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Water and Sediment Quality Status of the Toplluha River in Kosovo

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ABSTRACT

The surface water quality and level of metal contents in the contamination of the Toplluha river sediment were determined by means of statistical techniques and pollution indicators. The samples of water and sediments were taken in five different locations along the Toplluha river in the spring period 2013 and 2019 using standard methods for analysis. International standards (WHO 2004) were used to assess the quality of water. The samples of water in some of the locations were above these criteria levels. The heavy metal contents in the sediment were in the following order: Cu > Zn > Cr > Ni > Pb > Cd. For the evaluation of the heavy metal content, some factors were applied: enrichment factor (EF), pollution load index (PLI) and index of geoccumulation (Igeo). Cu and Pb have a significance enrichment according to the calculated EF values. The Igeo index values for Cu and Zn were at a higher level. The PLI index values were at a progressive high level from stations S3 to S5. Therefore, the preliminary treatment of the discharging waters is indispensable.

Keywords: water, sediment, quality, River, Toplluha, Kosovo

INTRODUCTION

Surface water, especially the quality of the waters and sediments of rivers is an important issue for evaluating the influence in humans. Anthropogenic chemicals can pollute special sources and degrade the ecosystem which influences the public health [Tepe & Çebi, 2017; Ustaoğlu, et al. 2017]. Many studies have been carried out on the surface waters in rivers with the purpose to control, prevent and monitor the water quality [Boyd, 2003; Tepe, et al., 2005, Wang, et al., 2013]. Monitored alteration can be carried out by physico-chemical parameters [Varol, et al. 2012], a few studies intended to attribute more causes to these variations [Morán-Tejeda, et al. 2011]. The differences in the water quality parameters are important in recognizing the important contributors [Tepe, 2009; Wu, et al., 2018]. The assessment of the analyzed physico-chemical parameters can be performed by comparison with national or international limit values. Using alternative techniques, such as multivariate statistical methods, enables assessing the water quality and environmental status of the study area [Ustaoğlu, et al., 2019]. Contaminated sediment matrix compared to the water column, creates a hazard in the ecosystem for a long time [Kara, et al. 2017]. Sediments play a role as a sink for heavy metals and other contaminants [Singh, et al. 2005]. Compared to the water column, the sediment layer is stationary and in the stable condition that prevents rapid re-suspension in the water and dissolution of biochemical pollutants [Yu, et al. 2016]. The Toplluha river is located in the southeastern part of the White Drin basin. In the southern part, the river is bordered by the catchment of the Lepenc and Prizren rivers, in the eastern is bordered by the river bifurcation, in the northeastern part of Carraleva river catchment, located in the northern part of the Mirusha river catchment, and in the western part of the Drin river [Shehu, et al., 2014]. The total length of the river is about 37 km and merges with Drini i Bardhë. Along this length, the river receives pollution from different sources. The agricultural run-off from the catchment area drains into the river directly or from its tributaries. Moreover, it receives wastewater and industrial water from the city of Suhareka and many villages. The purpose of this study was to analyze and interpret the data set obtained in 2013 and 2019.

MATERIAL AND METHODS

The study of this area was carried out in the spring of 2013 and 2019 at the same stations by taking the water samples and sediments from five different stations along the Toplluha river (Fig. 1). In the same sampling sites, the samples of water and sediment were taken in the spring season of the 2019 year. The sampling bottles were washed with acid a day before sampling. The sampling bottles were washed by using 1–3% HCl solution, rinsed with re-distilled water and finally were dried [Boyd and Tucker, 1992]. At the depth of 50 cm from surface water, the samples were taken and transported by the fridge to the laboratory for analysis. The sediment samples were taken at a depth of approximately 15 cm by mass of 200 g, using a portable sampler (Windaus-Labortechnik. GmbH&Co.KG.d-38678 Clausthal-Zellerfeld). The sediment was taken from the catcher, then the mass was divided into four pieces, a small amount of mass was taken from each piese and then mixed. The sediment samples transferred in a fridge to the central laboratory of the Chemistry Department, Faculty of Mathematical and Natural Sciences – University of Prishtina – Kosovo. The sediment samples were dried for 30 days at room temperature than in oven at 45 °C for 48 h to gain constant weight. The dried samples were then ground using a mortar and sieved through 0.045 mm, DIN 4188 sieve. The first station was located in a place called Buqallë (the “KT Solid”), at an altitude of 449.8 m, with coordinates: 42.370697, 20.876796. The second station was in the neighborhood of Bajraktari at the altitude of 392 m and the following coordinates: 42.357559, 20.835257. The third station of Toplluha Stream was in the middle of Suhareka town, at the latitude of 372 m, with the coordinates: 42.355916, 20.820561. The fourth station was beyond 0,216 km, at an altitude of 271 m and coordinates: 42.354766, 20.811004. The fifth station was at a long distance past 17.8 km with coordinates: 42.288032, 20.674592 in the bridge of Pirane village, before the Toplluha river joins with Drini i Bardhë. The Toplluha river receives domestic and industrial waste from The Suhareka and their vicinities. The wastewater from these activities is not treated and discharged directly into the river.

