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Ecological Risk Assessment of Heavy Metals in Sediment of Felent Stream, Sakarya River Basin, Turkey

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Abstract.- Many indices have been developed to evaluate the environmental risks of heavy metals in sediments. In the present study, two of these indices were used to determine the sediment quality of a polluted freshwater ecosystem. Sediment samples were collected seasonally from seven stations selected on Felent Stream and the accumulations of some heavy metals (As, Cr, Cu, Pb, Zn) in sediment were investigated seasonally. Potential ecological risk analysis (R_I) and biological toxicity test based sediment quality guidelines (mERM-Q) applied to the results to assess the environmental risks of heavy metals in the region (As, Cr, Cu, Pb, Zn). According to the results, Köprüören and Yoncalı Villages (F2 and F3 stations) where mining – agricultural sections of the study area were "high – medium priority site" according to mERM-Q and has "moderate ecological risk" according to R_I. Kütahya Province and estuary of stream (F6 and F7 stations) where urban sections of the study area had "high – medium priority site" and "medium – low priority site" respectively according to mERM-Q.

Keywords: Felent Stream, heavy metal, rsk assessment.

INTRODUCTION

The contamination of freshwater with heavy metals has become a matter of concern over the last few decades as a result of anthropogenic activities (Voegborlo *et al.*, 1999; Dirilgen, 2001; Vutukuru, 2005). Heavy metals, which are significant pollutants for invertebrates, fishes and humans, have devastating effects on the ecological balance of environment and diversity of aquatic organisms (Vosyliene and Jankaite, 2006; Farombi *et al.*, 2007; Atıcı *et al.*, 2008).

Felent Stream is one of the most prominent branches of Porsuk Stream (Sakarya River Basin) used for irrigation, industrial water supply, receiving domestic wastes and fishing activities. In addition to the geologic structure of the Felent Stream Basin, silver mining facility, intensive agricultural applications and solid waste storage area located in the downside of the basin are the main contamination factors for the region (Tokatlı *et al.*, 2013).

In the present study, arsenic, chromium, copper, lead and zinc concentrations in sediment of Felent Stream Basin were determined seasonally. Also "Potential Ecological Risk Index" and "Biological Risk Index" were used to assess the heavy metal contamination in sediments of the basin.

MATERIALS AND METHODS

Study area and collection of samples

Felent Stream, which is the most important branches of Porsuk Stream with length of 35 km and the average flow rate of 0.56 m^3/s, is exposed to agricultural, domestic and industrial pollution and carries this pollution into the Sakarya River through the Porsuk Stream (Anonymous, 2006). Map of Felent Stream Basin and selected stations were given in Figure 1. Samples were collected seasonally between the dates of March 2011 – December 2011.

Sediment samples were collected from the stream and reservoir by using sediment dipper and Ekman grab taking small portions from the center of the dipper and grab with a polyethylene spoon to avoid contamination by metallic parts of the grab.

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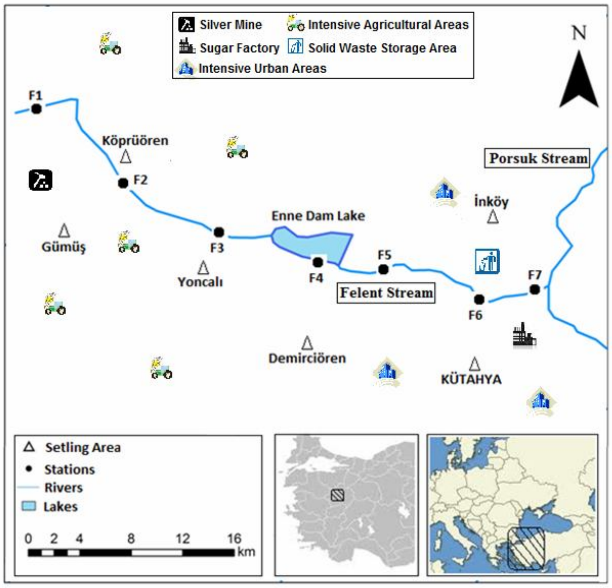

Fig 1. Felent Stream Basin and sampling points.

