Araştırma Makalesi *Research Article*

Türkiye'de Büyük Menderes Nehri'nde Ağır Metal Kirliliği Üzerine Bir Çalışma

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Öz

Bu araştırma Büyük Menderes Nehri'nde ağır metal kirliliğini saptamak amacı ile yapılmıştır. Büyük Menderes nehrinde seçilen 8 istasyondan 13 yıl boyunca alınan su örneklerinde Cu, Zn, Mn, Pb, Cd ve Fe parametreleri değerlendirilmiştir. Bakır Yenipazar Köprüsü'nde (10.02 ± 9.86) en düşük, Sarayköy Köprüsü'nde (18.46 ± 17.48) en yüksek; çinko Aydın köprüsünde en düşük (32.07 ± 18.14), Sarayköy Regülatöründe en yüksek (65.19 ± 55.54); mangan Adıgüzel Barajı'nda en düşük (41.61 ± 35.38), Sarayköy Regülatöründeki en yüksek (148.36 ± 105.02); kurşun, Adıgüzel Barajı'nda en düşük (4.01 ± 3.96), Yenipazar Köprüsü'nde en yüksek (9.95 ± 8.62); kadmiyum Söke Regülatörü'nde en düşük (2.37 ± 2.18), Sarayköy Köprüsü'nde en yüksek (2.61 ± 2.18); demir Adıgüzel Barajı'nda en düşük (77.21 ± 72.47), Söke Regülatöründe en yüksek (330.07 ± 306.24) olarak tespit edilmiştir. Sonuç olarak Büyük Menderes Nehri'nin kirlilik tehdidi altında olmadığı saptamıştır.

Anahtar Kelimeler: Büyük menderes nehri, Ağır metal kirliliği; Su kalitesi, Türkiye

A Study About of Heavy Metal Pollution in the Büyük Menderes River in Turkey

Abstract

This study has been conducted to find out the heavy metal pollution of Büyük Menderes River in Aydın. Water samples having been taken from 8 stations of the Buyuk Menderes for 13 years were examined in terms of Cu, Zn, Mn, Pb, Cd and Fe. The values were measured as the lowest in the Yenipazar Bridge (10.02±9.86) and the highest in the Sarayköy Bridge (18.46±17.48) for copper; the lowest in the Aydın Bridge (32.07±18.14) and the highest in the Sarayköy Regulator (65.19±55.54) for zinc; the lowest in the Adıgüzel Dam (41.61±35.38) and the highest in the Sarayköy Regulator (148.36±105.02) for manganese; the lowest in the Adıgüzel Dam (4.01±3.96) and the highest in the Yenipazar Bridge (9.95±8.62) for lead; the lowest in the Söke Regulator (2.37±2.18) and the highest in the Sarayköy Bridge (2.61±2.18) for cadmium; the lowest in the Adıgüzel Dam (77.21±72.47) and the highest in the Söke Regulator (330.07±306.24) for iron. Finally, it has been observed that Büyük Menderes River is not under the threat of pollution.

Keywords: Büyük menderes river, Heavy metal, Water quality, Turkey

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1. Introduction

Heavy metals are one of the most serious pollutants in our natural environment due to their toxic effect, persistence and bioaccumulation problems (Tam and Wong 2000). Heavy metals which are moved with water become extremely dilute and subside at the bottom of water by forming solid compounds as carbonate, sulfate, sulfur and become rich in this region. The heavy metal concentrations in waters always increase due to limited absorption capacity of sediment layer (Kahvecioğlu et al. 2008). The main sources of contamination include mining wastes, landfill leaches, municipal wastewater, urban runoff and industrial wastewaters, particularly from the electroplating, electronic and metal-finishing industries. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans (Sharma 2015).

At this point, when heavy metals exceed the concentration limits, they cause a toxic effect to both water and the body of creatures which they live in. Especially, if this effect is in the body of a creature, it changes by its type and structure of metal ions. Therefore, the maximum concentration limit must be determined and kept under control in foods obtained from water sources and regular drinking water. That's why determining heavy metal level of waters is so significant to detect pollution levels.

