PRELIMINARY ASSESSMENT OF ANTHROPOGENIC CONTRIBUTION AND INFLUENCING FACTORS ON MAJOR ELEMENTS AND TOTAL ORGANIC CARBON IN TAZLĂU RIVER SEDIMENTS, ROMANIA

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Abstract: The concentration of major elements (Si, Al, Ca, Mg, Na, K, Ti, Fe, Mn and P), as well as the total organic carbon (TOC) were studied in surface sediments from 29 sampling points in Tazlău River catchment.
The river sediments are characterized by lower concentrations of the studied major elements in almost all sampling points, with the exception of *s3* sample, where the concentrations slightly exceed the geochemical threshold. The mean values of major elements in Tazlău river sediments are in decreasing order of Si (75.74 wt%) > Al (4.44 wt%) > Ca (3.39 wt%) > Fe (2.47 wt%) > K (1.56 wt%) > Mg (0.65 wt%) > Ti (0.34 wt%) > Na (0.30 wt%) > P (0.09 wt%) > Mn (0.04 wt%). The pollution load index (PLI) values for Fe and Mn elements in Tazlău River sediment were found to be from 0.50 to 2.42 and are confirming that *s3* sampling point is moderately contaminated (PLI > 1).

Keywords: Major elements; sediments; Tazlău River; TOC, background; PLI

1. Introduction

Investigation of the chemical composition of river sediments is an important approach because the human activity can strongly influence the environmental quality of the fluvial systems (Dinelli et al., 2005). Strong urbanization and industrialization in recent years has resulted in increases heavy metals concentration discharged into the rivers.

Tazlău basin, with a total area of 1117 km^2 located in the central-eastern part of the Eastern Carpathians and Subcarpathians overlaps three distinct geological units: Tarcău nappe, Vrancea nappe (external flysch) and molasse sediments (pericarpathian nappe). Geological surface in the Eastern Carpathian region is primary composed by bituminous rocks (menilites, bituminous shale and brown marl) which have a high content of organic matter (Ţabără et al., 2015). Total organic carbon (TOC) has a major influence on chemical and biological process that take place in sediments (Agah et al., 2013).

The main objectives of this study are as follows: (1) to determine the major elements and total organic carbon in sediment samples collected from Tazlău River and, (2) to evaluate how different sampling locations are polluted with Mn and Fe.

2. Material and methods

2.1. Samples preparation

Twenty-nine stream sediment samples were collected from Tazlău River and some of its main tributaries at an equidistance of 3-4 kilometers (Fig. 1). Each sample was sieved and the fraction less than 0.63 mm diameter was used for analysis by X-ray fluorescence spectrometry (XRF).

The major elements measurements were carried out with an EDXRF Epsilon 5 Spectrometer at Geology department from "Alexandru Ioan Cuza" University, Iași.

To measure the total organic carbon (TOC%) the sediment samples were treated for 24 hours with 4N HCl, washed with distilled water, dried at 60° C and analyzed on Elementar EURO EA 3000 equipment.

2.2. Metal pollution assessment in Tazlău River sediments

Interpolation maps were made only for Fe and Mn elements by using the kriging method. The assessment of anthropogenic contribution of Fe and Mn in Tazlău River sediments was possible by determining the geochemical background and pollution load index (PLI). Geochemical background was calculated as Reimann et al. (2005) suggested:

$$Geochemical\ background = Median\ \pm 2MAD$$

In order to evaluate the degree of contamination with Fe and Mn, the pollution load index (PLI) was calculated in this study according to the formula used by Ali et al. (2016), Islam et al. (2015) and Maftei et al. (2014):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots CF_n)^{1/n}$$

where CF is the ratio obtained by dividing concentration of the studied metal in sediment to the background value: $CF_{metals} = C_{metal}/C_{background}$. Therefore, the values greater than 1 indicate pollution and the values smaller than 1 indicate that the sediments are unpolluted.