Chemical analysis

Sediment samples were dried for 3 h at 105°C for element analyses. Then, all sediment samples were placed (0.25g of each sample) in Pyrex reactors of a CEM Mars Xpress 5 microwave digestion unit. $HClO_4$:HNO_3 acids of 1:3 proportions were inserted in the reactors respectively. Samples were mineralized at 200°C for thirty minutes. Afterwards, the samples were filtered in such a way as to make their volumes to 100 ml with ultra-pure distilled water.

Element levels were determined by Inductively Coupled Plasma-Optic Emission Spectrophoto-metric (Varian 720 ES) method. The element analyses were recorded as means triplicate measurements, and the wavelengths used for element analysis were given in Table III (EPA, 1998; EPA, 2001).

Sediment quality indices

Potential ecological risk index (R_I)

The potential ecological risk index was developed to assess ecological risks for aquatic pollution control. The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. It was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of heavy metals and the response of the environment and can be calculated with the following formula (Hakanson, 1980);

$$R_I = \sum E_r^i$$

$$E_r^i = T_r^i C_f^i$$

$$C_f^i = C_0^i / C_n^i$$

Where "R_I" is calculated as the sum of all risk factors for heavy metals in sediments, "E_r^i" is the monomial potential ecological risk factor, "T_r^i" is the toxic response factor for a given substance that accounts for the toxic requirement and the sensitivity requirement (Table I), "C_f^i" is the contamination factor, "C_0^i" is the concentration of metals in the sediment and "C_n^i" is a reference value for metals (Table I). The scale of "R_I" was given in Table II.

Table I.- Reference values (C_n^i), toxicity coefficients (T_r^i), effect range low (ERL) and effect range medium (ERM) values of heavy metals in sediment (Hilton *et al.*, 1985; EPA, 2005)

Elements	R_I		mERM-Q	
	C_n^i	T_r^i	ERL	ERM
As	15.00	10.00	33.00	85.00
Cr	60.00	2.00	80.00	145.00
Cu	30.00	5.00	70.00	390.00
Pb	25.00	5.00	35.00	110.00
Zn	80.00	1.00	120.00	270.00

Biological risk index (mERM-Q)

The sediment quality guidelines (SQGs) were developed from biological toxicity test of the benthic environment and classified into three levels by ERL (effect range low) and ERM (effect range medium) as rarely (<ERL), occasionally (ERL – ERM) or frequently (≥ERM) associated with adverse biological effects (EPA, 2005). A mean ERM quotient (mERM–Q) is proposed for assessing the potential effects of multiple heavy metal contamination in sediment and can be calculated with the following formula (Long *et al.*, 2005);

$$mERM-Q = \left(\sum_{i=1}^{n} ERM-Q_i\right) \Big/ n$$

$$ERM-Q_i = C_i / ERM_i$$

Where “mERM–Q” is the effect range median quotient of multiple metal contamination, “Ci” is the total content of selected metal, “ERMi” is the ERM value of selected metal (Table I) and ‘‘n’’ is the number of selected metals. The scale of “mERM–Q” was given in Table II.

RESULTS

The potential ecological risk indices monomial (E^i_r) and multinomial (R_I) and biological risk indices monomial (ERM–Qi) and multinomial (mERM–Q) for each station and seasons were identified and given in Table III.

According to the results of monomial potential ecological risk indices (E^i_r), arsenic posed moderate and considerable ecological risk at F2 and F3 stations. Also, lead posed moderate ecological risk at F2 station in rainy seasons (autumn and winter), when the peak data were recorded for arsenic in the same area. Copper and lead posed moderate ecological risk at solid waste storage area (F6 station) in summer season. The potential ecological risk indices for monomial regulators indicted that the intensity of the five heavy metals sorted as As > Pb > Cu > Zn > Cr, respectively (Table III).

According to the results of multinomial potential ecological risk indices (R_I), F2 and F3 stations exhibited moderate ecological risk in all seasons except dry season (summer). Also, F6 station exhibited moderate ecological risk in summer season. The potential ecological risk indices for multinomial regulators indicted that the ecological risk of Felent Stream Basin in terms of five heavy metals sorted as F2 > F3 > F6 > F7 > F4 > F1 > F5,respectively (Fig. 2).

According to the results of monomial biological risk indices (ERM–Qi), arsenic posed high – medium priority side in spring and autumn seasons and posed high priority side in winter season at F2 and F3 stations. Chromium posed high – medium priority side at F1, F2, F3 and F6 station in winter season. Lead posed high priority side in rainy seasons (spring, autumn and winter) at Köprüören Village (F2 station) and in dry season (summer) at solid waste storage area (F6 station). Zinc posed high–medium priority side at F2 and F3 stations and high priority side in winter season at Köprüören Village. Also, copper posed high–medium priority side at solid waste storage area in dry season. The biologically risk of contamination to sediments of Felent Stream Basin followed the order as Pb > Zn > As > Cr > Cu,respectively (Table III).