Many studies in the literature have focused on heavy metal pollution of water resources worldwide (Reza and Singh 2010; Nair et al. 2010, Hassan et al. 2010; Arslan et al. 2011; Akobundu 2012; Touraj 2015; Hayati et al. 2017). The Büyük Menderes river has a 584-km length and is the longest river in the Aegean Region in Turkey. The Büyük Menderes river basin is affected by human activities like industry, agriculture, urbanization, and tourism, as well as obstacles that hinder the movement of migratory fish and reduce water quality. While the river used to be a valuable water source for fishing and drinking water, today it cannot even be used as a quality source of irrigation water at many points due to these pressures and effects (Koç 2008). The study area is important tourist attraction. Therefore, it is necessary to assess the quality of the river water. The purpose of this study was to evaluate the concentrations and average distributions of heavy metals in Menderes River water using atomic spectrometry (AAS).

2. Material and Methods

2.1. Study area

The Büyük Menderes River is located in the western Anatolia, southwest Turkey, between 37° 6'–38° 55' North and 27°–30° 36' East. Borders of the basin which constitutes 3.2 % of Turkey's land surface includes parts of Aydın, Uşak, Denizli, Muğla, Afyon, Isparta, Burdur and İzmir provinces. With 584 km, it is the longest river in the Aegean Region. Many lateral streams feed the river, with the main tributaries being the Çine, Banaz, Çürüksu and Akçay rivers. The majority of small tributaries dry out in summer. As an important river system, the Büyük Menderes includes wetlands such as Işıklı Lake, Bafa Lake, and the Büyük Menderes River Delta. It is also a very important river basin in terms of biodiversity, being subject to the effects of both the Mediterranean and continental climates. The locations of the eight stations selected for this study are shown in Fig. 1. The stations were chosen deliberately to identify the degradation of the quality of the water as a result of the urban pollution observed in the area. Station 1 is the Adıgüzel Dam. In this dam, this problem results from the industrial residues which contain leather and textile as well as waste materials coming from Uşak. Station 2 is constituted by the Yenice Regulator. It is 32 km away from the Adıgüzel Dam where pollution stems from domestic waste and pesticides. Station 3 is the Sarayköy Bridge which is influenced by the wastes coming from the Denizli-Sarayköy sewage system, the geothermal plant nearby, and a textile factory. Station 4 is the Feslek Regulator. The Büyük Menderes River is polluted by domestic wastes coming from the nearby residential and industrial areas. Station 5 is the Yenipazar Bridge which is polluted by the water coming from the Akçay tributary in the Yenipazar Bridge. Station 6 is the Aydın Bridge which is affected mainly by untreated wastewater coming from the industrial zones and municipal sewage treatment plants nearby. Station 7 is the Koçarlı Bridge which merges with the Menderes following the Cine and İkizdere streams. Station 8 is the Söke Regulator, stations of which are polluted by the domestic wastes and pesticide packages coming from the nearby areas.
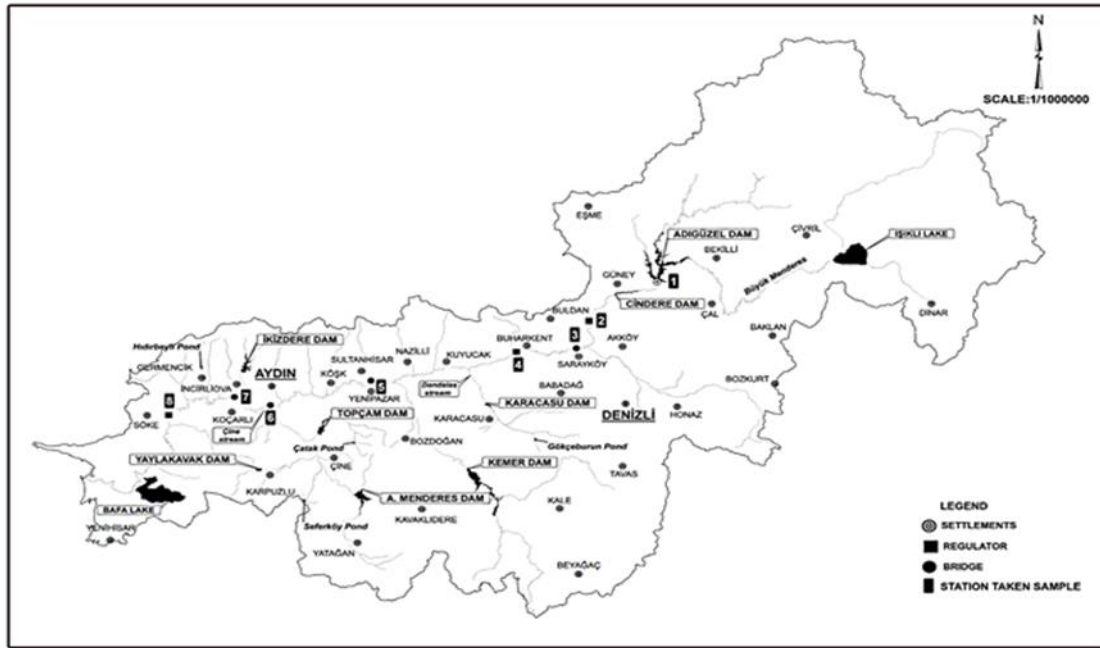
Figure 1. The sample stations from the Büyük Menderes River

