

Heavy Metals Content in Water, Sediment, and Fish (*Mugil cephalus*) From Koycegiz Lagoon System in Turkey: Approaches for Assessing Environmental and Health Risk

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ABSTRACT

The concentration of heavy metals (Hg, Cd, As, Cu, Pb, Cr, and Zn) in the water, sediment and fish (*Mugil cephalus*) were investigated from different sites on Köyceğiz Lagoon System. Potential ecological risk analysis of heavy metal concentrations in sediments underlined considerable ecological risk for two sites of the lagoon during winter and spring. The ratio of transfer factors of Hg, Cr, Cu, Zn, and As in fish from water was higher than 1, which means that fish undergo bioaccumulation of these elements from lagoon water. The determination of individual Target Hazard Quotients (THQs) in fish tissue indicated safe levels for the local people, but there is a possible risk in terms of total THQ because the highest THQ value of As suggests that they may experience a certain degree of adverse health effect.

Keywords: Bioaccumulation, Ecological risk, Health risk, Köyceğiz, Target hazard quotients.

INTRODUCTION

Many aquatic systems have been contaminated by a variety of pollutants such as organics, inorganics, and heavy metals. Contaminants can also have serious effects on human health and organisms inhabiting the surrounding ecosystems (Apostol and Gavrilescu, 2009; Prabu *et al.*, 2011; Sing and Agrawal, 2013). The problem of heavy metals pollution of water, sediment and fish has received increasing attention in the last few decades in developing countries such as Turkey (Yorulmaz *et al.*, 2015). The increased urbanization, population growth and touristic activities have aggravated the metal pollution on south west of Turkey (Genç and Yilmaz, 2015). Heavy metals discharged into the lagoon environment can damage fish species diversity as well as ecosystems, due to their long persistence and toxicity (Ebrahimpour *et al.*, 2011, Saha and

Zaman, 2011). Sediments act as sinks and are known as potential sources of heavy metal in lagoon systems. In addition, results of reported literature have shown that water-sediment interaction in aquatic systems play an important role in bio monitoring metals accumulation processes (Thouzeau *et al.*, 2007).

Fish are well known for their major role in the aquatic food-web and they can take up and accumulate high metal concentrations (Mansour and Sidky, 2002). The results of many reported studies underlined that heavy metals in fish inhabiting polluted waters can be considerably accumulated by these organisms without causing mortality. For these reasons, the estimation of risk potential for human consumption of fish accumulating high quantities of heavy metals in their tissues is very important (Oglu *et al.*, 2015). Mulletts such as *M. cephalus*, *Liza aurata*, *L. ramada* and *L. saliens* have been considered as bio indicators and are generally used in

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pollution and risk assessment of aquatic systems (Guilherme *et al.*, 2008; Zorita *et al.*, 2008). In addition, *M. cephalus* is considered as one of the fish species commonly consumed by local population (Yilmaz, 2009).

The aims of this study were threefold: (1) To evaluate the heavy metal content in the water, sediment and *M. cephalus* of the Köyceğiz Lagoon system, (2) To assess the ecological risk of the sediment, and (3) To estimate health risk of heavy metals in the fish.

MATERIALS AND METHODS

Sampling Area

The Köyceğiz Lagoon System has been an interesting area for scientific studies at all times since the lagoon is a system of vital importance in south west of Turkey, not only from the physical point of view but also because of touristic and land based activities

in the area (Figure 1). The importance of Köyceğiz Lagoon System is due to several factors: (1) Most attractive tourist sites of the region are concentrated in the area, (2) The Lagoon System is a Specially Protected Natural Area administrated by the Authority of Specially Protected Areas (Bayari *et al.*, 1995); (3) The population that inhabit almost the whole Lagoon System Territory is increasing, and (4) Several river systems flow into the Köyceğiz Lake.

Sampling and Analyses

Water and sediment samples were seasonally collected during 2010 in eight selected stations throughout Köyceğiz Lagoon System (Figure 1). Fish were also caught every season but from different areas of the lagoon system since *M. cephalus* is a cosmopolitan species inhabiting coastal waters of the tropical and subtropical zones of all seas and often entering into estuaries and rivers.