Physicochemical analysis

According to the standard methods [APHA/AWWA/WEF, 2012], the water samples were collected, and transported to laboratories. The water samples were collected in polyethylene bottles of three-liters for quantifying chemical properties. The water sample bottles were coded by date and sampling sites.

Before filling, the sampling bottles were rinsed several times with the water from the sampling point and transported to the laboratory in the fridge. In order to analyze BOD_5, the glass bottles were used washed with 1–2%

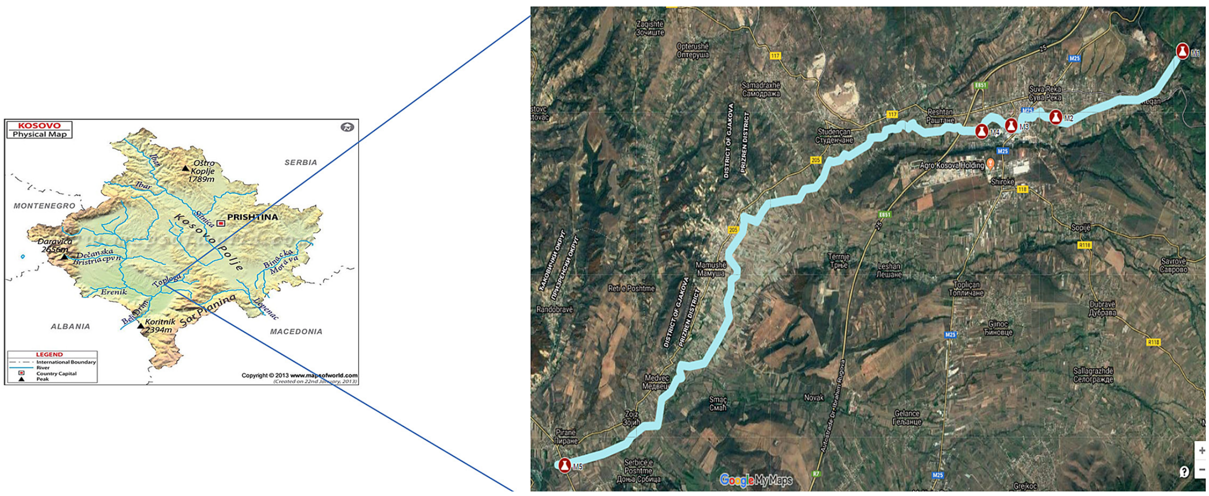


Fig. 1. Map of the study area of Toplluha river of Suhareka district urban area, Kosovo

HCl solution, rinsed with re-distilled water and then dried. The chemicals used were of analytic grade, p.a. The following parameters of water quality: temperature (T), pH, dissolved oxygen (DO), saturation dissolved oxygen (DOS), electrical conductivity (EC), total dissolved solids (TDS) were measured with: WTW 340i instrument, aqualytic pc Compact Instruments, pH-meter CONSORT C830 instrument. COD, TOC, BOD_5, PO_4^{3-}, P_{tot}, NH_4^+, NO_2^-, Cl^-, SO_4^{2-}, NO_3^-, N_{anorg}, N_{org}, N_{total}, surfactants (detergents) were measured with S.F.M. SECOMAMA UV Instruments, photometry WTW S-12.

Sediment heavy metal analysis

The concentration of sediment heavy metals was determined according to the EPA Method 3050B (SW-846): Acid Digestion of Sediments, Sludge's, and Soils. In the research, 1 g of the oven-dried and sieved sediment samples were digested with 5 ml HNO_3+10 ml HF +10 ml $HClO_4$ under warm conditions until completely dissolved. The samples were filtered through a 0.45 µm filter prior to the analysis. The calibration standards were prepared from a multi-element standard (Fluka analytical, Germany). The samples were analyzed three times for heavy metal concentrations as mg kg^{-1} dry weight using an AAS instrument (Analytik Jena ContrAA 300, Germany).

Assessment of sediment contamination

The pollution load index (PLI), contamination factor (CF), enrichment factor (EF) and geoaccumulation index (I_{geo}) were used to determine the metal contamination in the sediments of the Toplluha river. According to [Suresh, et al., 2011], it can be calculated as an integral approach of the pollution load index of heavy metals and assess the sediment quality. The PLI is defined as the nth root of the multiplications of the contamination factor of metals (CF).

$$PLI = (CF1 \times CF2 \times CF3 \times ... \times CFn)^{1/n}$$

For assessing the quality of sediment, the PLI index provides a simple comparative means. The value of zero indicates unpolluted, a value of one indicates baseline levels of pollutants and above one indicates progressive deterioration of the sediment [Tomlison, et al., 1980]. Where CF_{metals} is the ratio between the content of each metal to the background values (background value from Dutch list) in sediment and content of each metal from the samples of the study area in sediment, $CF_{metals} = C_{metal} / C_{background}$

The contamination factor values are interpreted as follows: CF < 1 indicates no or low pollution; 1 ≤ CF < 3 is moderate pollution; 3 ≤ CF < 6 is considerable pollution; and CF ≥ 6 is very high pollution [Hakanson, 1980; Kadhum, et al., 2016]. In order to assess the degree of pollution from heavy metals, the index of the geo-accumulation (I_{geo}) can be determined. According to [Muller, G, 1969], I_{geo} is interpreted and calculated as follows:

$I_{geo} = \log2 [Cn / 1.5Bn]$, where Cn is the measured concentration in the sediment for the analyzed metal n, Bn is the background value for the metal n and factor 1.5 is used due to of possible variations of the background data of lithological variations. [Rudnick and Gao, 2003].