2.2. Sampling and Analysis

The quality of the water was measured at 8 stations, namely the Adıgüzel Dam, the Yenice Regulator, the Sarayköy Bridge, the Feslek Regulator, the Yenipazar Bridge, the Aydın Bridge, the Koçarlı Bridge, the Söke Regulator).Water samples were collected in polyethylene bottles (washed with detergent, then with deionized water, 2 M nitric acid (Merck), then with deionized water again, and finally with surface water). Samples were acidified with 10 % HNO3, placed in an ice bath and brought to the laboratory. The samples were filtered through a 0.45 µm micropore membrane filter and kept at -20 °C until the analysis was conducted (Alam et al. 2001). The frequency of sampling was monthly. Heavy metal accumulation in the water samples was detected by means of Atomic Absorption device (Fifield and Haines 1997). Analyses of water samples were performed according to the international standard methods (Apha 2005) in the State Hydraulic Works 21st Region Directorate Quality Control Laboratory. The one-way analysis of variance (ANOVA) was conducted to evaluate among the sample stations. The Tukey multiple range test was used to discriminate between means. All statistical analyses were performed in the SPSS version 21 statistical software (IBM, New York, NY), and statistical decisions were based on an alpha of 0.05. The distribution of the data was illustrated via Box-Plot Graphs.

3. Results and Discussion

The copper value was the lowest in the Yenipazar Bridge (10.02±9.86 µg/l) and the highest in the Sarayköy Bridge (18.46±17.48 µg/l) as presented in Table 1.

Table 1. Results of heavy metal analyses of water samples taken from the Büyük Menderes River

Stations	Copper (µg/l)	Zinc (µg/l)	Manganese (µs/cm)	Lead (µg/l)	Cadmium (µg/l)	Iron (µs/cm)
Adıgüzel	10.41±9.98[c]	43.55±41.49[bc]	41.61±35.38[b]	4.01±3.96[e]	2.50±2.01[ab]	77.21±72.47[e]
Yenice	11.79±11.64[bc]	58.93±58.21[ab]	134.92±134.56[a]	7.92±7.56[bc]	2.50±2.09[ab]	151.32±149.92[d]
Sarayköy	18.46±17.48[a]	65.19±55.54[a]	148.36±105.02[a]	6.45±6.43[cd]	2.61±2.18[a]	176.19±172.09[d]
Feslek	14.39±14.14[abc]	64.30±63.93[a]	141.63±120.05[a]	5.88±5.87[de]	2.55±2.02[ab]	262.50±207.64[bc]
Yenipazar	10.02±9.86[c]	33.12±22.60[c]	123.61±82.37[a]	9.95±8.62[a]	2.52±2.15[ab]	267.90±267.03[ab]
Aydın	17.28±15.92[a]	32.07±18.14[c]	148.26±112.55[a]	5.92±5.82[de]	2.56±2.22[a]	202.84±178.17[cd]

| Koçarlı | 15.33±8.85[ab] | 54.68±50.32[ab] | 133.07±118.48[a] | 9.01±8.81[ab] | 2.50±2.09[ab] | 318.71±304.98[ab] |
| Söke | 12.25±11.10[bc] | 53.19±42.98[ab] | 132.61±115.83[a] | 7.23±4.57[bcd] | 2.37±2.18[b] | 330.07±306.24[a] |

