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Base alteration of some heavy metal concentrations on local and seasonal in Bartin River

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Abstract Fresh water resources have always been an extremely invaluable economic and strategic resource in the world. There are about 1.4 billion people who have no access to pure water resources mainly due to the discharge of 95% of unpurified wastewater and 70% of industrial wastes into water resources in underdeveloped and developing countries. More than half of the world's rivers are contaminated. Eighty percent of diseases are caused by contaminated waters in developing countries. Among the pollutants in these streams, heavy metals are of particular significance, as heavy metals do not dissolve and degenerate easily in nature. They also tend to bio-accumulate. This is why determining heavy metal concentrations is of great importance because it can help detect risk zones and risk levels. This study aims to determine the alteration of some heavy metal concentrations during a year in Bartin River on a point and seasonal base. Within the scope of the study, samples were collected from 5 chosen locations on Bartin River during a year and the alteration of Cu, Fe, Zn, Mn, Ni, and Pb concentration amounts were determined monthly. As a result of the study, it was determined that there were various rates of contamination with heavy metals at all stations, and that the amount of all studied heavy metal concentrations decreased depending on seasonal alteration when precipitation and hence the flow rates were high, and the highest concentrations were calculated in samples that were collected from L3 and L5 stations. Results shows that some of the toxic metals' accumulations are higher than the suggestion of value, which recommended that the Bartin River is to some extent a toxic metal polluted river and that animals are not totally safe. Since this study constitutes a sample, all international samples should be controlled especially in the Organized Industrial Zone and foundation areas and the wastewater entering the river should be controlled and the pollution source should be determined and precautions should be taken. According to the results of the study, it also shows the water quality of the rivers in general. Pollution levels of rivers should be taken into account in the use of river water and care should be taken to use river water directly or indirectly in agricultural activities that may cause harm to human health. The results of this study can be a guide for identifying suitable areas to use the water of rivers. In future river planning, these studies will have an important guide value.

Keywords Heavy metal concentrations · Heavy metal pollution · Suitable areas · Pollution · Air pollution

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Introduction

Cities transformed into huge production centers as an effect of the industrial revolution which led to a rapid urbanization and population increase in these regions (Singh et al. 2003; Delpla et al. 2009; Lechler et al. 2000; Swennen et al. 1994; Kaya 2009; Kaya et al. 2009; Yucedag et al. 2018; Kaya et al. 2018a, b). The rapid urbanization and population increase are the main reason of many problems such as traffic density, environmental pollution, deforestation, and global warming (Miller et al. 2004; Mortimer 1985; Sharma et al. 2007; Haiyan and Stuanes 2003; Muller et al. 2008; Fernandes 1997; Kaya 2010; Cetin et al. 2010; Cetin 2015a, b; Cetin and Sevik 2016a, b; Cetin 2017; Cetin et al. 2019; Varol et al. 2019; Cetin et al. 2018a, 2018b, c, d, e, f, g). Environmental pollution is of great significance among these problems (Cetin 2016a, b, c, d; Cetin et al. 2017; Sevik and Cetin 2015; Sevik et al. 2017a, b; Kaya et al. 2018a, b). It is reported that approximately 6.5 million people die every year due to reasons caused by air pollution (Lechler et al. 2000; Swennen et al. 1994; Miller et al. 2004; Mortimer 1985; Sharma et al. 2007; Haiyan and Stuanes 2003; Mossi 2018; Cetin et al. 2017; Cetin et al. 2018b; Cetin and Sevik 2016b; Sevik et al. 2017b, 2018; Cetin et al. 2017). The situation is similar with the water pollution. Water has always been an extremely valuable, economic, and strategic resource in the world. It is even more so as a result of the damage occurring rapidly on fresh water resources. There are about 1.4 billion people who have no access to pure water resources mainly due to the discharge of 95% of unpurified wastewater and 70% of industrial wastes into water resources in underdeveloped and developing countries. More than half of the world's rivers are contaminated. Eighty percent of diseases are caused by contaminated waters in developing countries (Singh et al. 2003; Delpla et al. 2009; Lechler et al. 2000; Swennen et al. 1994; Miller et al. 2004; Mortimer 1985; Sharma et al. 2007; Haiyan and Stuanes 2003; Muller et al. 2008; Fernandes 1997).

Streams play a major role as they have the ability of collecting pollutants from both air and soil and they can carry the pollutants to very long distances from the pollutant sources and spread the pollution in the environment. Therefore, in recent years, stream pollution has been one of the most important research subjects, and metal pollution of water resources has attracted attention due to its toxicity, abundance, and permanence (Delpla et al. 2009; Lechler et al. 2000; Swennen et al. 1994; Miller et al. 2004; Yuan et al. 2011; Islam et al. 2015).

Various heavy metals, especially large quantities of dangerous chemicals, have been released into rivers due to the rapid urbanization (Su et al. 2013; Islam et al. 2015). The release of domestic and industrial wastes into rivers leads to increased levels of pollution in river water (Islam et al. 2015; Venugopal et al. 2009).