Figure 1. Köyceğiz Lagoon System and sample points (Google Earth).

Table 1. Reference values (C_n^i) and toxicity coefficients (T_r^i) of heavy metals in sediments (Hilton *et al.*, 1985).

| Heavy metals | Hg | Cd | As | Cu | Pb | Cr | Zn |
|--------------|-----|-----|----|----|----|----|----|
| C_n^i | 0.2 | 0.5 | 15 | 30 | 25 | 60 | 80 |
| T_r^i | 40 | 30 | 10 | 5 | 5 | 2 | 1 |

Table 2. Terminology used to describe the risk factor E_r^i and R_I as suggested by Hakanson (1980).

| E_r^i | Potential ecological risk for single regulator | R_I | Ecological risk for all factors |
|---------------------------|------------------------------------------------|----------------------|---------------------------------|
| $E_r^i \leq 40$ | Low | $R_I \leq 95$ | Low |
| $40 \leq E_r^i \leq 80$ | Moderate | $95 \leq R_I < 190$ | Moderate |
| $80 \leq E_r^i \leq 160$ | Considerable | $190 \leq R_I < 380$ | Considerable |
| $160 \leq E_r^i \leq 320$ | High | $R_I \geq 380$ | Very high |
| $E_r^i \geq 320$ | Very high | | |

In total, 32 water and sediment samples and 70 fish samples (20 for winter, 27 for spring, 10 for summer and 13 for autumn) were collected. After collecting the samples, they were placed in an ice box, transported to the laboratory, washed with ultrapure water (Direct-Q 8UV Germany) and kept in a freezer (-20°C) before analysis. The liver, muscle and gill tissues were dissected using stainless steel knife which had been cleaned with acetone and distilled water prior to use. Water samples were collected at the surface in 40 mL acid-washed polyethylene sample bottles, taking care not to incorporate sediment into the samples. Water samples were filtered and analyzed directly. At each point, composite sediment samples were collected using standard protocol (USEPA, 2001). Each sediment sample was air dried at 105°C and sieved using a 2-3 mm. The operating conditions for fish and sediments were carried out applying the same procedure suggested by Karadede and Unlu (2000) and (Berghof speedway MWS-3+) digestion system was used. The elements were analyzed using ICP/AES (Optima 2000-Perkin Elmer), which is a fast multi-element technique with a dynamic linear range and moderate-low detection limits (Sturgeon, 2000). Standard reference materials, DORM-2 (for muscle), DOLT-2 (for liver) -National Research Council Canada SPS-SW1 (for water) and WQB1 (for sediment)- National Water Research Institute were used to analyze the heavy metals. Replicate analysis of these reference

materials showed good accuracy, with recovery rates for heavy metals between 92 and 107% for fish, 92 and 104% for sediment and between 94 and 102% for water. The absorption wavelengths and detections limits were 228.804 nm and $0.001 \mu\text{g g}^{-1}$ for Cd, 324.75 nm and $0.01 \mu\text{g g}^{-1}$ for Cu, 220.35 nm and $0.0042 \mu\text{g g}^{-1}$ for Pb, and 206.20 nm and $0.0059 \mu\text{g g}^{-1}$ for Zn, 276.716 nm and $0.0071 \mu\text{g g}^{-1}$ for Cr, 253.652 nm and $0.0610 \mu\text{g g}^{-1}$ for Hg, 193.696 nm and $0.0530 \mu\text{g g}^{-1}$ for As, respectively.

The potential ecological Risk Index (R_I) is a methodology developed by Hakanson (1980) to assess the degree of heavy metal pollution in sediments (Mora *et al.*, 2004; Zheng *et al.*, 2008).

$$R_I = \sum E_r^i, \quad E_r^i = T_r^i C_f^i, \quad C_f^i = C_o^i / C_n^i \quad (1)$$

Where, R_I is calculated as the sum of all Risk factors for heavy metals in sediments, E_r^i is the potential risk of individual heavy metal, T_r^i is the Toxic-response factor for a given heavy metal, as shown in Table 1. C_f^i is the Contamination coefficient, C_o^i is the present Concentration of heavy metals in the sediment, and C_n^i is a reference value for heavy metals (Table 1). The grading standards of potential ecological risk of heavy metals in sediment are listed in Table 2.