The differences were observed to be significant in all of the 8 stations ($p < 0.05$). The copper was the lowest (5.83±1.26 µg/l) in 2003 and the highest (31.29±23.62 µg/l) in 2005. The difference between the years during which the study was conducted was found to be statistically significant ($p < 0.05$) (Figure 2).
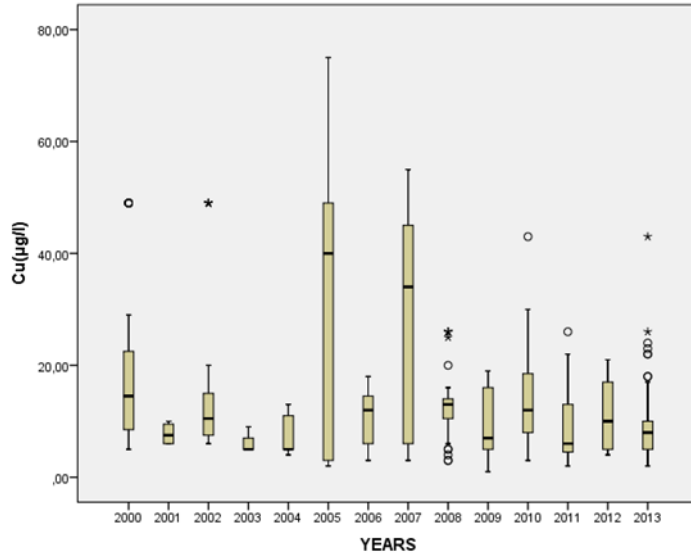

Figure 2. Change graphics of Cu values in the Büyük Menderes River during 2000-2013

The average copper metal level was reported to 1.55 µg/l, 10 µg/l, 13.25 µg/l, 27µg/l, 105µg/l and 2.48µg/l in the Brahmani, Ganga, Hazar, Sira, Subarnarekha and Euphrates rivers (Reza and Singh 2010, Aktar et al. 2010, Touraj 2015, Herojeet et al. 2015, Manoj and Chaudhury 2012, Hassan et al. 2010). According to WHO (1993), standard value of copper is 100 µg/l. Present findings are lower than standard. Some of the most important factors which cause copper to increase in the water are reported to be pesticides, cooling water discharge, textile industry, and car and lorry brake linings. Processed agriculture is heavily practiced in the Büyük Menderes Plain throughout the selected stations of the river and pesticides and fertilizers are also heavily used. The proximity of the stations to main roads is also another important factor. The zinc value was measured as the lowest in the Aydın Bridge (32.07±18.14) and the highest in the Sarayköy Regulator (65.19±55.54) as presented in Table 1. In all of the 8 stations, significant differences were determined in the annual zinc levels ($p < 0.05$). The zinc was measured as the lowest (11.60±5.67) in 2002 and the highest (111.29±78.70) in 2010. There were differences between all the years, and these differences were found to be statistically significant ($p < 0.05$) (see Figure 3).
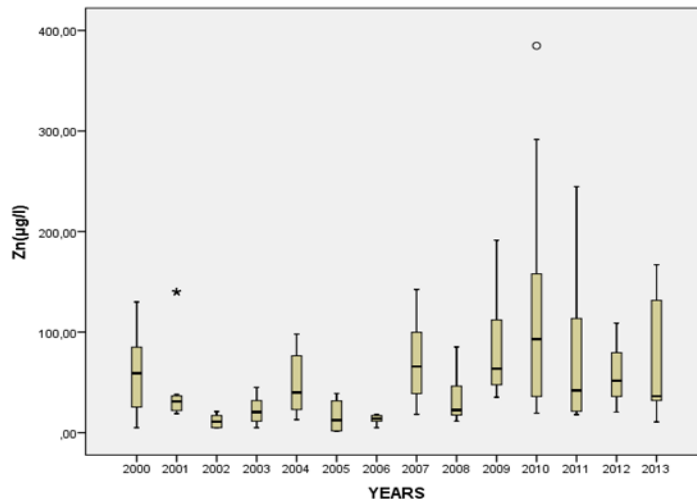

Figure 3. Change graphics of Zn values in the Büyük Menderes River during 2000-2013