According to the results of multinomial biological risk indices (mERM–Q), Köprüören and Yoncalı Villages exhibited high – medium priority side in rainy seasons and solid waste storage area exhibited high – medium priority side in dry season. The biological risk indices for multinomial regulators indicted that the biologically risk of contamination to sediments of Felent Stream Basin in terms of five heavy metals followed the order as F2 > F3 > F6 > F7 > F4 > F1 > F5,respectively (Fig.3).

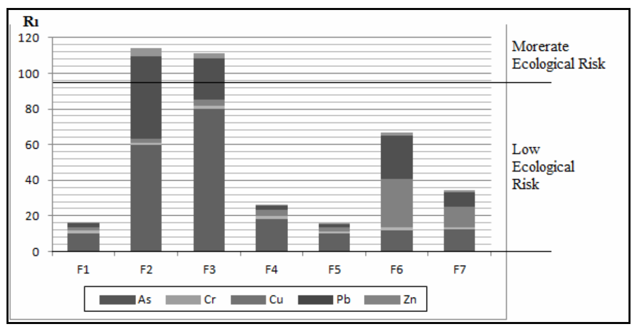

Fig. 2. Multinomial potential ecological risk indices (R_I) in Felent Stream.

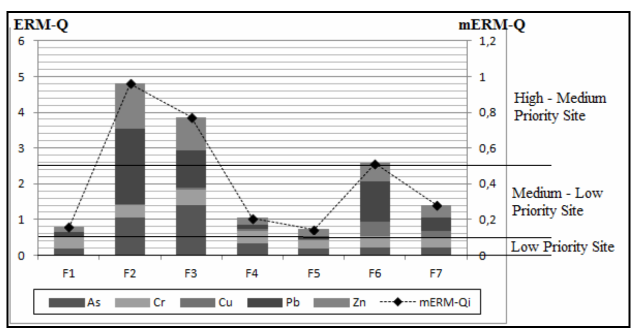

Fig. 3. ERM quotient (ERM-Q) and mean ERM quotient (mERM-Q) in Felent Stream.

Table II.- Scale used to describe the risk factors of E^i_r, R_I, ERM-Qi and mERM-Q (Hakanson, 1980; Long *et al.*, 2005).

Assessment of potential ecological risk				Assessment of biological risk	
E^i_r	Potential ecological risk for monomial factor	R_I	Potential ecological risk for multinomial factors	ERM-Qi and mERM-Q	Biological toxicity risk for monomial and multinomial factors
< 40	Low ecological risk	< 95	Low ecological risk	< 0.1	Low priority side
40 – 80	Moderate ecological risk	95 – 190	Moderate ecological risk	0.1 – 0.5	Medium-low priority side
80 – 160	Considerable ecological risk	190 – 380	Considerable ecological risk	0.5 – 1.5	High-medium priority side
160 – 320	High ecological risk	> 380	Very high ecological risk	> 1.5	High priority side
> 320	Very high ecological risk				

Table III.- Heavy metal risk indices in sediment of Felent Stream.