Transmission of metals from sediment to fish tissues is studied using a methodology called Transfer Factor (TF). It



is calculated as a ratio of concentration of a specific metal in fish tissue to the concentration of the same metal in sediment, both represented in the same units. *TF* of heavy metal in fish from lagoon ecosystem, which include water and sediment, was given as the quotient of

$$TF = \frac{\text{concentration of pollutant in fish}}{\text{heavy metal concentration in water or sediment}} \quad (2)$$

Target Hazard Quotient (THQ) is a powerful tool for estimating and analyzing heavy metal pollution. Several methods for the determination of potential risks for human health affected by heavy metal in fishes have been proposed. *THQ*, which is the ratio between the exposure and the reference doses (a Reference Dose or *RfD*), is quantitative estimate of health risks for noncarcinogenic effects (Yi *et al.*, 2011). *THQ* were developed by EPA in the US for the assessment of potential health risks associated with heavy metals pollutants (USEPA, 2000). This risk estimation method has recently been used by Chien *et al.* (2002) and proved to be valid and useful (Cardwell *et al.*, 1999; Hall *et al.*, 2000; Wang *et al.*, 2002). If the ratio of *THQ* is less than 1, it means the exposed population is assumed to be safe, and $1 < THQ < 5$ means that the exposed population is in a level of concern interval.

The models for estimating *THQ* were (Chien *et al.* 2002):

$$THQ = \frac{EFr \times ED_{tot} \times FIR \times C}{RfDo \times BWa \times ATn} \times 10^{-3} \quad (3)$$

$$\text{Total THQ (TTHQ)} = THQ \text{ (toxicant 1)} + THQ \text{ (toxicant 2)} + THQ \text{ (toxicant 3)} + \dots + THQ \text{ (toxicant n)} \quad (4)$$

Where, *THQ* is the Target Hazard Quotient; *EFr* is Exposure Frequency (365 d yr⁻¹); *ED_{tot}* is the Exposure Duration (77 years, average lifetime); *FIR* is the Food Ingestion Rate (g d⁻¹); *C* is the heavy metal

Concentration in fish (mg g⁻¹); *RfDo* is the oral Reference Dose (mg kg⁻¹ d⁻¹, Table 3); *BWa* is the average adult Body Weight (71.5 kg); and *ATn* is the Average exposure Time for non-carcinogens (365 d yr⁻¹ number of exposure years, assuming 77 years (TSI, 2010; 2013)).

To assess the correlation among heavy metals concentrations in sediments and fish tissues from the Köyceğiz Lagoon System, Pearson correlation and Kruskal-Wallis test followed by Mann-Whitney *U* test were performed by comparing the concentrations obtained for every season in the different samples. The potential ecological Risk Index (*R_i*), Transfer Factor (TF) and THQs (Target Hazard Quotients) calculations, Kruskal-Wallis followed by Mann-Whitney-*U* test were performed by means of the statistical software SPSS 20.0 and Microsoft EXCEL for Windows.

RESULTS AND DISCUSSION

Relationship between Heavy Metals Levels in Fish Tissue and in the Environment

The results of heavy metals concentrations of the water, sediments and fish tissue are presented in Table 4.

Concentrations of heavy metals in the sediment were 1,000-100,000 times higher than those in the water. Some previous studies have reported similar results (Demirak *et al.*, 2006; Kir *et al.*, 2007). The heavy metals concentrations were 10-1,000 times higher in fish than in water, but lower than in the sediments (Table 1). Fish fauna has generally higher levels of Hg, As, Cu, Cr and Zn compared with water, but lower levels when compared with sediment, except for As. Considering the heavy metals concentrations in sediment from the Köyceğiz Lagoon System, in spring,

Table 3. Oral reference doses of heavy metals (USEPA, 2009).