3. Results and discussion

3.1. Geochemical distribution of major elements and TOC in surface sediments

The major elements composition and total organic carbon values are listed in Table 1. The Pearson's correlation coefficients between major elements and TOC of 29 sediment samples were calculated and presented in Table 2.

Table 1. Major elements concentrations in Tazlău River sediments and geochemical background calculated for Fe and Mn.

	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	TOC
						wt%					
s1	0.60	0.57	7.75	75.22	0.05	1.88	1.78	0.43	0.06	3.57	0.66
s2	0.38	0.63	6.70	75.47	0.06	1.72	1.79	0.36	0.06	3.31	0.59
s3	1.64	2.69	7.91	66.04	0.09	2.25	5.91	0.54	0.10	5.14	1.32
s4	0.46	0.96	6.10	75.65	0.09	1.86	2.84	0.43	0.05	3.36	0.68
s5	0.19	0.47	5.70	75.63	0.06	1.60	2.05	0.33	0.05	2.82	0.51
s6	0.18	0.65	4.67	74.96	0.09	1.56	2.20	0.38	0.04	2.45	0.49
s7	1.41	0.84	2.50	74.87	0.11	1.40	7.32	0.27	0.07	2.59	0.53
s8	0.03	0.65	5.04	74.36	0.08	1.72	2.96	0.38	0.05	2.98	0.57
s9	0.19	0.61	4.85	74.51	0.10	1.66	3.06	0.39	0.05	2.88	1.25
s11a	0.80	0.99	6.63	69.81	0.10	1.97	4.09	0.53	0.06	3.29	0.80
s11b	0.11	0.43	3.86	78.79	0.11	1.51	2.07	0.26	0.03	2.19	0.44
s12	0.13	0.64	4.91	76.51	0.11	1.68	3.02	0.39	0.04	2.61	1.04
s13	0.02	0.23	3.63	79.18	0.07	1.42	2.59	0.25	0.02	1.90	0.40
s14a	0.03	1.34	7.14	69.34	0.07	2.04	5.03	0.59	0.06	3.40	0.61
s14b	0.03	0.23	2.85	81.20	0.09	1.29	2.23	0.25	0.02	1.71	0.35
s15a	0.02	0.37	3.01	78.07	0.07	1.34	2.26	0.23	0.02	1.62	0.48
s15b	0.02	0.42	4.68	74.13	0.10	1.61	3.43	0.36	0.05	2.38	0.67
s16a	0.04	0.44	3.61	74.17	0.08	1.45	3.19	0.34	0.03	1.92	0.55
s16b	0.02	0.33	2.89	80.14	0.11	1.28	2.73	0.19	0.02	1.62	0.76
s18	0.04	0.66	2.82	81.42	0.08	1.31	2.56	0.27	0.02	1.54	0.41
s19	1.35	0.79	3.32	73.77	0.08	1.40	3.56	0.30	0.02	1.78	0.47
s21a	0.35	0.69	4.05	79.32	0.06	1.56	3.13	0.30	0.03	1.97	0.57
s21b	0.09	0.19	2.76	77.30	0.09	1.32	3.47	0.21	0.03	1.61	0.34
s22	0.03	1.02	4.61	74.89	0.05	1.60	4.11	0.29	0.04	2.24	0.73
s23	0.06	0.39	2.27	81.07	0.08	1.13	2.58	0.18	0.02	1.26	0.38
s24	0.05	0.42	3.46	75.05	0.14	1.45	4.84	0.38	0.04	2.14	0.36
s25	0.06	0.48	4.03	73.97	0.10	1.52	5.09	0.34	0.05	2.36	0.60
s26	0.04	0.45	4.22	71.86	0.10	1.54	5.18	0.36	0.05	2.85	0.42
s28	0.29	0.23	2.93	79.76	0.08	1.26	3.35	0.23	0.03	2.16	0.79

	Geochemical background	Geochemical threshold	Mean content
Fe	1.34 – 3.39	3.39	0.04
Mn	0.02 – 0.07	0.07	2.29