St.	E^i_r					R_I	ERM-Q_i					mERM-Q
	As	Cr	Cu	Pb	Zn		As	Cr	Cu	Pb	Zn	
Spring season												
F1	11.21	1.28	1.65	2.01	0.53	16.67	0.20	0.26	0.03	0.09	0.16	0.15
F2	**52.27**	1.57	3.24	34.62	4.68	**96.37**	**0.92**	0.32	0.05	**1.57**	**1.39**	**0.85**
F3	**84.08**	1.34	3.47	21.70	4.23	**114.82**	**1.48**	0.28	0.05	**0.99**	**1.25**	**0.81**
F4	13.51	1.86	3.34	1.19	0.42	20.31	0.24	0.38	0.05	0.05	0.12	0.17
F5	14.71	0.92	3.81	1.60	0.81	21.86	0.26	0.19	0.06	0.07	0.24	0.16
F6	10.02	0.87	24.33	21.66	2.30	59.19	0.18	0.18	0.37	**0.98**	**0.68**	0.48
F7	15.93	1.43	4.67	5.16	1.34	28.53	0.28	0.30	0.07	0.23	0.40	0.26
Summer Season												
F1	3.87	0.38	0.80	1.23	0.20	6.47	0.07	0.08	0.01	0.06	0.06	0.05
F2	16.73	0.63	0.75	17.00	2.04	37.15	0.30	0.13	0.01	**0.77**	**0.60**	0.36
F3	**55.07**	1.87	3.20	12.98	4.01	77.13	**0.97**	0.39	0.05	**0.59**	**1.19**	**0.64**
F4	7.40	0.75	1.87	1.48	0.50	11.99	0.13	0.15	0.03	0.07	0.15	0.11
F5	4.40	0.53	1.58	1.36	0.34	8.21	0.08	0.11	0.02	0.06	0.10	0.07
F6	12.13	0.81	**66.83**	**45.80**	1.39	**126.96**	0.21	0.17	**1.03**	**2.08**	0.41	**0.78**
F7	10.80	0.56	31.93	10.36	0.75	54.40	0.19	0.12	0.49	0.47	0.22	0.30
Autumn Season												
F1	14.24	2.18	2.20	3.55	0.60	22.76	0.25	0.45	0.03	0.16	0.18	0.21
F2	**78.67**	1.81	2.15	**64.00**	4.66	**151.28**	**1.39**	0.37	0.03	**2.91**	**1.38**	**1.22**
F3	**88.76**	1.90	3.35	25.83	2.19	**122.02**	**1.57**	0.39	0.05	**1.17**	**0.65**	**0.77**
F4	26.93	2.23	7.95	3.37	1.08	41.57	0.48	0.46	0.12	0.15	0.32	0.31
F5	13.07	1.37	3.12	2.01	0.85	20.41	0.23	0.28	0.05	0.09	0.25	0.18
F6	13.37	1.26	13.61	17.49	1.69	47.41	0.24	0.26	0.21	**0.80**	**0.50**	0.40
F7	11.12	1.56	4.65	8.22	1.28	26.83	0.20	0.32	0.07	0.37	0.38	0.27
Winter Season												
F1	12.17	2.62	1.77	2.60	0.64	19.80	0.21	**0.54**	0.03	0.12	0.19	0.22
F2	**90.40**	2.88	2.50	**68.98**	5.79	**170.55**	**1.60**	**0.60**	0.04	**3.14**	**1.71**	**1.42**
F3	**91.82**	3.24	3.01	30.94	2.08	**131.08**	**1.62**	**0.67**	0.05	**1.41**	**0.61**	**0.87**
F4	24.47	2.30	1.70	2.99	0.74	32.19	0.43	0.48	0.03	0.14	0.22	0.26
F5	7.38	1.64	1.80	1.85	0.80	13.47	0.13	0.34	0.03	0.08	0.24	0.16
F6	11.51	3.23	4.21	13.98	1.53	34.45	0.20	**0.67**	0.06	**0.64**	0.45	0.40
F7	11.55	1.88	3.52	9.92	1.50	28.38	0.20	0.39	0.05	0.45	0.44	0.31

Notes: E^i_r is the monomial and R_I is the multinomial heavy metal potential ecological risk indices; ERM-Qi is the monomial and mERM-Q is the multinomial biological risk index; bold types indicate the sample sites with moderate and considerable ecological risk for “potential ecological risk index” and high-medium and high priority side for “biological risk index”.

DISCUSSION

Arsenic is associated with ores mined for metals, and may enter the environment during the mining and smelting of these ores, and it is clearly known that most anthropogenic releases of arsenic are to land or soil, primarily in the form of pesticides or solid wastes (ATSDR, 2005a). Silver mine located at the Gümüş Village, intensive agricultural activities carried on especially upstream of the basin, and pesticides used unconsciously may be caused the extreme arsenic accumulations in the sediment of F2 and F3 stations.