| Heavy metal | Hg | Cd | Pb | Cr | Cu | Zn | As |
|------------------------------------------------------|------------------------|----------------------|----------------------|-----|----------------------|----------------------|----------------------|
| <i>RfDo</i> , (mg kg ⁻¹ d ⁻¹) | 1.6 x 10 ⁻⁴ | 1 x 10 ⁻³ | 4 x 10 ⁻³ | 1.5 | 4 x 10 ⁻² | 3 x 10 ⁻¹ | 3 x 10 ⁻⁴ |

Table 4. Mean concentrations ($\mu\text{g g}^{-1}$) of heavy metal accumulation in water, sediment and fish tissue for each season (mean \pm SEM).

| | Hg | Cd | As | Cu | Pb | Cr | Zn |
|---------------------|------------------|------------------|-------------------|--------------------|-------------------|---------------------|----------------------|
| Winter | | | | | | | |
| Water (n= 8) | 0.001 \pm 0.00 | 0.034 \pm 0.00 | 0.00 \pm 0.00 | 0.066 \pm 0.00 | 0.074 \pm 0.00 | 0.00 \pm 0.00 | 0.087 \pm 0.00 |
| Sediment (n= 8) | 0.239 \pm 0.04 | 1.880 \pm 0.07 | 0.343 \pm 0.22 | 28.653 \pm 5.65 | 10.419 \pm 1.49 | 307.119 \pm 86.69 | 67.380 \pm 23.10 |
| Fish muscle (n= 20) | 0.008 \pm 0.00 | 0.087 \pm 0.03 | 0.557 \pm 0.20 | 5.777 \pm 2.56 | 1.087 \pm 0.17 | 0.915 \pm 0.10 | 35.212 \pm 6.16 |
| Fish gill (n= 20) | 0.034 \pm 0.01 | 0.042 \pm 0.01 | 0.290 \pm 0.03 | 1.123 \pm 0.44 | 1.518 \pm 0.18 | 1.506 \pm 0.26 | 18.223 \pm 3.10 |
| Fish liver (n= 20) | 0.099 \pm 0.02 | 0.150 \pm 0.02 | 1.025 \pm 0.12 | 13.658 \pm 3.09 | 1.641 \pm 0.17 | 3.292 \pm 0.677 | 51.890 \pm 5.97 |
| Spring | | | | | | | |
| Water (n= 8) | 0.001 \pm 0.00 | 0.724 \pm 0.03 | 0.020 \pm 0.01 | 0.055 \pm 0.00 | 0.062 \pm 0.00 | 0.00 \pm 0.00 | 0.074 \pm 0.00 |
| Sediment (n= 8) | 0.436 \pm 0.13 | 0.718 \pm 0.12 | 0.498 \pm 0.35 | 35.221 \pm 7.93 | 7.735 \pm 1.18 | 532.30 \pm 85.31 | 56.087 \pm 28.56 |
| Fish muscle (n= 27) | 0.00 \pm 0.00 | 0.481 \pm 0.08 | 0.796 \pm 0.15 | 43.425 \pm 9.25 | 0.210 \pm 0.09 | 3.198 \pm 1.09 | 92.598 \pm 13.20 |
| Fish gill (n= 27) | 0.00 \pm 0.00 | 0.003 \pm 0.00 | 0.030 \pm 0.01 | 2.066 \pm 0.12 | 0.264 \pm 0.12 | 3.178 \pm 1.27 | 29.214 \pm 8.30 |
| Fish liver (n= 27) | 0.00 \pm 0.00 | 0.033 \pm 0.02 | 0.114 \pm 0.02 | 3.157 \pm 0.58 | 0.578 \pm 0.15 | 1.919 \pm 0.30 | 43.355 \pm 8.05 |
| Summer | | | | | | | |