Material and methods

The study was conducted on Bartin River. Bartin River rises in Ilgaz Mountains, which are located on borders of Kastamonu and Karabük cities; it flows to the north through Bartin and disembogues into the Black Sea. The water depth of Bartin river was measured at a minimum of 1.0 m and maximum 8.5 m in various points according to the seasonal alteration data in 2004 (Turoğlu and Özdemir 2005). According to the publication of Bartin station by DSİ in 2000, the highest average flow rate was 175 m^3/s in January and the lowest average flow rate was 4.5 m^3/s in July (DSHWSPD, Directorate of State Hydraulic Works Survey and Plan Department 2005). According to these data, the average highest and lowest water flow rates per year is $5.5 \times 10^9 - 0.14 \times 10^9$ m^3/year and Bartin River carries 2.8 billion m^3 of water per year.

Within the scope of the study, samples were collected from 5 different points at Kozcağız (L1), Kemer Köprü (L2), Organized Industrial Zone (L3), Orduyeri (L4), and Gürgen Fountain (L5). The locations of the points on the map from where the samples were collected are presented in Fig. 1.

Samples from the points shown in Fig. 1 were collected on a monthly basis in 2017 and the amounts of heavy metal concentrations in these samples were measured. Heavy metals in water samples were determined by Atomic Absorption Spectrophotometer. Thus, the change in Cu, Fe, Zn, Mn, Ni, and Pb concentrations in 5 different locations in Bartin River was determined and the obtained values were tabulated and illustrated with the help of graphs.

Findings

As a result of the study, the mean values of Cu concentrations on a monthly basis depending on locations, *F*

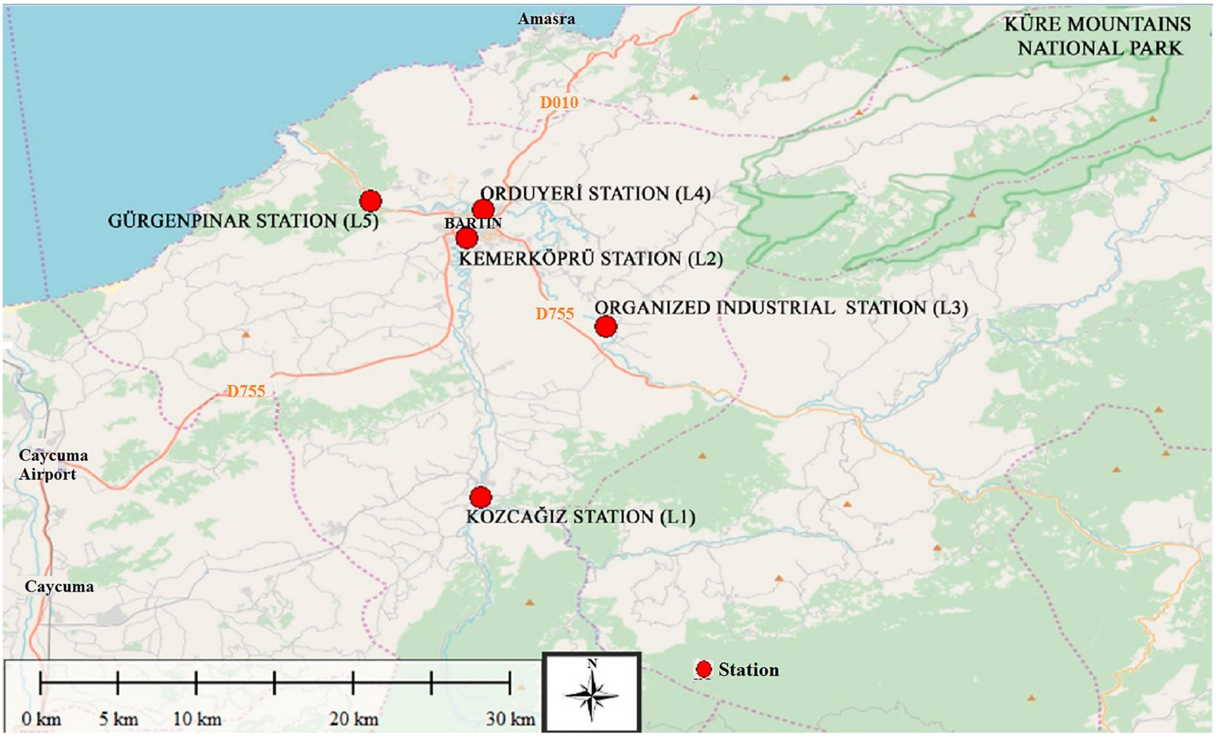

Fig. 1 Points from where the samples were collected

value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 1.

When Table 1 is examined, it can be observed that the alteration of Cu concentration in the five stations in all months is statistically significant at a 99.9% confidence

Table 1 The alteration of Cu concentration on a monthly basis depending on location

Months	Location					*F* value	Sig
	L1	L2	L3	L4	L5		
Jan	0.008 c	0.005 b	0.018 e	0.003 a	0.015 d	81.783	0.000
Feb	0.009 b	0.007 ab	0.021 d	0.005 a	0.013 c	79.818	0.000
Mar	0.004 b	0.000 a	0.012 d	0.004 b	0.009 c	166.500	0.000
Apr	0.008 a	0.009 a	0.026 c	0.007 a	0.019 b	80.725	0.000
May	0.012 a	0.011 a	0.043 c	0.009 a	0.023 b	130.957	0.000
Jun	0.012 a	0.010 a	0.042 c	0.009 a	0.032 b	121.607	0.000
Jul	0.014 a	0.013 a	0.041 c	0.010 a	0.028 b	91.446	0.000
Aug	0.013 a	0.012 a	0.048 c	0.011 a	0.036 b	123.869	0.000
Sep	0.015 b	0.014 b	0.044 c	0.009 a	0.033 d	112.085	0.000
Oct	0.016 b	0.015 b	0.043 d	0.008 a	0.034 c	103.777	0.000
Nov	0.015 b	0.011 a	0.035 d	0.008 a	0.026 c	84.587	0.000
Dec	0.012 c	0.009 b	0.017 d	0.005 a	0.019 d	45.855	0.000