The value of the geoacumulation index was interpreted as $I_{geo} \leq$ 0-practically unpolluted; $0 \leq I_{geo} \leq$1-unpolluted to moderately polluted; $1 \leq I_{geo} \leq$ 2-moderately polluted; $2 \leq I_{geo} \leq$ 3-moderately to heavily polluted; $3 \leq I_{geo} \leq$ 4-heavily polluted; $4 \leq I_{geo} \leq$5-heavily to extremely polluted and $5 \leq I_{geo}$-extremely polluted.

The values of enrichment factor (EF) of heavy metals have commonly been used to assess the anthropogenic pollution. Fe was chosen as the normalizing element to identify the anomalous metal contributions [Yang, et al., 2003]. The EFs were calculated using the following equation: $EF = (C / Fe)_{sample} / (C/Fe)_{background}$, where $(C/Fe)_{sample}$ and $(C/ Fe)_{background}$ represent the heavy metal to Fe ratios in our study and in the background sample, reference ERR respectively. Generally, the enrichment factor (EF), can be interpreted as: <2: minimal; 2–5: moderate; 5–20: significant; 20–40: very high; >40 extremely high [Zhang and Liu, 2002; Andrews and Sutherland, 2004].

Statistical analysis

The data were statistically analyzed using the Minitab 16 package. The results of heavy metals in water and sediment were calculated by using the means and standard deviations. Microsoft Excel 2010 software was used for other calculations.

RESULTS AND DISCUSSION

The annual mean of the measured water parameters with their minimum, maximum and standard deviation values in the period 2013 and 2019 were shown in (Table 1). Additionally, the differences among parameters were indicated with superscripts. The annual mean of water quality parameters: temperature, pH, DOS%, DO mgL^{-1}, and TUR in two periods were not significantly different between the stations in the Toplluha river ($p>0.05$). On the other hand, EC, WSS, TSS, COD, BOD_5, TOC, NH_4^+, NO_3^-, NO_2^-, N_{anorg}, N_{org}, N_{tot}, PO_4^{3-}, P_{tot}, Cl^-, and SO_4^{2-} were significantly different between the sampling sites ($p<0.05$, Table. 1). While assessing the relationships among water quality parameters the Pearson Correlation Index was used (Table 2). Through the size of coefficient, the relation is defined as follows; 0.9–1; highest, 0.7–0.89; higher, 0.5–0.69; medium, 0.26–0.49; low, 0.0–0.25; very low. In the case of a decrease in a parameter by an increase in other parameters, usually displayed negative values constitute an inverse relation. For example, a high negative correlation between dissolved oxygen saturation and all other parameters except Turbidity and water-soluble solids was observed. The same correlation occurred between dissolved oxygen and other parameters. On the other hand, minimum and maximum positive correlations were shown at EC: 0.134–0.957, WSS: 0.333–0.835, TSS: 0.535–0.816, COD: 0.570–0.931, BOD_5: 0.713–0.927, TOC: 0.611–0.935, DET: 0.621–0.823, NH_4^+: 0.528–0.923, NO_3^-: 0.610–0.857, NO_2^-: 0.678–0.895 to other parameters. A similar correlation was observed for nitrogen forms, phosphorus forms, chlorides, and sulphates.

Figure 2 shows the dendrogram of Euclidian distance and means similarities of 22 physico-chemical parameters between the sampling sites in the Toplluha river. According to the obtained results, the similarities between sampling sites appear to be gathered in two clusters.

The obtained results show a significant similarity between the sampling sites, even though

Table 1. Physico-chemical parameters of the Toplluha river stations (Min-Max-Mean, StDev)