| Water (n= 8) | 0.001 \pm 0.00 | 0.054 \pm 0.05 | 0.001 \pm 0.00 | 0.001 \pm 0.00 | 0.001 \pm 0.00 | 0.155 \pm 0.15 | 0.001 \pm 0.00 |
| Sediment (n= 8) | 0.001 \pm 0.00 | 0.669 \pm 0.10 | 0.001 \pm 0.00 | 24.471 \pm 5.81 | 4.426 \pm 1.05 | 243.957 \pm 39.71 | 265.956 \pm 104.07 |
| Fish muscle (n= 10) | 0.086 \pm 0.07 | 1.427 \pm 0.13 | 1.375 \pm 0.287 | 32.268 \pm 7.97 | 0.652 \pm 0.43 | 2.902 \pm 0.33 | 121.106 \pm 25.06 |
| Fish gill (n= 10) | 0.00 \pm 0.00 | 0.238 \pm 0.00 | 0.014 \pm 0.00 | 0.510 \pm 0.142 | 0.090 \pm 0.09 | 3.480 \pm 0.40 | 5.975 \pm 5.97 |
| Fish liver (n= 10) | 0.000 \pm 0.00 | 0.318 \pm 0.04 | 0.268 \pm 0.21 | 0.810 \pm 0.15 | 0.320 \pm 0.11 | 5.812 \pm 3.38 | 25.158 \pm 1.75 |
| Autumn | | | | | | | |
| Water (n= 8) | 0.001 \pm 0.00 | 4.435 \pm 0.15 | 0.001 \pm 0.00 | 0.001 \pm 0.00 | 8.101 \pm 1.31 | 2.672 \pm 0.80 | 0.712 \pm 0.07 |
| Sediment (n= 8) | 0.001 \pm 0.00 | 0.795 \pm 0.17 | 0.001 \pm 0.00 | 30.430 \pm 6.21 | 4.639 \pm 1.07 | 388.50 \pm 69.43 | 20.937 \pm 17.12 |
| Fish muscle (n= 13) | 0.00 \pm 0.00 | 0.478 \pm 0.09 | 0.598 \pm 0.239 | 38.099 \pm 21.31 | 0.779 \pm 0.35 | 1.738 \pm 0.58 | 92.739 \pm 24.90 |
| Fish gill (n= 13) | 0.006 \pm 0.00 | 0.116 \pm 0.02 | 0.277 \pm 0.14 | 0.250 \pm 0.14 | 0.585 \pm 0.33 | 1.746 \pm 0.62 | 20.323 \pm 4.47 |
| Fish liver (n= 13) | 0.00 \pm 0.00 | 0.074 \pm 0.01 | 0.301 \pm 0.17 | 0.363 \pm 0.21 | 0.200 \pm 0.10 | 3.247 \pm 1.28 | 20.214 \pm 8.97 |
| Average | | | | | | | |
| Water (n= 32) | 0.001 \pm 0.00 | 1.149 \pm 0.34 | 0.005 \pm 0.00 | 0.030 \pm 0.00 | 2.059 \pm 0.69 | 0.706 \pm 0.28 | 0.218 \pm 0.17 |
| Sediment (n= 32) | 0.169 \pm 0.04 | 1.016 \pm 0.10 | 0.210 \pm 0.10 | 29.694 \pm 3.15 | 6.805 \pm 0.72 | 367.972 \pm 39.64 | 102.590 \pm 31.63 |
| Fish muscle (n= 70) | 0.012 \pm 0.00 | 0.476 \pm 0.06 | 0.758 \pm 0.10 | 29.901 \pm 5.69 | 0.626 \pm 0.11 | 2.220 \pm 0.46 | 78.897 \pm 8.42 |
| Fish gill (n= 70) | 0.011 \pm 0.00 | 0.061 \pm 0.01 | 0.154 \pm 0.03 | 1.270 \pm 0.16 | 0.682 \pm 0.11 | 2.432 \pm 0.53 | 21.780 \pm 3.69 |
| Fish liver (n= 70) | 0.029 \pm 0.00 | 0.109 \pm 0.01 | 0.436 \pm 0.07 | 5.435 \pm 1.13 | 0.788 \pm 0.10 | 3.035 \pm 0.52 | 39.301 \pm 4.23 |