The average zinc metal level was reported to be 5.00 µg/l, 20 µg/l in the San Andres Lagoon, Argungu rivers (Va´zquez-Sauceda et al. 2011; Obaroh et al. 2015). According to WHO (1993), Standard value of zinc in water is 3000 µg/l. Present findings of river are within the standard level. The fact that the pollution rate was found to be high in Sarayköy is associated with the presence of the geothermal facility in the region. The manganese value was measured as the lowest in the Adıgüzel Dam (41.61±35.38) and the highest in the Sarayköy Regulator (148.36±105.02) as presented in Table 1. In all of the 8 stations, significant differences were determined in the annual manganese levels ($p < 0.05$). The manganese was measured as the lowest (70.31±52.51) in 2005 and the highest (218.18±156.18) in 2012. There were differences between all the years, and these differences were found to be statistically significant ($p < 0.05$) (see Figure 4).
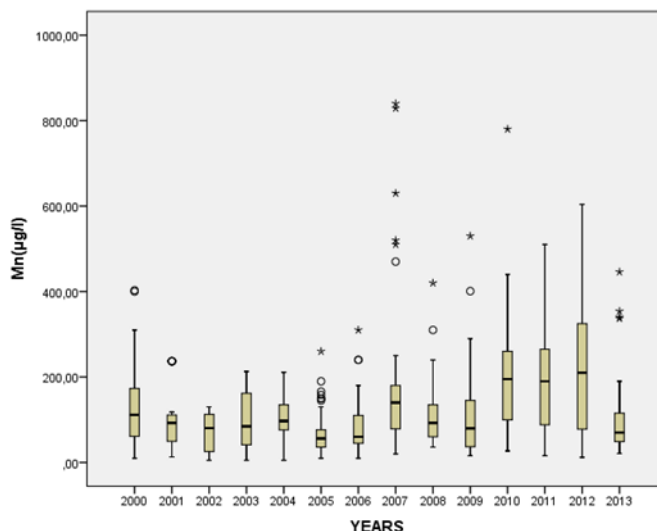

Figure 4. Change graphics of Mn values in the Büyük Menderes River during 2000-2013

Manganese is formed in domestic wastewater, industrial wastes and receiving river environment. Manganese has the lowest toxic effect among all heavy metals. In general terms, manganese data values are found within acceptable limits. While the Adıgüzel station has values quite below these limits, other stations fall into the moderately polluted water group in terms of manganese. In another study conducted by Arıman et al. 2007, the manganese averages in following rivers were reported as follows; 91 µg/l in Yeşilırmak, 134 µg/l in Abdal, 358 µg/l in Mert, 206 µg/l in Kürtün, 928 µg/l in Engiz and 310 µg/l in Kızılırmak. The average manganese metal level was reported to be 76 µg/l, 116 µg/l, 73.3 µg/l, 313.9 µg/l and 6.12 µg/l in the Subarnarekha, Hazar, Odra, Sirsa and Euphrates rivers (Manoj and Chaudhury 2012, Touraj 2015, Adamiec 2002, Herojeet et al. 2015, Hassan et al. 2010). The lead value was measured as the lowest in the Adıgüzel Dam (4.01±3.96) and the highest in the Yenipazar Bridge (9.95±8.62) as presented in Table 1. In all of the 8 stations, significant differences were determined in the annual manganese levels ($p < 0.05$). The lead was measured as the lowest (1.17±1.35) in 2008, and the highest (18.50±5.16) in 2003. There were differences between all the years, and these differences were found to be statistically significant ($p < 0.05$) (see Figure 5).
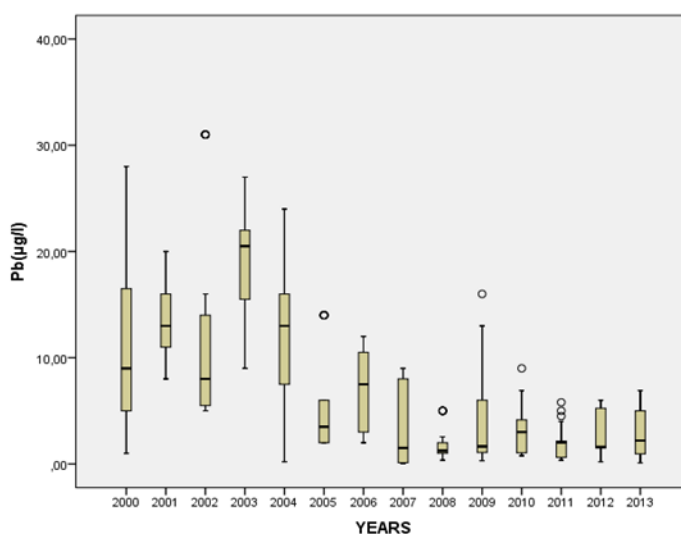