Table 2 The alteration of Cu concentration based on location for all months

Months	Location				
	L1	L2	L3	L4	L5
Jan	0.008 b	0.005 b	0.018 b	0.003 a	0.015 bc
Feb	0.009 b	0.007 c	0.021 bc	0.005 b	0.013 ab
Mar	0.004 a	0.000 a	0.012 a	0.004 ab	0.009 a
Apr	0.008 b	0.009 d	0.026 c	0.007 c	0.019 cd
May	0.012 c	0.011 ef	0.043 ef	0.009 de	0.023 de
Jun	0.012 c	0.010 de	0.042 e	0.009 de	0.032 gh
Jul	0.014 bc	0.013 gh	0.041 e	0.010 e	0.028 fg
Aug	0.013 c	0.012 fg	0.048 f	0.011 e	0.036 h
Sep	0.015 cd	0.014 hi	0.044 ef	0.009 de	0.033 h
Oct	0.016 d	0.015 i	0.043 ef	0.008 cd	0.034 h
Nov	0.015 cd	0.011 ef	0.035 d	0.008 cd	0.026 ef
Dec	0.012 c	0.009 d	0.017 ab	0.005 b	0.019 cd
F value	32.491	53.662	44.998	25.580	41055
Sig	0.000	0.000	0.000	0.000	0.000

level. The highest values are obtained at L3 and L5 locations respectively, and the values of the other three locations are quite close to each other. The differences between the locations are quite evident; for example, the value measured at L3 location in August is approximately 4.36 times higher than the measured value at L4 location; and the measured value at L5 is calculated as 3.27 times higher than the value measured at the L4 location. Table 2 shows the change of Cu concentration based on location throughout the year.

It was determined that Cu concentrations showed a significant change in the different locations in the different months. Cu concentrations decreased significantly in almost all of the sampling locations of the study in March. This alteration is observed more clearly especially in L3 and L5. The alteration in the concentration of Cu based on location for all months is given as a graph in Fig. 2.

The mean values of Fe concentrations on a monthly basis depending on locations, *F* value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 3.

As seen in Table 3, the alteration of Fe concentration in all months depending on locations is statistically significant at least at a 99.9% confidence level. When the alteration of Fe concentration depending on location is examined, it is observed that the values obtained in L1, L2, L4, and L5 locations are very close to each other, whereas the values obtained in L3 location are

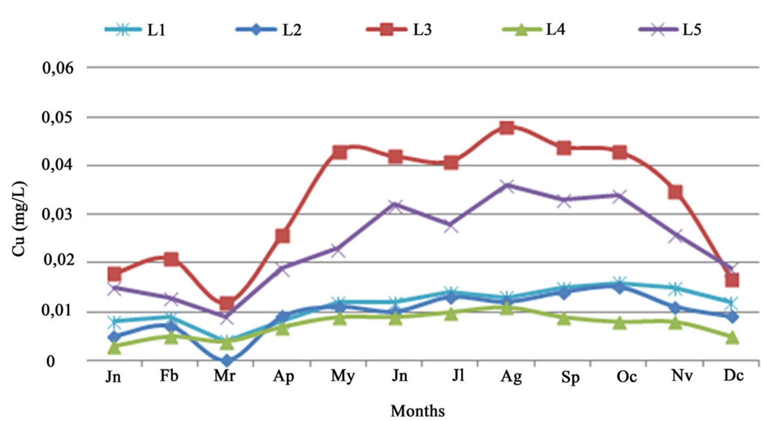

Fig. 2 The alteration of Cu concentration based on location for all months

Table 3 The alteration of Fe concentrations on a monthly basis depending on location

Months	Locations					*F* value	Sig
	1	2	3	4	5		
Jan	0.872 a	0.928 a	1.526 b	0.926 a	0.875 a	23.397	0.000
Feb	0.884 a	0.936 a	1.554 b	0.914 a	0.933 a	23.469	0.000
Mar	0.732 a	0.762 a	1.488 b	0.886 a	0.825 a	33.715	0.000
Apr	0.843 a	0.830 a	1.714 b	0.918 a	0.955 a	37.933	0.000
May	0.746 a	0.760 a	1.863 b	0.923 a	0.862 a	59.356	0.000
Jun	0.812 a	0.793 a	2.074 b	0.942 a	0.866 a	68.947	0.000
Jul	0.706 ab	0.652 a	1.979 c	0.867 b	0.874 b	78.014	0.000
Aug	0.641 ab	0.566 a	2.321 d	0.833 bc	0.877 c	114.264	0.000
Sep	0.764 a	0.754 a	2.356 c	0.934 ab	1.034 b	87.169	0.000
Oct	0.871 a	0.863 a	2.278 b	0.948 a	1.008 a	71.346	0.000
Nov	0.852 a	0.858 a	2.193 b	0.956 a	0.975 a	67.613	0.000
Dec	0.792 a	0.784 a	2.072 c	0.933 a	0.886 a	69.931	0.000

much higher. Table 4 shows the alteration of the Fe concentrations based on locations for all months.