Parameters	S1		S2		S3		S4		S5		Mean	STDev	Min	Mead	Max
	2013	2019	2013	2019	2013	2019	2013	2019	2013	2019					
T (◦C)	16	12.5	16.4	11.8	17.6	13.1	18.3	13.8	19.3	12.9	15.17	2.68	11.8	14.9	19.3
pH (0–14)	8.39	7.98	7.89	6.99	7.51	9.12	7.4	8.8	8.12	7.55	8.03	0.73	6.9	7.95	9.10
DOS (%)	110	95	98	85	86.7	72.3	62.2	54.9	95.6	71.8	82.8	17.64	54.00	85.50	110.0
DO (mg L$^{-1)}$	10.1	9.48	9.7	8.3	8.01	6.12	5.6	3.9	9.2	4.8	7.15	2.23	3.90	815	1010
EC (μS/cm)	482	597	506	789	602	869	601	1150	586	978	716	2216	4820	6015	1150
WSS (mgL^{-1})	253	398	253	412	303	592	299	471	298	313	359.2	1086	253.0	308.0	592.0
TUR (NTU)	19.5	16.8	18.2	14.5	13.6	20.5	13.2	18.4	12.2	14.8	16.47	288	12.2	17.3	20.5
TSS (mgL^{-1})	0	1.99	5.6	7.2	17.4	28.5	17	22.1	22.2	17.8	13.98	963	0.00	17.20	28.50
COD (mgL^{-1})	1.2	0.8	5.9	4.7	6.5	8.1	8.8	11.4	3.5	4.2	5.51	334	0.80	5.30	11.40
BOD_5 (mgL^{-1})	0.2	0.6	0.5	1.12	2.4	8.99	3.9	8.12	1.9	6.4	3.44	3.27	0.20	2.15	8.99
TOC (mgL^{-1})	0.4	0.9	1.7	2.8	1.9	5.2	3.2	8.9	1.5	6.3	3.28	271	0.40	2.35	8.90
DET (mgL^{-1})	0	0	0.2	0.1	2	5.4	3.8	6.4	1	7.5	3.64	2909	0.00	1.50	7.50
NH_4^+ (mgL^{-1})	<0.01	0.005	<0.01	0.3	3.87	5.62	2.58	4.32	1.2	3.16	2.106	203	0.001	1.89	5.62
NO_3^- (mgL^{-1})	10.9	21.5	66	60.2	35.1	78.2	62	98.5	25.1	52.1	50.96	2755	10.90	56.15	98.50
NO_2^- (mgL^{-1})	0.042	0.29	0.495	2.11	1.36	2.98	2.2	4.16	0.45	1.29	1.53	132	0.042	1.32	4.16
N_{anorg} (mgL^{-1})	0.45	0.35	1.65	2.15	4.216	3.15	4.08	5.16	1.64	2.31	2.51	116	0.35	2.23	5.16
N_{org} (mgL^{-1})	0.09	0	0.331	0.541	0.843	1.26	0.81	1.11	0.32	0.51	0.581	0419	0.00	0.52	1.26
N_{tot} (mgL^{-1})	0.541	0.32	1.98	2.45	5.05	6.18	4.89	6.15	1.97	3.15	3.26	217	0.32	2.8	6.18
PO_4^{3-} (mgL^{-1})	0.088	0	0.219	0.911	0.911	1.47	0.63	0.999	0.13	0.887	0.62	049	0.00	0.75	1.47
P_{tot} (mgL^{-1})	0.042	0.011	0.091	0.17	0.381	1.98	0.24	0.87	0.09	0.45	0.433	0602	0.011	0.205	1.98
Cl^- (mgL^{-1})	13.4	12.2	13.4	22.4	20.5	102.5	20.5	147.2	15.2	68.7	43.6	471	12.2	20.5	147.2
SO_4^{2-} (mgL^{-1})	28.9	35.5	49.9	112.2	78.4	154.5	64.6	187.9	30.3	134.2	87.6	566	28.9	71.5	187.9

Explanation: T – temperature, pH – log hydrogenium ion, DOS – dissolved oxygen saturation, EC – electrical conductivity, WSS – water soluble solids, TUR – turbidity, TSS – totalsuspended solids, COD – chemical oxygen demand, BOD_5 – biological oxygen demand, TOC – total organc carbon, DET – detergents(surfactants), NH_4^+ – ammonium ion, NO_3^- – nitrate ion, NO_2^- – nitrite ion, Na_{norg} – anorganic nitrogen, N_{org} – organic nitrogen, N_{tot} – total nitrogen, PO_4^{3-} – phosphate ion, P_{tot} – phosphorus total, Cl^- – chloride ion, SO_4^{2-} – suphate ion.

Table 2. Pearson correlation between Physico-chemical parameters of the Toplluha river