The major elements abundance is described by Si dominance, values ranging from 66.04 wt% to 81.42 wt% (Table 1). Silica does not show any specific relationships with phosphor and the negative correlation with all elements suggest a dilution effect due the higher quartz content in sediments (Maharana et al., 2018). The mean values of major elements in Tazlău river sediments are in decreasing order of Si (75.74 wt%) > Al (4.44 wt%) > Ca (3.39 wt%) > Fe (2.47 wt%) > K (1.56 wt%) > Mg (0.65 wt%) > Ti (0.34 wt%) > Na (0.30 wt%) > P (0.09 wt%) > Mn (0.04 wt%). The variable contents of Al, Fe, Ca and K may suggest the feldspars control in sediments. The distribution of Fe, Ti, K and Mn is similar with Al concentrations, showing a strong positive correlation with Pearson coefficients between 0.76 and 0.95 at $p < 0.05$ and $n = 29$ (Table 2).

TOC content in Tazlău River surface sediments ranges between 0.34 wt% and 1.32 wt% with a mean of 0.61 wt%. The maximum value of TOC was recorded in *s3* sample point located near of natural gases exploitation area. Biological input characterized by nutrient availability can significantly contribute in carbon absorption and water chemistry. The highest concentration of TOC recorded in *s3* sampling site

could be due to the organic matter decomposition through the biological process that occurs in sediments (Kamaruzzam et al., 2009).

According to Environmental Protection Agency of United State (Agah et al., 2013, USEPA, 2002), TOC in sediments river is evaluated based to the following categories: ≤ 1% - low impact, between 1% to 3% - intermediate impact and > 3% high impact. Therefore, in Tazlău River sediments, the carbon level was found to be in the range of low to medium impact. The geochemical correlation between the total organic carbon and Fe and Mn (pairs TOC-Fe and TOC-Mn), can suggest the same local source for the higher concentrations, especially in *s3* sampling point.

A highest relationship described by r can being significant at $p < 0.05$ and has been obtained between the pairs $K_2O – TiO_2$, $Fe_2O_3 – Al_2O_3$, $K_2O – Al_2O_3$, $MnO – Fe_2O_3$ and $K_2O – Fe_2O_3$ (Table 2).

Table 2. Pearson correlation matrix between major elements and TOC in Tazlău river sediments (n = 29).

	Si	Ti	Al	Fe	Mg	Mn	Ca	Na	K	P	TOC
Si	1										
Ti	**-0.84**	1									
Al	**-0.70**	**0.86**	1								
Fe	**-0.79**	**0.83**	**0.90**	1							
Mg	**-0.72**	**0.68**	**0.63**	**0.77**	1						
Mn	**-0.80**	**0.77**	**0.76**	**0.93**	**0.74**	1					
Ca	**-0.59**	0.32	0.02	0.32	**0.49**	**0.55**	1				
Na	**-0.48**	0.31	0.30	**0.51**	**0.65**	**0.56**	**0.47**	1			
K	**-0.81**	**0.93**	**0.95**	**0.93**	**0.77**	**0.83**	0.24	0.39	1		
P	-0.12	0.03	-0.30	-0.07	-0.07	0.10	**0.44**	0.04	-0.12	1	
TOC	**-0.47**	**0.49**	**0.52**	**0.63**	**0.60**	**0.60**	0.21	0.36	**0.59**	0.07	1

Values in bold are different from 0 with a significance level alpha <0.05

3.2. Estimating the level of pollution of Fe and Mn in Tazlău River sediments

Fe and Mn are considered the most important environmental contaminants due to their toxicity and risk that they pose. In this study Fe is one of the most abundant elements and its concentration ranges between 1.26 wt% and 5.14 wt% with the highest contents recorded in *s3* sampling point (Fig. 2). The concentration of Mn in Tazlău River sediments is characterized by a uniformity of data with a low dispersion degree. The Mn concentration is slightly exceeding the geochemical threshold in *s3* sampling point and the chemical composition ranges between 0.02 wt% and 0.10 wt% (Fig. 2).