According to the results presented in the table, it was determined that there was no statistically significant difference at a 95% confidence level in alteration values of Fe concentrations measured in L4 and L5 stations; and the alteration values of Fe concentration measured at the L1 station was statistically meaningful at a 95% confidence level; while the alteration values of Fe concentration measured at L2 and L3 stations were statistically meaningful at a 99.9% confidence level. Particularly, the alteration in L3 location is remarkable. It was determined that Fe concentration was at its lowest level in January, February and March, and then it started to rise and reached its peak in August in this station. The alteration of Fe concentrations based on the location depending on months is given in Fig. 3 as a graph.

Table 4 The alteration of the Fe concentration based on locations depending on months

Months	Locations				
	1	2	3	4	5
Jan	0.872 cd	0.928 d	1.526 ab	0.926	0.875
Feb	0.884 d	0.936 d	1.554 ab	0.914	0.933
Mar	0.732 abc	0.762 bc	1.488 a	0.886	0.825
Apr	0.843 bcd	0.830 cd	1.714 abc	0.918	0.955
May	0.746 abcd	0.760 bc	1.863 bcd	0.923	0.862
Jun	0.812 bcd	0.793 bcd	2.074 def	0.942	0.866
Jul	0.706 ab	0.652 ab	1.979 cde	0.867	0.874
Aug	0.641 a	0.566 a	2.321 ef	0.833	0.877
Sep	0.764 abcd	0.754 bc	2.356 f	0.934	1.034
Oct	0.871 cd	0.863 cd	2.278 ef	0.948	1.008
Nov	0.852 bcd	0.858 cd	2.193 def	0.956	0.975
Dec	0.792 bcd	0.784 bc	2.072 def	0.933	0.886
F	3.063	5.900	8.596	,512	1.683
Sig	,011	,000	,000	,876	,138

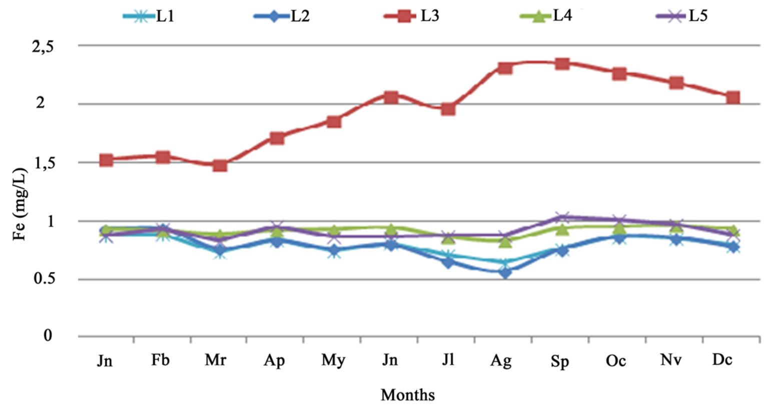

Fig. 3 The alteration of Fe concentration based on the location depending on months

The mean values of Zn concentration on a monthly basis depending on locations, *F* value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 5.

As seen in Table 5, the alteration of Zn concentration in all months due to locations is statistically significant at least at a 99.9% confidence level. In terms of the Duncan test results, it is seen that L4 location is in the first homogeneous group in all months and L3 is in the last homogeneous group in all months. Generally, the lowest values in all months were obtained in L4 and the highest values were obtained in L1 location, while the values of the other three locations were very close to each other and they were generally in the same homogeneous groups according to the Duncan test results. Table 6 shows the alteration of Zn concentration based on location for all months.

According to the results presented in the table, it was determined that the alteration of Zn concentrations was statistically significant at least at a 99.9% confidence level at all locations. In general, Zn concentrations were higher in May and November months. The alteration of Zn concentrations based on the location for all months is given in Fig. 4 as a graph.

The mean values of Mn concentration on a monthly basis depending on locations, *F* value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 7.

When Table 7 is examined, it is observed that the alteration of Mn concentrations as in other heavy metals

Table 5 The alteration of Zn concentration on a monthly basis depending on location

Months	Locations					*F* value	Sig
	1	2	3	4	5		
Jan	0.134 b	0.147 bc	0.272 d	0.091 a	0.172 c	49.970	0.000
Feb	0.132 b	0.102 ab	0.326 d	0.093 a	0.186 c	84.308	0.000
Mar	0.147 b	0.144 b	0.248 c	0.112 a	0.174 b	29.681	0.000
Apr	0.195 b	0.182 b	0.335 c	0.126 a	0.213 b	40.027	0.000
May	0.228 b	0.216 b	0.472 c	0.133 a	0.234 b	67.869	0.000
Jun	0.257 ab	0.263 ab	0.478 d	0.142 a	0.331 c	51.237	0.000
Jul	0.261 b	0.2855 bc	0.435 d	0.148 a	0.325 c	37.835	0.000
Aug	0.302 b	0.318 b	0.486 c	0.158 a	0.362 b	39.498	0.000
Sep	0.291 b	0.303 bc	0.484 d	0.162 a	0.358 c	39.900	0.000
Oct	0.252 b	0.263 b	0.4736 c	0.153 a	0.302 b	48.712	0.000
Nov	0.244 bc	0.214 b	0.458 d	0.145 a	0.291 c	54.464	0.000
Dec	0.174 ab	0.157 a	0.372 c	0.142 a	0.206 b	56.325	0.000