Para-meters	T (°C)	pH (0–14)	DOS (%)	DO (mgL^{-1})	EC (µS/cm)	WSS (mgL^{-1})	TUR (NTU)	TSS (mgL^{-1})	COD (mgL^{-1})	BOD_5 (mgL^{-1})	TOC (mgL^{-1})	DET (mgL^{-1})	NH_4^+ (mgL^{-1})	NO_3^- (mgL^{-1})	NO_2^- (mgL^{-1})	Na_{norg} (mgL^{-1})	N_{org} (mgL^{-1})	N_{tot} (mgL^{-1})	PO_4^{3-} (mgL^{-1})	P_{tot} (mgL^{-1})	Cl^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})
T (°C)	1.000																					
pH (0–14)	-0.204	1.000																				
DOS (%)	0.195	-0.028	1.000																			
DO (mgL^{-1})	0.248	-0.056	0.964	1.000																		
EC (µS/cm)	-0.572	0.192	-0.786	-0.850	1.000																	
WSS (mgL^{-1})	-0.613	0.547	-0.509	-0.464	0.645	1.000																
TUR (NTU)	-0.551	0.592	0.001	-0.136	0.314	0.395	1.000															
TSS (mgL^{-1})	0.150	0.188	-0.690	-0.686	0.568	0.508	-0.092	1.000														
COD (mgL^{-1})	0.076	0.037	-0.834	-0.751	0.571	0.423	0.031	0.677	1.000													
BOD_5 (mgL^{-1})	-0.301	0.386	-0.829	-0.886	0.833	0.701	0.379	0.816	0.695	1.000												
TOC (mgL^{-1})	-0.395	0.195	-0.871	-0.928	0.957	0.559	0.328	0.641	0.729	0.893	1.000											
DET (mgL^{-1})	-0.230	0.166	-0.841	-0.943	0.817	0.425	0.288	0.727	0.621	0.927	0.898	1.000										
NH_4^+ (mgL^{-1})	-0.066	0.271	-0.751	-0.783	0.647	0.597	0.184	0.872	0.726	0.903	0.723	0.823	1.000									
NO_3^- (mgL^{-1})	-0.304	0.079	-0.794	-0.732	0.717	0.572	0.279	0.535	0.883	0.713	0.814	0.621	0.582	1.000								
NO_2^- (mgL^{-1})	-0.311	0.159	-0.883	-0.827	0.807	0.715	0.164	0.647	0.880	0.805	0.850	0.680	0.744	0.875	1.000							
Na_{norg} (mgL^{-1})	0.133	-0.089	-0.840	-0.777	0.569	0.333	-0.158	0.700	0.931	0.658	0.692	0.642	0.787	0.716	0.834	1.000						
N_{org} (mgL^{-1})	-0.072	0.122	-0.800	-0.757	0.631	0.641	0.115	0.814	0.897	0.826	0.721	0.693	0.910	0.784	0.894	0.885	1.000					
N_{tot} (mgL^{-1})	0.021	0.087	-0.834	-0.792	0.608	0.543	0.043	0.822	0.918	0.814	0.723	0.725	0.923	0.756	0.867	0.937	0.985	1.000				
PO_4^{3-} (mgL^{-1})	-0.372	-0.017	-0.715	-0.724	0.708	0.690	0.206	0.696	0.689	0.796	0.708	0.694	0.847	0.703	0.814	0.715	0.904	0.857	1.000			
P_{tot} (mgL^{-1})	-0.325	0.505	-0.538	-0.561	0.582	0.835	0.508	0.722	0.570	0.855	0.611	0.636	0.838	0.610	0.687	0.476	0.814	0.743	0.814	1.000		
Cl^- (mgL^{-1})	-0.416	0.481	-0.744	-0.804	0.906	0.709	0.508	0.638	0.686	0.909	0.935	0.810	0.757	0.761	0.841	0.615	0.736	0.711	0.690	0.757	1.000	
SO_4^{2-} (mgL^{-1})	-0.550	0.158	-0.797	-0.839	0.947	0.715	0.383	0.609	0.704	0.867	0.935	0.799	0.753	0.825	0.892	0.676	0.798	0.758	0.870	0.731	0.913	1.000

Explanation: see Table 1.

they are divided into two groups. The total heavy metal concentrations for each sampling site found in water in this study and comparison to the WHO water standard (2004) are shown in Table 3. The mean heavy metal concentrations were observed in water in a decreasing order of Pb > Zn > Cd > Fe > Cr > Ni > Mn >Cu. The mean concentrations of Pb, Zn, Cd, Fe, Cr, Ni, Mn and Cu were 0.185, 0.171, 0.0259, 0.623, 0.0595, 0.243, 0.283 and 0.246 mg L^{-1}. The result showed that Pb, Zn, and Cd were found higher, Fe, Ni, and Cr increased slightly, while Mn and Cu were under the limit. The flow of the rivers, waste disposal, location of the industries, and

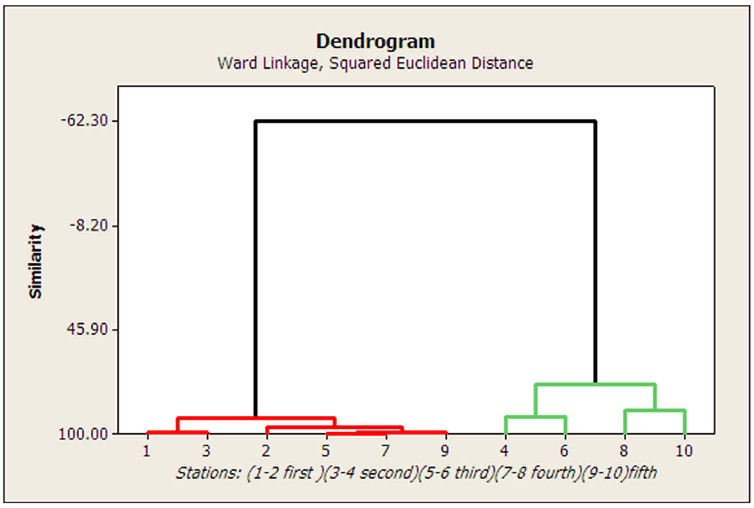


Fig. 2. Dendogram of Euclidian distance and similarity at stations in the Toplluha river

Table 3. Total heavy metals concentration (in mg/L) in the water of the Toplluha river