The *s3* sampling point is located near natural gas drillings and the studies describe the association between oil and natural gases extraction processing with environmental pollution by heavy metals (Adesodun and Mbagwu, 2008, Essiett et al., 2010, Muniz, 2004, Yang et al., 2015).

The calculated pollution load index (PLI) values of Fe and Mn elements in sediments are summarized in Fig. 3. The values range from 0.50 to 2.42 and are confirming that *s3* sampling point was moderately contaminated (PLI > 1).

The higher PLI values recorded in *s3* sampling point indicate that Mn is the major contributor to the sediment pollution (percentage contributions for each element: 53.87 % - Mn and 46.13% - Fe). Therefore, the higher PLI observed in *s3* sample might be due to the anthropogenic effects already explained.

For the other sampling points that exceed the value of 1, the PLI indicates a certain uniformity based on the following percentages: *s3* (11.07%) > *s1* (7.22%) > *s11a* (7.00%) > *s14a* (6.80%) > *s2* (6.62%) > *s7* (6.51%) > *s4* (6.46%) > *s9* (6.01%) > *s8* (5.99%) > *s26* (5.76%) > *s5* (5.60%) > *s25* (5.47%) > *s12* (5.14%) > *s15b* (5.05%) > *s24* (4.71%) > *s6* (4.60%).

As a general overview the sources could be controlled by human as well as environmental factors such as geogenic input, oil and gas drilling, pesticides and fertilizers used in agricultural soils, or natural disasters. For example, the *s1* and *s2* sampling points are located in a natural background area without any anthropogenic source. Nevertheless, the high values identified in this region might be of natural source, controlled by the lithogenic substrate of the sediments (external flysch). For the rest of sampling points the PLI values that slightly exceeded the threshold could accumulate from a variety of sources such as industrial and

agricultural activities, traffic, atmospheric deposition or rainfalls, since the downstream area of the basin is a very populated one and several local agricultural activities are present.

However, because the PLI values are slightly exceeding the value of 1 the human impact seems under control and safe. Of course, further investigations are required in order to control the health of the ecosystem and the contaminants caused by anthropogenic activities.

4. Conclusions

The chemical analysis of sediments in Tazlău River and its catchment indicate a high content of SiO_2 and anthropogenic pollution in *s3* sampling point with some heavy metals (Fe and Mn) and organic carbon. The TOC content in Tazlău River surface sediments range between 0.34 wt% and 1.32 wt% with a mean of 0.61 wt% and the maximum value was recorded in *s3* sample point located near natural gases exploitation area. The calculated pollution load index (PLI) values for Fe and Mn elements in sediments were found to be in the interval of 0.50 - 2.42 and are confirming that *s3* sampling point is moderately contaminated (PLI > 1).