summer and autumn, the data showed a highly significant positive correlation between Pb and Cd ($r < 0.921$, $r < 0.929$ and $r < 0.868$, respectively, $P < 0.01$). Moreover, there were significantly strong positive correlations between Zn and Cu in the same seasons ($r < 0.932$, $r < 0.739$ and $r < 0.955$, respectively, $P < 0.01$), whereas As did not show any significant correlation with any metal in any season. Several studies reported that the muscle of fish may not be a major repository of As. Nevertheless, our results showed a high As accumulation in fish muscle in every season. Seasonal statistical analysis showed that the significant differences were not found for As and Pb between spring and summer for all three fish tissues, but significant differences were observed for Cd in muscle in all seasons ($P < 0.05$), except between spring and autumn. Our results suggest that water temperature may affect the heavy metal accumulation in various organs. Higher temperatures in summer promote accumulation of Cd, As, and Zn in muscle. Although high accumulation of Cd was not observed in fish, concentration of Cd in fish muscle was close to the limit values ($0.50 \mu\text{g g}^{-1}$ for EU, 2006). The reason for this accumulation can be diet related because diet influences Cd accumulation in fish. Cd levels in carnivorous largemouth bass ($1.11 \mu\text{g g}^{-1}$ for *Micropterus salmoides*) and black crappie ($0.20 \mu\text{g g}^{-1}$ for *Pomoxis nigromaculatus*) are among the lowest whole-body trace metals concentration, while the more omnivorous warmouth ($1.43 \mu\text{g g}^{-1}$ for *Chaenobryttus gulosus*) and bluegill ($3.12 \mu\text{g g}^{-1}$ for *Lepomis macrochirus*) generally contain higher concentration (Murphy *et al.*, 1978). Our results support the hypothesis that the omnivorous fish such as *M. cephalus* are more able to accumulate Cd metals than other fishes. Pb accumulations in fish muscle were determined above the limit value in autumn and summer. It was observed that the highest Pb concentration in fish muscle and sediment was in winter when agricultural activities increase on Köyceğiz Lagoon System. A lot of study

indicates that gills are the major site of uptake of Pb, but, in the present study, the highest levels of Pb were found in liver. This situation can be explained considering that fish excrete Pb rapidly; therefore, Pb depuration generally reduces organ levels of Pb. However, in a 12-week depuration study, Holcombe *et al.* (1976) showed that liver continues to accumulate Pb for 2 weeks while the gill and kidney levels decrease. Our results support the theory that heavy metal concentration in sediment, water and uptake of heavy metal by fish could be altered by exposure time, season, differences in fish species, feeding type, climate, as well as by other factors. *M. cephalus* have been widely used as bioindicators of metal pollution studies which it showed the highest sensitivity to toxic effects of Cd, Pb and As.

Ecological Risk Assessment

The obtained potential ecological risk indices E_r^i and R_i for each site are listed in Table 5. According to these data, Cd showed considerable ecological risk at all sites in winter and also showed considerable ecological risk at Dalyan area in autumn. The considerable ecological risk for Cd found in winter is dangerous for benthic fish species because while Cd bound by metallothioneins and other proteins represents the so called 'detoxified Cd', Cd associated with higher molecular weight proteins ($> 20,000$ daltons) represents the potential for toxicity (Sorensen, 1991). Additionally, Hg showed considerable ecological risk at Dalyan area and high ecological risks at Sultaniye and Estuary area in spring. According to this, the control of the contamination sources of Hg in this area is highly suggested. Among the elements, Hg is one of the most hazardous to fish and other animals because of the tenacity with which Hg binds sulfhydryl groups. The high ecological risks of these Cd and Hg in lagoon ecosystems are consequences of their high toxic-response

Table 5. Potential heavy metal ecological risk indexes of the Köyceğiz Lagoon System.^a