Figure 5. Change graphics of Pb values in the Büyük Menderes River during 2000-2013

The average lead metal level was reported to be 23 µg/l, 4.4 µg/l, 1.77 µg/l, 17.9 µg/l and 0.10 µg/l in the Subarnarekha, Hazar, Odra, Sirsa and Euphrates rivers (Manoj and Chaudhury 2012, Touraj 2015, Adamiec 2002, Herojeet et al. 2015, Hassan et al. 2010). According to WHO (1993), the standard value of lead is 20 µg/l. Present findings of river are within the standard level. The cadmium value was measured as the lowest in the Söke Regulator (2.37±2.18) and the highest in the Sarayköy Bridge (2.61±2.18) as presented in Table 1. In all of the 8 stations, significant differences were determined in the annual cadmium levels (p<0.05). The cadmium couldn't detected in 2009 and measured the highest (5.79±0.41) in 2007. There were differences between all the years, and these differences were found to be statistically significant (p<0.05) (see Figure 6).
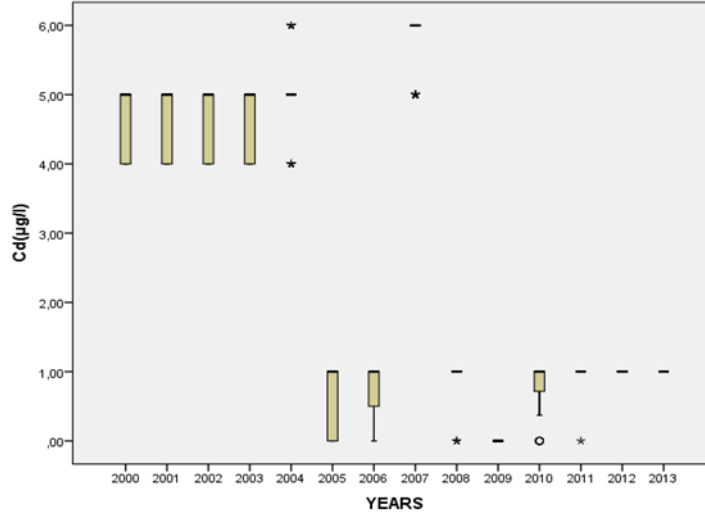

Figure 6. Change graphics of Cd values in the Büyük Menderes River during 2000-2013

The average cadmium metal level was reported to be 5 µg/l, 2.65 µg/l, 0.14 µg/l, 2.6 µg/l, 4.8 µg/l and 2.14 µg/l in the Ganga, Hazar, Odra, Sirsa, Subarnarekha and Euphrates rivers (Aktar et al 2010, Touraj 2015, Adamiec 2002, Herojeet et al. 2015, Manoj and Chaudhury 2012, Hassan et al. 2010). Cadmium is formed due to a good variety of reasons such as especially industrial waste in the environment, agricultural fertilizers and detergents. Standard value of cadmium is 3 µg/l for drinking and <1 mg/l for aquaculture. Present findings river exceeds the standard value in case of aquaculture but within acceptable for drinking. The iron value was measured as the lowest in the Adıgüzel Dam (77.21±72.47) and the highest in the Söke Regulator (330.07±306.24) as presented in Table 1. In all of the 8 stations, significant differences were determined in the annual iron levels (p<0.05). The iron was measured as the lowest (38.89±21.87) in 2012 and the highest (547.20±243.20) in 2004. There were differences between all the years, and these differences were found to be statistically significant (p<0.05) (see Figure 7).
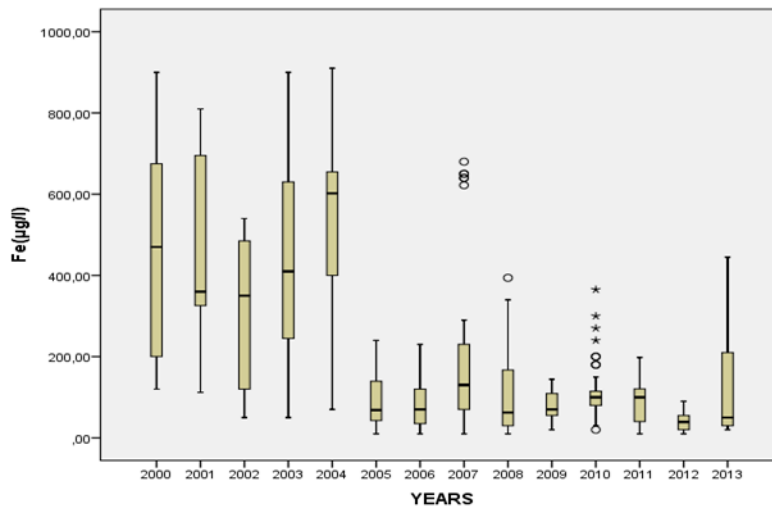