Table 6 The alteration of Zn concentration based on location for all months

Months	Locations				
	1	2	3	4	5
Jan	0.134 a	0.147 b	0.272 ab	0.091 a	0.172 a
Feb	0.132 a	0.0.102 a	0.326 bc	0.093 a	0.186 a
Mar	0.147 ab	0.144 b	0.248 a	0.112 ab	0.174 a
Apr	0.195 cd	0.182 bc	0.335 bc	0.126 bc	0.213 ab
May	0.228 de	0.216 c	0.472 e	0.133 bcd	0.234 b
Jun	0.257 ef	0.263 d	0.478 e	0.142 cde	0.331 cd
Jul	0.261 ef	0.2855 de	0.435 de	0.148 cde	0.325 cd
Aug	0.302 g	0.318 e	0.486 e	0.158 e	0.362 d
Sep	0.291 fg	0.303 e	0.484 e	0.162 e	0.358 d
Oct	0.252 e	0.263 d	0.474 e	0.153 de	0.302 c
Nov	0.244 e	0.214 c	0.458 e	0.145 cde	0.291 c
Dec	0.174 bc	0.157 b	0.372 cd	0.142 cde	0.206 ab
F	23.629	32.209	15.127	10.321	23.741
Sig	0.000	0.000	0.000	0.000	0.000

is statistically significant at least at a 99.9% confidence level in all months depending on location. According to the Duncan test results, the highest values are obtained at L3 location in all months, while the values obtained from other stations are very close to each other. Table 8 shows the alteration of Mn concentrations based on location for all months.

According to the results presented in the table, it was determined that the alteration of Mn concentrations was statistically significant at least at a 99.9% confidence level at all locations. Generally, although the Mn concentrations increased in summer months, the alteration of Mn concentrations in stations other than L3 station was not very high, whereas in L3 station it increased significantly after June, was quite high in July–August and then started to decrease. The alteration of Mn concentration based on locations for all months is given in Fig. 5 as a graph.

The mean values of Ni concentration, which is one of the metals subjected in this study, on a monthly basis for all locations, *F* value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 9.

When Table 9 is examined, it is seen that the alteration of Ni concentrations is also statistically significant at least at a 99.9% confidence level in all moths depending on locations. The highest values were obtained at L3 location and the values of the other four locations were closer to each other. Table 10 shows the alteration of Ni concentrations based on locations for all months.

According to the results presented in Table 10, it is determined that the alteration of Ni concentrations is

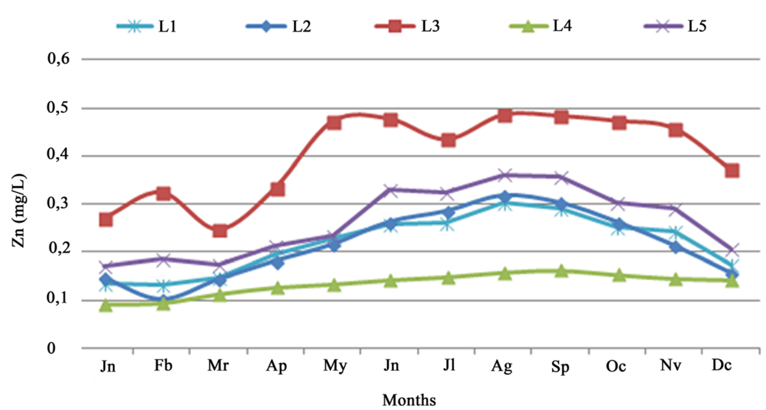

Fig. 4 The alteration of Zn concentration based on the location for all months

Table 7 The alteration of Mn concentrations on a monthly basis depending on location

Months	Locations					*F* value	Sig
	1	2	3	4	5		
Jan	0.031 a	0.052 b	0.108 c	0.023 a	0.056 b	93.431	0.000
Feb	0.038 b	0.063 c	0.112 d	0.021 a	0.058 c	91.927	0.000
Mar	0.022 a	0.045 b	0.106 c	0.025 a	0.055 b	100.951	0.000
Apr	0.037 a	0.056 b	0.103 c	0.028 a	0.058 b	73.467	0.000
May	0.045 a	0.063 b	0.137 c	0.032 a	0.063 b	93.007	0.000
Jun	0.054 b	0.067 bc	0.148 d	0.035 a	0.072 c	86.63	0.000
Jul	0.069 b	0.064 ab	0.252 c	0.043 a	0.075 b	151.636	0.000
Aug	0.0.071 ab	0.071 ab	0.0.265 c	0.052 a	0.084 b	142.605	0.000
Sep	0.055 a	0.078 ab	0.257 c	0.056 a	0.087 b	138.768	0.000
Oct	0.046 a	0.065 a	0.253 c	0.065 a	0.089 b	143.951	0.000
Nov	0.027 a	0.052 b	0.205 d	0.062 b	0.085 c	135.37	0.000
Dec	0.024 a	0.033 ab	0.188 d	0.043 b	0.080 c	167.792	0.000

statistically significant at least at a 99.9% confidence level at all locations. In general, it is observed that Ni concentrations have started to increase beginning from March and reached the highest levels in May–August and then started to decrease. The alteration of Ni concentrations based on location for all months is given in Fig. 6 as a graph.

The mean values of Pb concentrations, which is one of the most important metals subjected to this study, on a monthly basis depending on locations, *F* value and significance level calculated as a result of variance analysis and homogeneous groups resulting from Duncan test are given in Table 11.