| Sample Site | | E_r^i | E_r^i | E_r^i | E_r^i | E_r^i | E_r^i | E_r^i | R_i |
|-------------|----------------------|---------------|---------|---------|---------|----------|--------------|---------|---------------|
| | | Cd | Cr | Cu | Pb | Zn | Hg | As | |
| Winter | Namnam River | 114.78 | 6.69 | 4.74 | 2.54 | 0.60 | 17.6 | 0.00 | 146.98 |
| | Yuvarlakçay River | 120.90 | 30.06 | 2.96 | 0.47 | 0.53 | 53.6 | 0.27 | 208.54 |
| | Water treatment area | 132.42 | 10.19 | 10.84 | 3.31 | 2.68 | 105.2 | 0.00 | 264.93 |
| | Sultaniye | 92.88 | 5.45 | 1.94 | 1.70 | 3.06 | 39.8 | 0.11 | 144.83 |
| | Middle of the lake | 95.64 | 6.75 | 4.64 | 1.93 | 0.50 | 45.8 | 1.23 | 155.38 |
| | The entrance channel | 107.40 | 6.05 | 3.99 | 1.75 | 0.45 | 35.8 | 0.09 | 156.69 |
| | Dalyan area | 117.66 | 7.27 | 5.14 | 2.71 | 0.70 | 43.4 | 0.11 | 177.00 |
| | Estuary area | 121.14 | 9.38 | 3.91 | 2.22 | 0.43 | 41.6 | 1.88 | 178.82 |
| Spring | Namnam River | 17.70 | 30.98 | 3.57 | 0.61 | 0.39 | 20.8 | 0.00 | 75.95 |
| | Yuvarlakçay River | 56.94 | 26.97 | 7.38 | 2.08 | 1.06 | 29.4 | 0.00 | 123.84 |
| | Water treatment area | 71.94 | 17.35 | 13.88 | 2.21 | 4.19 | 62 | 0.61 | 171.59 |
| | Sultaniye | 45.00 | 8.186 | 4.34 | 1.12 | 0.35 | 171.6 | 0.00 | 231.22 |
| | Middle of the lake | 23.76 | 10.84 | 5.70 | 1.06 | 0.32 | 54.2 | 0.00 | 95.90 |
| | The entrance channel | 49.08 | 20.61 | 3.12 | 2.04 | 0.35 | 0.2 | 0.00 | 75.42 |
| | Dalyan area | 19.44 | 11.41 | 1.99 | 0.95 | 0.15 | 152.6 | 0.15 | 186.56 |
| | Estuary area | 61.08 | 15.55 | 6.93 | 2.28 | 0.63 | 207.2 | 0.00 | 293.84 |
| Summer | Namnam River | 15.90 | 13.71 | 2.12 | 0.15 | 0.01 | 0.2 | 0.00 | 32.10 |
| | Yuvarlakçay River | 46.98 | 4.762 | 3.62 | 1.27 | 2.05 | 0.2 | 0.00 | 58.89 |
| | Water treatment area | 33.96 | 5.21 | 8.40 | 0.74 | 4.48 | 0.2 | 0.00 | 53.00 |
| | Sultaniye | 23.40 | 3.69 | 3.58 | 0.47 | 3.02 | 0.2 | 0.00 | 34.38 |
| | Middle of the lake | 39.54 | 7.56 | 2.35 | 0.66 | 3.25 | 0.2 | 0.00 | 53.56 |
| | The entrance channel | 31.98 | 10.01 | 1.06 | 0.51 | 1.67 | 0.2 | 0.00 | 45.44 |
| | Dalyan area | 66.48 | 12.88 | 8.19 | 2.03 | 15.91 | 0.2 | 0.00 | 105.71 |
| | Estuary area | 63.12 | 7.19 | 3.28 | 1.23 | 5.04 | 0.2 | 0.00 | 80.07 |
| Autumn | Namnam River | 10.38 | 16.58 | 2.37 | 0.66 | 1.67E-05 | 0.2 | 0.00 | 30.20 |
| | Yuvarlakçay River | 19.32 | 15.25 | 4.56 | 0.00 | 0.13 | 0.2 | 0.00 | 39.47 |
| | Water treatment area | 38.70 | 8.81 | 11.97 | 1.04 | 2.34 | 0.2 | 0.00 | 63.07 |
| | Sultaniye | 39.06 | 6.21 | 4.72 | 0.40 | 1.67E-05 | 0.2 | 0.00 | 50.61 |
| | Middle of the lake | 61.08 | 10.20 | 5.39 | 1.28 | 0.04 | 0.2 | 0.00 | 78.21 |
| | The entrance channel | 63.72 | 26.53 | 4.23 | 0.98 | 0.14 | 0.2 | 0.00 | 95.82 |
| | Dalyan area | 108.12 | 12.15 | 3.42 | 2.05 | 1.67E-05 | 0.2 | 0.00 | 125.95 |
| | Estuary area | 41.22 | 7.82 | 3.88 | 0.98 | 0.12 | 0.2 | 0.00 | 54.24 |
| Average | | 60.96 | 12.26 | 4.94 | 1.36 | 1.70 | 33.87 | 0.14 | 115.26 |