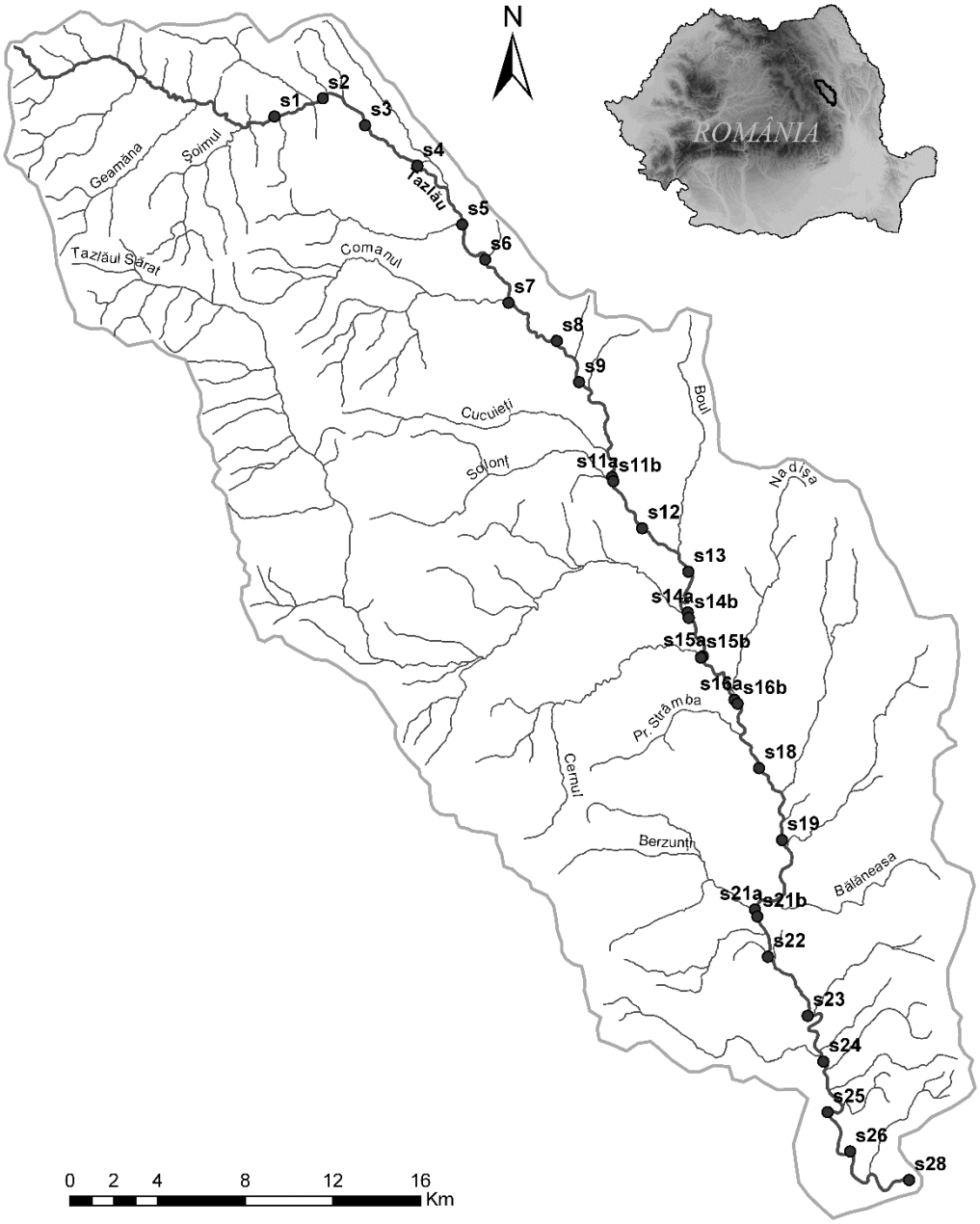

Fig. 1. Map of the study area with sampling sites.