Parameter	Sampling	Cr	Cd	Ni	Zn	Mn	Cu	Fe	Pb
M1	Springer 2013	0.034	0.023	0.008	0	0.07	0.052	0.058	0.054
	Springer 2019	0.069	0.078	0.012	0.0061	0.088	0.123	0.78	0.066
M2	Springer 2013	0.029	0.015	0.006	0.004	0.058	0	0.033	0.081
	Springer 2019	0.077	0.045	0.002	0.045	0.086	0.23	0.98	0.44
M3	Springer 2013	0.033	0.005	0.007	0	0	0	0.22	0.066
	Springer 2019	0.089	0.047	0.099	0.074	0.63	0.86	0.96	0.048
M4	Springer 2013	0.045	0	0.007	0	0	0	0.128	0.015
	Springer 2019	0.069	0.033	0.014	0.98	0.79	0.89	1.89	0.98
M5	Springer 2013	0.07	0.005	0	0.012	0.13	0.005	0.157	0.005
	Springer 2019	0.08	0.008	0.088	0.59	0.98	0.298	1.02	0.098
Mean		0.0595	0.0259	0.0243	0.171	0.283	0.246	0.623	0.185
StDev		0.02206	0.02487	0.0368	0.337	0.368	0.348	0.607	0.3057
Minimum		0.029	0	0	0	0	0	0.033	0.005
Median		0.069	0.019	0.0075	0.009	0.087	0.087	0.5	0.066
Maximum		0.089	0.078	0.099	0.98	0.98	0.89	1.89	0.98
WHO water standards (2004)		0.05	0.003	0.02	0.05	0.4	2.0	0.3	0.01

domestic system influence the variation of the heavy metal concentrations [Alam, K., 2003]. The mean concentration of Cu, Mn, Ni, and Cr was found lower but Pb, Zn, and Cd were higher in the Toplluha river than the WHO water standard (2004). As shown in Table. 4, the concentration of total heavy metals in the sediment at all sampling sites of the Toplluha river was much higher than Dutch Target and Intervention Values, 2000 (the New Dutch List). The mean concentration of total heavy metals in sediments was in the decreasing order of Cu > Zn > Cr > Ni > Pb > Cd. The mean concentration of Cu in the sediment was observed as 374.2 mg/kg which was higher than (D.L) the values 36 mg/kg. The anthropogenic activities such as the treatment of agricultural land with fertilizers and Cu pesticides might influence a higher concentration of Cu. The Zn concentration in the sediment was found as 345.8 mg/kg, which was higher than (D.L) values of 140 mg/kg. However, the high level of Zn indicates its higher input, which might have originated from the urban and industrial wastes. The Cr concentration in the sediment was observed 243.6 mg/kg which was higher than (D.L) values of 100 mg/kg. A higher concentration of

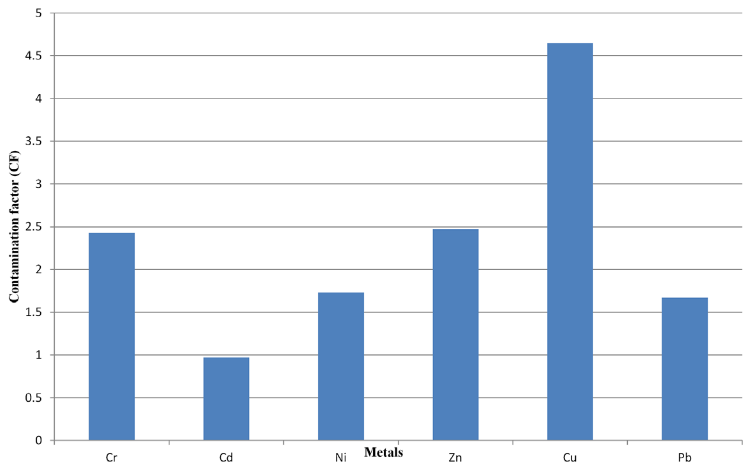
Table 4. Total heavy metals content (in mg/kg) in the sediment of the Toplluha river

Parameter	Sampling	Cr	Cd	Ni	Zn	Mn	Cu	Fe	Pb
M1	Springer 2019	120.2	0.05	62.5	89.6	522.2	29.8	11250	90.12
M2	Springer 2019	247	0.22	25.8	146.2	249.8	38.2	11325	91.32
M3	Springer 2019	253	0.69	49.5	378.5	422.5	97.82	14235	115.2
M4	Springer 2019	319	1.82	99.8	592.5	598.5	298.2	29355	198.15
M5	Springer 2019	279	1.11	65.2	522.2	711.2	374.2	24322	215.2
Mean		**243.6**	**0.778**	**60.6**	**345.8**	**500.8**	**167.6**	**18097**	**142**
StDev		66.73199	0.639544	24.06513	199.2615	157.1008	141.6632	7391.206	53.83177
Minimum		120.2	0.05	25.8	89.6	249.8	29.8	11250	90.12
Median		253	0.69	62.5	378.5	522.2	97.82	14235	115.2
Maximum		319	1.82	99.8	592.5	711.2	374.2	29355	215.2
Dutch Target and Intervention Values, 2000 (the New Dutch List)		100	0.8	35	140	/	36	/	85

Cr might be a consequence of direct discharge of untreated industrial and domestic wastes. The Ni and Pb concentration level in sediments are significant, Ni was found at 60.6 mg/kg, about twice higher than the (D.L) values of 35 mg/kg. The Pb level also is significant at 142.0 mg/kg, i.e. more one and half time than the (D.L) values of 85 mg/kg. The concentrations of Ni and Pb might be result of the geological composition of the soil, industrial and untreated domestic discharge.