When Table 11 is examined, it is observed that the alteration of Pb concentrations is statistically significant at least at a 95% confidence level depending on locations in all months except January. This alteration is significant at a 99% confidence level in February and March and 99.9% confidence level in other months. The highest values of Pb concentrations were obtained at L3 and L5 locations respectively. Table 12 shows the

Table 8 The alteration of Mn concentration based on location for all months

Months	Locations				
	1	2	3	4	5
Jan	0.031 bc	0.052 bc	0.108 ab	0.023 a	0.056 a
Feb	0.038 cd	0.063 de	0.112 ab	0.021 a	0.058 a
Mar	0.022 a	0.045 b	0.106 ab	0.025 ab	0.055 a
Apr	0.037 c	0.056 cd	0.103 a	0.028 abc	0.058 a
May	0.045 de	0.063 de	0.137 bc	0.032 bc	0.063 ab
Jun	0.054 f	0.067 e	0.148 c	0.035 c	0.072 bc
Jul	0.069 g	0.064 de	0.252 e	0.043 d	0.075 bcd
Aug	0.071 g	0.071 ef	0.265 e	0.052 e	0.084 cde
Sep	0.055 f	0.078 f	0.257 e	0.056 ef	0.087 de
Oct	0.046 e	0.065 de	0.253 e	0.065 g	0.089 e
Nov	0.027 ab	0.052 bc	0.205 d	0.062 fg	0.085 de
Dec	0.024 ab	0.033 a	0.188 d	0.043 d	0.080 cde
F	43.345	13.545	40.684	41.173	10.449
Sig	0.000	0.000	0.000	0.000	0.000

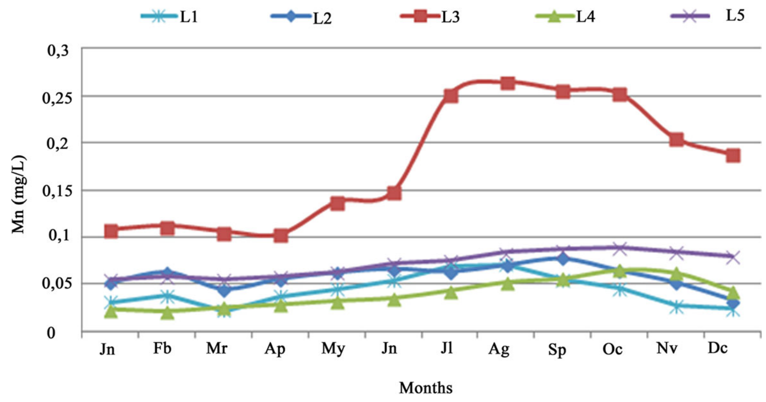

Fig. 5 The alteration of Mn concentration on location basis depending on months

alteration of Pb concentration based on locations for all months.

According to the results seen in Table 12, the change of Pb concentrations at all locations for all months was statistically significant at least at a 99.9% confidence level. In general, Pb concentrations have started to increase beginning from March, they have been at very high levels beginning from May and have started to decrease with a slow decline starting from August. The alteration of Pb concentrations based on location for all months is given as a graph in Fig. 7.

Results and discussion

According to the results of heavy metal analysis performed in water samples that were collected within this study, it was determined that there is a heavy metal contamination in all stations at various rates. The water quality criteria determined in terms of heavy metal content consider all water as the highest criterion if only one heavy metal content exceeds the criterion (Official Gazette 2004; Official Gazette 2012). It can be said that the alteration of all heavy metals depending on months generally decreases due to the high rainfall periods and in high flow rate seasons.

As a general assessment of all heavy metals considering all stations, water taken from the L2 station is the least polluted with Fe and Zn and is classified as clean from Fe and Zn contamination.

The L1 station has similar characteristics to the L2 station. L3 station exists in quality class II for all metals; the L4 station is less polluted with Fe and exists in clean water quality class in terms of the other metals. The

Table 9 The alteration of Ni concentration on a monthly basis depending on location

Mohths	Locations					F value	Sig
	1	2	3	4	5		
Jan	0.007 b	0.007 b	0.016 d	0.001 a	0.009 c	85.375	0.000
Feb	0.009 b	0.009 b	0.017 d	0.004 a	0.013 c	51.000	0.000
Mar	0.004 b	0.000 a	0.013 c	0.000 a	0.000 a	477.000	0.000
Apr	0.009 c	0.005 a	0.0.022 d	0.006 ab	0.008 bc	95.500	0.000
May	0.014 a	0.015 ab	0.031 c	0.012 a	0.018 b	49.346	0.000
Jun	0.016 ab	0.017 ab	0.030 c	0.014 a	0.019 b	28.910	0.000
Jul	0.017 a	0.015 a	0.030 b	0.016 a	0.018 a	25.269	0.000
Aug	0.018 ab	0.018 ab	0.033 c	0.017 a	0.022 b	26.580	0.000
Sep	0.016 b	0.013 a	0.024 c	0.016 b	0.019 b	18.439	0.000
Oct	0.009 b	0.004 a	0.021 d	0.013 c	0.015 c	74.260	0.000
Nov	0.011 c	0.008 b	0.019 d	0.005 a	0.011 c	53.705	0.000
Dec	0.008 c	0.005 b	0.016 d	0.003 a	0.009 c	81.964	0.000