Silver can be found in natural environments in compounds with other elements especially with lead (ATSDR, 1990). In a study performed in Emet Stream that is in the domain area of a silver mine in Kütahya Province, significant positive correlations were reported between lead and silver accumulations in sediment of Emet Stream Basin ($p<0.05$) (Tokatlı, 2012). Also the lead accumulations detected in sediment of Emet Stream were significantly lower than detected in Felent Stream (Tokatlı *et al.*, 2012a). In the present study, extreme Pb concentrations detected in sediment of Köprüören Village (discharge point of a silver mine to the system) reflect that geologic structure of the basin and mineral processing of the silver mine can be the main lead sources of the system. It was stated in another study that the sediments of sites downstream of a copper mine plant in Tigris River (Turkey) showed significant enrichment with lead (Varol and Şen, 2012). Also, pesticides used in agricultural lands contain significant quantities of lead, and it is known that hunting activities have a significant effect on the lead contamination in the environment (one shot contains 32 gr lead) (Akman *et al.*, 2004; ATSDR, 2007). Therefore, use of pesticides and hunting activities carried on the rural areas of the system thought to be the prime causes of high lead accumulation in the upstream.

If we compare the data of the present study with another study performed in Felent Stream, it can be said that arsenic and lead levels in sediment of Felent Stream extremely increased in the course of time (Tokatlı *et al.*, 2012b).

Fertilizers have a significant impact on zinc transition to the soil, and rains can speed up this process (ATSDR, 2005b). Peak Zn levels of the present study were observed in mining – agricultural sections of Felent Stream Basin (F2 and F3 stations). Tokatlı (2012) reported that transportation of zinc compounds as a result of soil washing during the rainy season in the Emet Stream Basin (one of important agricultural area of Turkey) is significantly speeding up. As similar to this declaration, Zn accumulation in sediment of the entire basin increased during the rainy seasons.

The chromium level in soils depends on the composition of the rock structure from which the soils were formed, and rain helps to remove chromium from the air and washes chromium compounds out of many soils so that it eventually moves into the surface water (Fishbein, 1981; Merian, 1984; ATSDR, 2000). As similar to this information significant increase of Cr accumulations in sediment of Felent Stream Basin were determined in rainy seasons.

Copper, zinc and lead accumulations detected in the solid waste storage area (F6 station) were significantly higher than the other stations located in the downstream of the basin. According to the results of a study performed in India, one of the most important sources of lead and copper in lake sediments of Katedan Industrial Development Area is the random dumping of hazardous solid waste (Govil *et al.*, 2012). Arslan *et al.* (2011, 2012) reported that solid waste storage area of Kütahya Province is under effect of an important inorganic contamination, and this pollution has become a limiting factor for the aquatic life.

According to data observed, almost all element levels have decreased in the lenthic section of the basin (in Enne Dam Lake). This may be due to the resting of the water in the reservoir, and these results reflect that Enne Dam Lake has a significant cleaning capacity for the system. In a study performed in Yangtze River Basin in China, heavy metal levels in sediments were higher in the lakes than river (Yi *et al.*, 2011). Heavy metal levels may be high in sublittoral and profundal sediment samples collected from especially input sections of natural lenthic systems. In the present study, lenthic sediment samples were collected from the littoral zone and the sampling point was close to the output of reservoir. Köse reported that (2012) Porsuk Dam

Lake constructed on the Porsuk Stream (Sakarya River Basin) has an important cleaning capacity and water–sediment quality of the basin were significantly rising at the stations, which were close to the output of the reservoir. Also as similar to the present study, it was stated that water–sediment characteristics of the dam–out station was similar to the stream–source station in the Porsuk Stream Basin (Köse, 2012).

CONCLUSIONS

Some sample sites in the upstream (F2 and F3 stations) and in the downstream (F6 and F7 stations) of Felent Stream presented high ecological risk.

According to the potential ecological risk index for a single regulator, arsenic posed a moderate to considerable risk whereas lead posed a moderate risk. According to the biologic risk index for a single regulator, arsenic posed a high–medium to high priority chromium posed a high–medium priority; lead posed a high–medium to high priority and zinc posed a high–medium priority.

The ecological risk for all factors (R_I) showed that 25% of sampling sites were in the category of moderate risk, and the biological risk for all factors (mERM-Q) showed that 28.57% of sampling sites were in the category of high – medium priority.

The present study clearly presents the necessity and availability of the ecological risk assessment indices. As a result of the study, the direct discharge of a silver mine waste water and discharge of untreated industrial and domestic waste to the system should be prevented; use of pesticides and fertilizers in agricultural activities should be limited, and incentives should be provided to the agriculturalist supported by professionals. In epitome, control of the quantity and concentration of input contaminants and reduction of the stream pollution load are the most effective measures to improve the quality of the Felent Stream Basin.

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