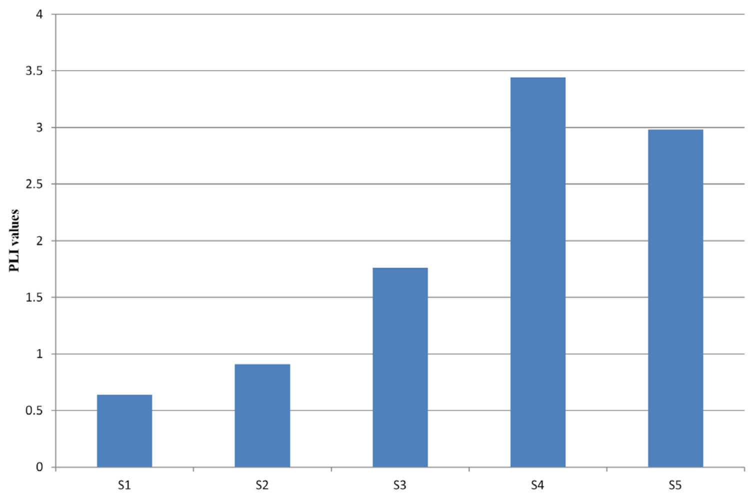
According to the CF shown in Figure 3; the sediment pollution level of river was found as in low pollution (CF<1) class, Cd, other metals-Ni, Pb, and Cr were found in moderate pollution ($1 \leq CF < 3$), Cu in considerable pollution ($3 \leq CF < 6$) and Zn in very high pollution ($CF \geq 6$). The calculated (PLI) pollution load index values of metals in the sediment are summarized in Figure 4 ranging from 0.64 to 3.44 and confirming that the sediments of the studied river were a baseline to progressive deterioration (PLI>1). However, the higher PLI values indicated that Cr, Ni, Pb, Zn, and Cu are the great contributors to the sediment pollutions in the studied river. Higher PLI values were observed in the S3, S4, and S5 sampling site which might be due to the effects of urban activities.

Figure 5 represents the geoacumulation index (I_{geo}) values of the studied heavy metals. Among the studied metals, the geoacumulation index (I_{geo}) values showed the decreasing order of Cu > Zn > Cr > Ni > Pb > Cd. Among the sites, the range of the geoacumulation index (I_{geo}) values for Cd, Pb, Ni, Cr, and Zn were 0.01–0.45, 0.21–0.50, 0.14–0.57, 0.24- 0.64 and 0.12–0.84 respectively, indicating unpolluted to



*Low degree (CF<1), moderate degree(1<CF<3), considerable degree (3<CF<6) and very high degree (CF>6) (Loska et al., 1997)

Fig. 3. Contamination factor (CF) of heavy metals in the sediment of the Toplluha river



PLI=0 (perfection), PLI=1 (Baseline level), PLI>1 progresive deterioration (Tamilson et al., 1980)

Fig. 4. Pollution load index (PLI) value of heavy metals in the sediment of Toplluha river

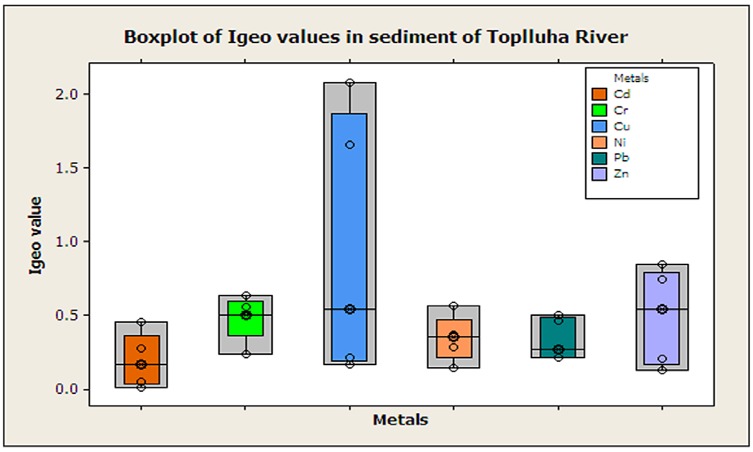


Fig. 5. Geoacumulation index (I_{geo}) value of heavy metals in the sediment of Toplluha river

the moderately polluted status of the sediment. In turn the geoacumulation index (I_{geo}) values for Cu were 0.16–2.08 and indicate moderately to heavily polluted sediment. Normalization techniques such as Enrichment factor (EF) are widely used to categorize the metal fractions associated with sediments. The spatial distributions of the calculated EF for each heavy metals were displayed in Figure 6. The mean enrichment factor (EF) values of all the studied metals suggested their enrichments in the surface sediments of the Toplluha river. Except for the Cd, the enrichment factor value of which was found at a low level, all other metals were in the significant to a high level indicating strong human influence on the metal in sediment pollution.