Table 10 The alteration of Ni concentrations based on locations for all months

Months	Locations				
	1	2	3	4	5
Jan	0.007 b	0.007 cd	0.016 ab	0.001 a	0.009 bc
Feb	0.009 bc	0.009 d	0.017 abc	0.004 bc	0.013 de
Mar	0.004 a	0.000 a	0.013 a	0.000 a	0.000 a
Apr	0.009 bc	0.005 bc	0.022 de	0.006 d	0.008 b
May	0.014 d	0.015 f	0.031 f	0.012 e	0.018 fg
Jun	0.016 e	0.017 fg	0.030 f	0.014 f	0.019 g
Jul	0.017 e	0.015 f	0.030 f	0.016 g	0.018 fg
Aug	0.018 e	0.018 g	0.033 f	0.017 g	0.022 h
Sep	0.016 e	0.013 e	0.024 e	0.016 g	0.019 g
Oct	0.009 bc	0.004 b	0.021 cde	0.013 ef	0.015 ef
Nov	0.011 c	0.008 d	0.019 bcd	0.005 cd	0.011 cd
Dec	0.008 b	0.005 bc	0.016 ab	0.003 b	0.009 bc
F	38.804	70.210	26.958	113.287	52.213
Sig	0.000	0.000	0.000	0.000	0.000

samples taken from L5 station were classified as quality class II in terms of Cu, Zn, and Fe heavy metals contamination; quality class I in terms of Ni and Mn, Fe heavy metals contamination.

It was determined that L5 station was in water quality class II in terms of Cu, Zn, and Fe; class I in terms of Ni and Mn and class I–II in terms of Pb. As a result, although pollution by heavy metal ions shows variable values, the heavy metal content was determined to be above the acceptable amounts, and unfortunately, it is estimated that these values will increase in the following years.

According to the study conducted by Water Management (2005), in 2004 Pre-sea pollution measurement values of Bartin River of DSİ Drinking Water General Directorate the amount of cadmium was quite high and the amount of Fe was above the limit values in terms of heavy metal content. Similar results have been demonstrated in studies conducted on different streams. Okur et al. (2001) analyzed and calculated the content of Fe, Cu, Pb, Cr, and Al below the criterion data while they reported that Zn, Mn, and Co values reached the pollution level in water of the Büyük Menderes River. Toroğlu et al. (2006) reported that heavy metal pollution in all stations for Cu, Fe, Zn, Mn, Ni, and Pb is very high in Aksu River and its branches and this situation is caused by the absence of treatment plant in at least a part of the surrounding industrial facilities.

Among the pollutants poured into the Bartin River from the industrial facilities in the region, heavy metals are of great significance as they are toxic even at low concentrations for human health. Although micronutrients such as

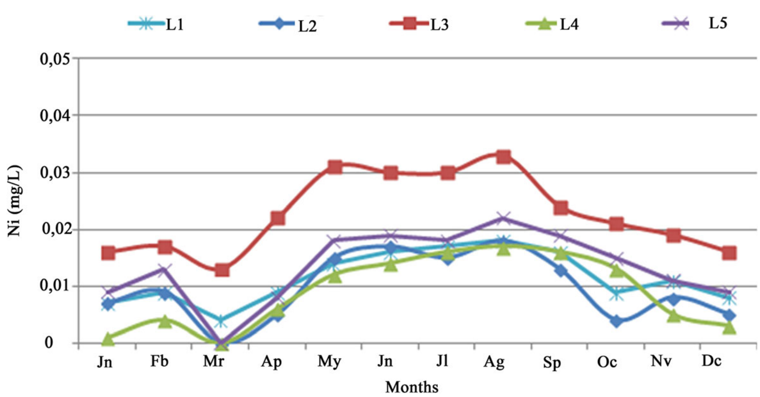

Fig. 6 The alteration of Ni concentrations based on location for all months

Table 11 The alteration of Pb concentrations on a monthly basis depending on location

Months	Locations					*F* value	Sig
	1	2	3	4	5		
Jan	0.0061 a	0.00612 a	0.0074 b	0.0063 a	0.0066 ab	2.415	0.118
Feb	0.00687 a	0.00702 a	0.0098 b	0.007 a	0.0065 a	6.770	0.007
Mar	0.00563 a	0.00532 a	0.0073 b	0.0062 a	0.0058 a	8.010	0.004
Apr	0.00734 a	0.00752 a	0.0156 c	0.0073 a	0.0097 b	45.312	0.000
May	0.00859 a	0.00862 a	0.0185 c	0.008 a	0.0114 b	48.425	0.000
Jun	0.0086 a	0.00852 a	0.0177 c	0.0082 a	0.0136 b	43.603	0.000
Jul	0.00921 a	0.00932 a	0.0163 c	0.0089 a	0.0124 b	21.254	0.000
Aug	0.0099 a	0.00977 a	0.0186 c	0.0103 a	0.0142 b	29.069	0.000
Sep	0.0098 b	0.00984 b	0.0183 d	0.00743 a	0.0127 c	47.695	0.000
Oct	0.0097 b	0.01012 b	0.0176 d	0.0065 a	0.0123 c	36.789	0.000
Nov	0.00909 b	0.00912 b	0.0171 c	0.0061 a	0.0097 b	45.685	0.000
Dec	0.00761 b	0.00712 b	0.0153 c	0.0039 a	0.0078 b	59.432	0.000

