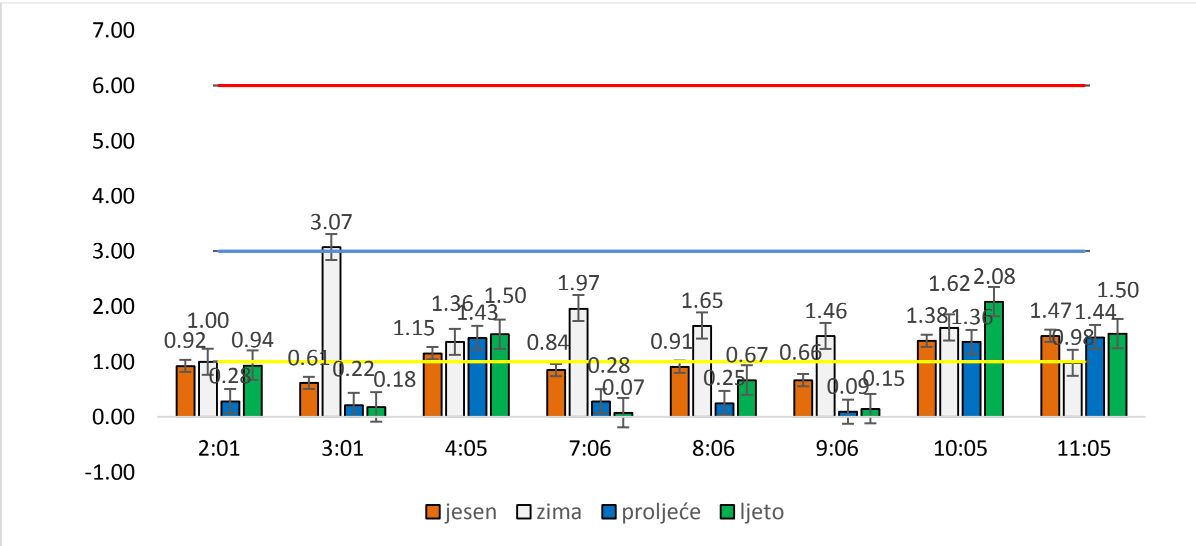

Figure 6. Graphical representation of contamination factors for Mn in sediment

Regarding the degree of iron sediment contamination, it is mostly very small (0.05) to moderate contamination (2.65) (Figure 7). The exceptions are the high degree of contamination due to the impact of Gostelja in Oskovo (6.39) and the very high degree of contamination due to the impact of wastewater from various effluents in Banovići on the Litva river watercourse (value KF = 29 in winter, not shown in the diagram).

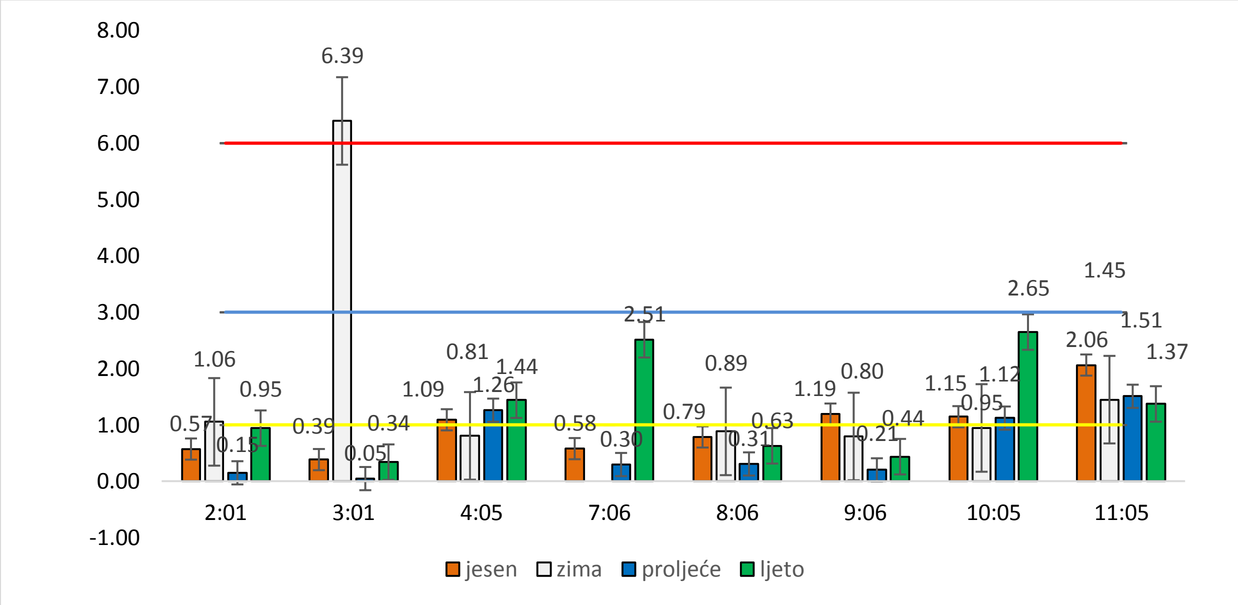

Figure 7. Graphical representation of contamination factors for Fe in sediment

IV. CONCLUSION

Assessing the impact of individual watercourses based on the contamination factor for sediment, we conclude that it is mostly a moderate to high impact, depending on which element it is. The most pronounced effect of Oskova on Spreč is on average CF of 2.55 for Cd; all the way to a high 5.04 for Ni. This is in line with expectations as wastewater from mines and separations is mostly discharged into selected tributaries.

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