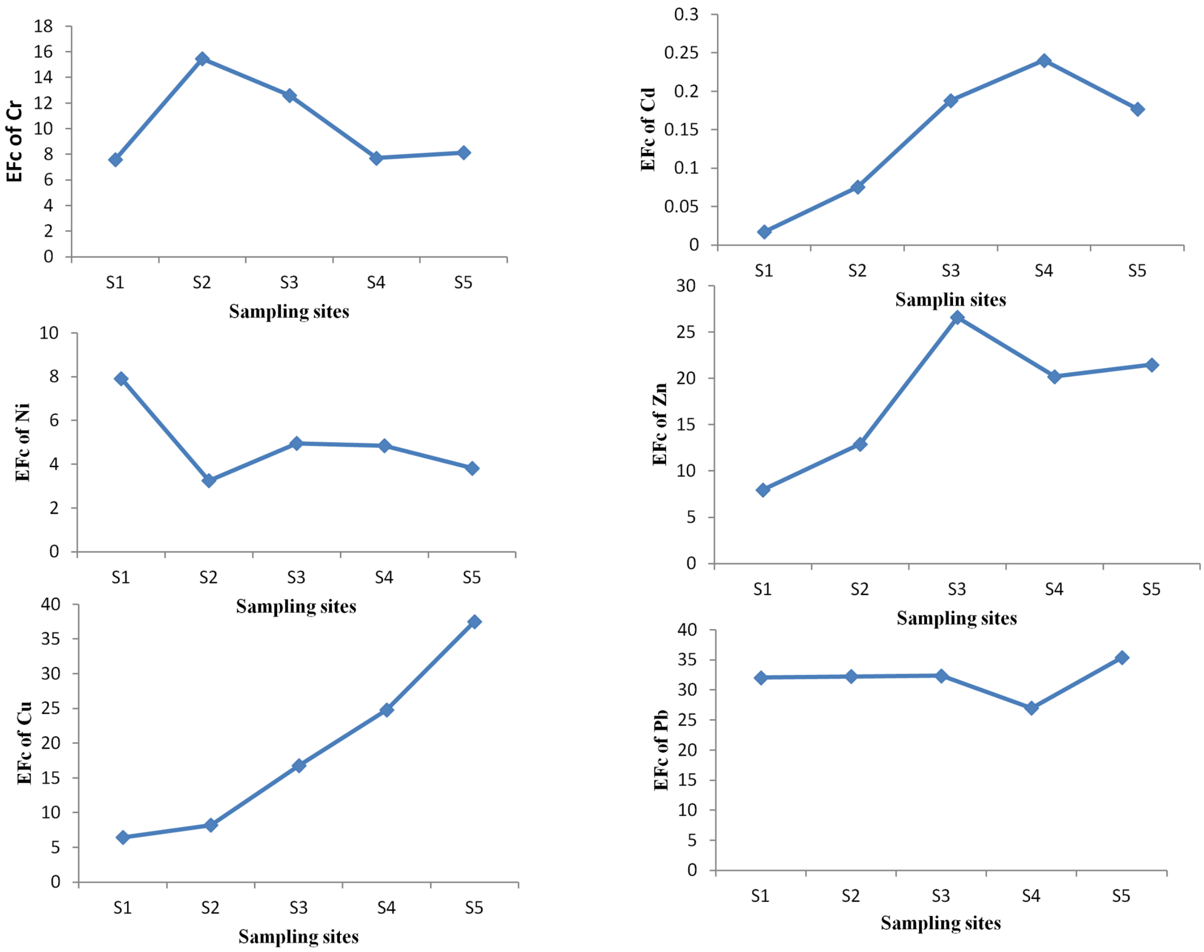


Fig. 6. Enrichment factor (EF) values for heavy metals in the sediments of sampling sites of Toplluha river.

CONCLUSIONS

The spatial distribution and variation of contaminants in water and sediments (especially heavy metals) in the water of Toplluha river, were identified on a scientific basis. The water column is the indicator of temporary pollution that can show variation in a short period of time. The sediment of the river represents more steady situations that cannot change rapidly.

A comprehensive understanding of the water quality trend in both the short and long term is very important for the sustainability of the river water. The water quality parameters and their mean values were evaluated according to the WHO water standard (2004), and Dutch Target and Intervention Values (DTIV), 2000 (the New Dutch List). Along the river stream, varying values of the parameter, ranging from S2 to S5 exhibit persistent contamination with the organic and inorganic pollutants, an anionic surfactant, ammonium nitrogen, nitrite and nitrate. Nitrogen found in class II, COD, BOD_5, Ptot, PO_4^{3-} found in classes from III to V, as well as DO, DOS%, EC and pH found in classes from I to III. Heavy metals in water were in class from I to V, especially in the sample sites S4 and S5.

The characteristics of heavy metals pollution (Cr, Cd, Ni, Zn, Cu, and Pb) in the sediment of the Toplluha river, was investigated using the factors described above. The results demonstrated that the concentration of all heavy metals in the sediment samples was considerably higher than the average shale values except Cd. These higher concentrations of metals can pose a considerable ecological risk in the Toplluha river.

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