Mn, Zn, Cu, Fe, Ni are necessary for living organisms including plants, they can have harmful effects at high levels. Metals such as Pb have a severely toxic effect on organisms even at low levels (Shahid et al. 2017). Numerous studies have been conducted regarding the importance of the subject on both heavy metals in the contents of streams (Liang et al. 2016; Marrugo-Negrete et al. 2017; Zhang et al. 2017: Singh et al. 2003; Delpla et al. 2009; Lechler et al. 2000; Swennen et al. 1994; Miller et al. 2004; Mortimer 1985; Sharma et al. 2007; Haiyan and Stuanes 2003; Muller et al. 2008; Fernandes 1997), lakes (Ahmed et al. 2002; Ahmed et al. 2003; Ahmad et al. 2010; Singh et al. 2003; Delpla et al. 2009), and in the atmosphere (Ozel et al. 2015; Saleh, 2018, Turkyilmaz et al. 2018a, b, c, d, e; Sevik et al. 2018; Miller et al. 2004; Mortimer 1985; Sharma et al. 2007; Haiyan and Stuanes 2003;).

There are important industrial facilities around Bartin River and its branches. The leading industrial sectors in

Table 12 The alteration of Pb concentrations based on locations for all months

Months	Locations				
	1	2	3	4	5
Jan	0.0061 ab	0.00612 ab	0.0074 a	0.0063 b	0.0066 ab
Feb	0.00687 b	0.00702 bc	0.0098 b	0.007 bc	0.0065 ab
Mar	0.00563 a	0.00532 a	0.0073 a	0.0062 b	0.0058 a
Apr	0.00734 bc	0.00752 bc	0.0156 c	0.0073 bc	0.0097 cd
May	0.00859 cd	0.00862 cd	0.0185 d	0.008 cd	0.0114 de
Jun	0.0086 cd	0.00852 cd	0.0177 cd	0.0082 cd	0.0136 ef
Jul	0.00921 d	0.00932 d	0.0163 cd	0.0089 de	0.0124 ef
Aug	0.0099 d	0.00977 d	0.0186 d	0.0103 e	0.0142 f
Sep	0.0098 d	0.00984 d	0.0183 d	0.00743 bc	0.0127 ef
Oct	0.0097 d	0.01012 d	0.0176 cd	0.0065 b	0.0123 ef
Nov	0.00909 d	0.00912 d	0.0171 cd	0.0061 b	0.0097 cd
Dec	0.00761 bc	0.00712 bc	0.0153 c	0.0039 a	0.0078 bc
F	10.117	9.889	29.493	12.750	20.471
Sig	0.000	0.000	0.000	0.000	0.000

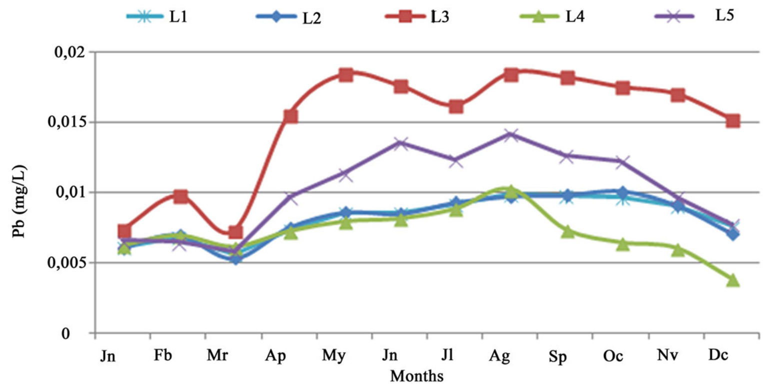

Fig. 7 The alteration of Pb concentrations based on location for all months

the province are textile and apparel industry, chemistry, coal and plastic industry, stone and soil based industry, forest products and furniture industry, and food industry (Bartin Governorship 2013). According to the Provincial Environmental Situation Report of the Bartin Governorate in 2012, there are 206 companies that have industry registry in these sectors. As also stated in the report that industrial enterprises in the province are generally located in the Organized Industrial Zone and there is no wastewater treatment plant belonging to the Organized Industrial Zone and it is in the construction phase. However, it is also stated that most of the industrial facilities in the province have wastewater treatment plants. It has also been reported that there is no treatment plant for the treatment of domestic wastewater of the province and the sewage water flows directly to the river without any treatment from the central settlements of Hasankadi, Kumluca and Kozcağız towns and Bartin Province which are settled collectively around the river.

Conclusions

The industrial usage of water resources in Bartin River Basin for the purposes of process, cooling, cleaning, and so on, the industrial wastewater, agricultural activities—the use of fertilizers and pesticides—contamination caused by excessive and improper irrigation, domestic usage, domestic wastewater, and solid waste disposal in stream beds are all pollution factors in the Bartin River. In addition, Bartin Stream is still on the receiving end for many pollutants without treatment. The existing pollution sources in the settlement areas are affecting the river negatively. It is believed that the industrial activities and the pollutants transported via water from the neighboring provinces cause the increase of heavy metal contamination in Bartin River.

The results of the study reveal that especially the samples that were collected from L3 and L5 stations contain the highest concentrations of heavy metals. The wastewater that gets mixed into the river from these locations should be checked and precautions should be taken by determining the source of pollution.

The results of the study also reveal the water quality of Bartin River in general. Pollution levels of the river must be considered in use of Bartin River water and caution must be exercised in for agricultural activities that may be harmful to human health be it directly or indirectly. The results of this study may be directive for the determination of suitable areas to use the water of Bartin River.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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