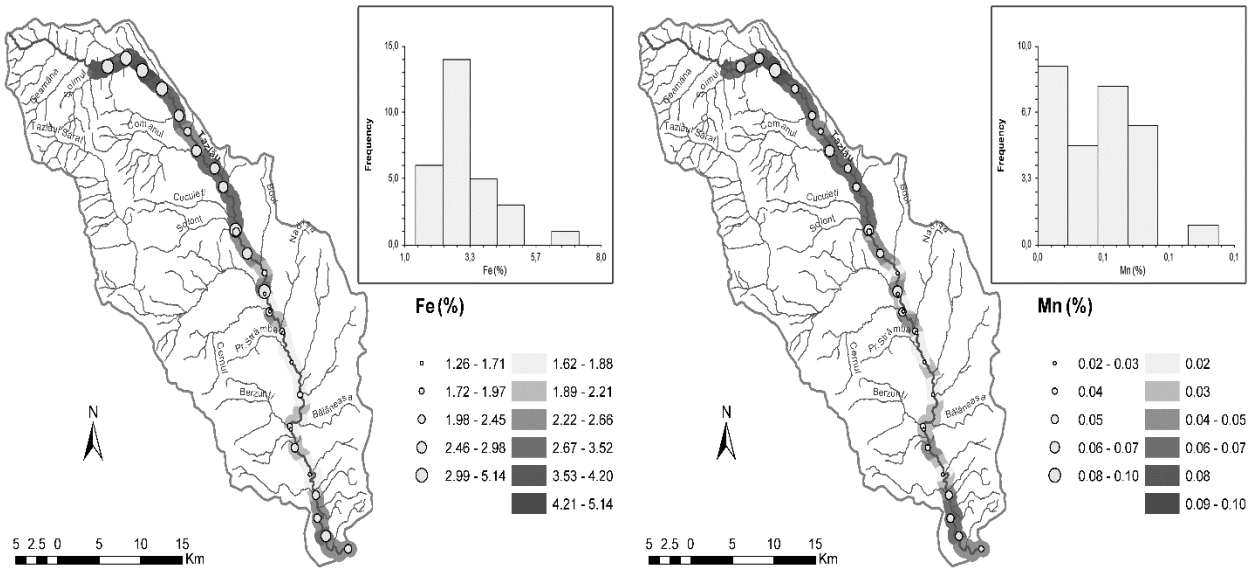

Fig. 2. Distribution map of Fe and Mn (%) in Tazlău River sediments.

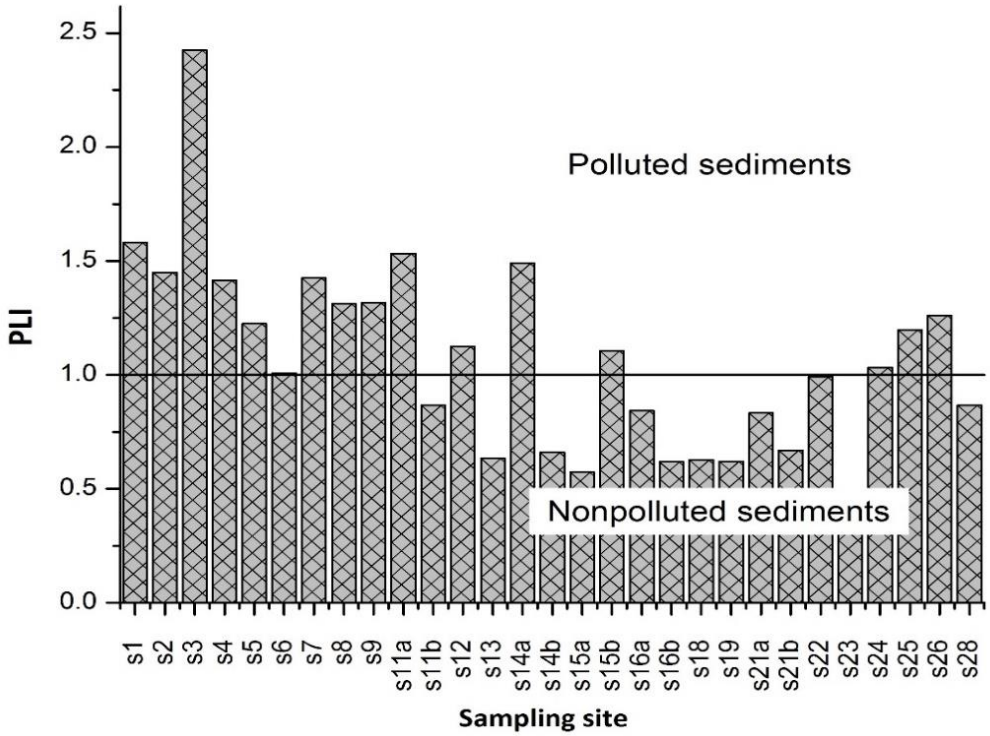

Fig. 3. Pollution load index value of Fe and Mn (%) metals in Tazlău River sediments.

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