Figure 7. Change graphics of Fe values in the Büyük Menderes River during 2000-2013

In the study conducted on some rivers in the Central Black Sea, the iron averages in following rivers were reported as follows; 14 µg/l in Yeşilırmak, 29 µg/l in Abdal, 20 µg/l in Mert, 59 µg/l in Kürtün, 311 µg/l in Engiz and 553 µg/l in the Kızılırmak (Arıman et al. 2007). The average iron metal level was reported to be 800 µg/l, 480 µg/l, 23.33 µg/l, in the Ganga, Damodar, Brahmani rivers

(Aktar et al 2010, Chatterjee et al., 2010, Reza and Singh, 2010). In the Büyük Menderes River, there is no pollution in terms of Fe. Table 2 shows the results of the heavy metal samples statistical parameters computed using the chemical data.

Table 2. Result of heavy metal samples statistical parameters computed using the chemical data

Stations	Copper (µg/l)	Zinc (µg/l)	Manganese (µs/cm)	Lead (µg/l)	Cadmium (µg/l)	Iron (µs/cm)
n	84	84	84	84	84	84
Mean	13.76	50.63	125.51	7.05	2.51	223.34
Std. deviation	0.40	1.45	3.73	0.16	0.01	5.34
Minimum	12.95	47.77	118.17	6.73	2.48	212.84
Maximum	14.53	53.49	132.85	7.37	2.54	233.84

To observe the relationships among the studied elements, a correlation analysis was conducted. A correlation coefficient nearer to +1 or −1 indicates a perfect linear relationship between the two parameters. Table 3 shows the results of the Pearson correlation coefficients, which indicated various levels of relationships among the studied elements. As Table 3 shows, strong positive relationships (>0.5) were found between Cd and Cu, Fe and Cd, Pb and Fe, Pb and Cd. A negative relationship (−0.216) was found between Pb and Cu. The closest relationship (0.59) was the positive one between Cd and Fe.

Table 3. Coefficient correlation between the 6 elements in the River waters of Menderes

	Cd	Cu	Fe	Mn	Pb	Zn
Cd	1	0.058	0.595**	-0.049	0.524**	-0.118
Cu	0.058	1	-0.010	0.066	-0.216**	0.068
Fe	0.595**	-0.010	1	0.000	0.584**	0.004
Mn	-0.049	0.066	0.000	1	-0.009	0.224**
Pb	0.524**	-0.216**	0.584**	-0.009	1	-0.165**
Zn	-0.118**	0.068	0.004	0.224**	-0.165**	1

** Correlation coefficient were found >0.50

4. Conclusion

Studies on the dimensions of pollution in water resources must be conducted routinely in environmental terms. Direct interaction of both organism varieties in resource and waters with the environment requires prospective pollution inventories towards such resources. According to the evaluation made under the light of data obtained from ongoing studies at eight stations of the Menderes River for thirteen years, it can be seen that the river is not under the threat of intense pollution factors. Within the scope of these observations, significant precautions must be taken and this type of studies must be improved and conducted frequently.

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