^a The highest values in the table were shown in bold



factors. For other metals (Cr, Cu, Pb, Zn, and As), the potential ecological risk indexes were low. On the other hand, average risk assessment values for all metals in the sample sites indicate considerable ecological risk, except for the area of Namnam River. The potential ecological risk of the seven heavy metals decreased in the following sequence $Cd > Hg > Cr > Cu > Zn > Pb > As$. Consequently, the concentrations of Cd and Hg found in the sediments of the lagoon system represent the main concern according to human health risk. Ecological Risk Index (RI) was generally higher in the Dalyan area compared to the other stations, perhaps due to the pollution and the human disturbances produced by boats and shipping traffic travelling from sea to the lake.

Transfer Factor

Transfer Factor (TF) is a powerful tool for processing the bioaccumulation information for water, sediment, and fish. Heavy metals entering into the water body would be absorbed in sediments (Yi *et al.*, 2011) and can be accumulated by fish. *TF* can be an appropriate measure for the assessment. *TF* for water, sediment, and fish are listed in Table 6.

The results showed that the transfer factor of Hg, Cr, Cu, Zn and As in fish from water was greater than 1, and this means that fish undergo bioaccumulation of these elements from lagoon water. The order of transfer factor was as follows: $Cu > Zn > As > Hg > Cr > Pb > Cd$. The transfer factor of water was greater than sediments and this demonstrates that the fish bioaccumulate these elements, except As, from the water. Since the transfer factor of As for water and sediment are greater than 1, this shows a bioaccumulation of As in fish from both water and sediment.

Health Risk from Consuming Fish

Since it was demonstrated that heavy metals in fishes threaten the health of aquatic animals and humans, the assessments and control of the sources of heavy metal pollution is of great importance. Estimates of fish consumption of Turkey indicate that the population consumes 20 g/day of fish (FAO, 2008). *THQ* for individual metals and the total *THQ* from consumption of fish by general population in Köyceğiz Lagoon System are estimated. The *THQ* of each metal due to fish consumption is generally less than 1. Result show that this area will not confront a significant potential health risk by intake of a single metal through consumption of fish. But, it has been reported that exposure to two or more pollutants may result in additive or interactive effects (Hallenbeck, 1993). *THQ* values of Cd, Cu, and As were higher than the comparable values for Hg, Pb, Cr, and Zn for inhabitants of Köyceğiz Lagoon System. The potential health risk for Cr was the lowest, which may be ascribed to its higher oral reference dose. Arsenic (As), the major risk contributor for population in Köyceğiz Lagoon System, accounted for 60% of the total *THQ*. The other highest risk contributor element was Cu, contributing with about 18% of the total *THQ*. The next highest risk contributor element was Cd with 11%. The risk contributions of Pb and Zn were relatively low at about 3 and 6%, respectively. Both Cr and Hg contributions were low and similar at about 0.5%. This result shows that As, Cu, and Cd are the dominant contributors while relatively minor risk derives from Cr and Hg for inhabitants of Köyceğiz Lagoon System. The estimated *THQ* for individual metals decreased in the following sequence: $As > Cu > Cd > Zn > Pb > Hg > Cr$. The reason for the major risk of

Table 6. Transfer Factor (TF) of heavy metals in fish from the Köyceğiz Lagoon System.

| Elements | Hg | Cd | Pb | Cr | Cu | Zn | As |
|----------------|--------|--------|--------|--------|--------|--------|--------|
| Sediement/Fish | 0.1055 | 0.2118 | 0.1028 | 0.0069 | 0.4098 | 0.4544 | 2.1321 |
| Water/fish | 17.871 | 0.1873 | 0.3397 | 3.628 | 393.73 | 213.01 | 79.077 |

THQ for As can be due to the two-sided exposure from both water and sediment as calculated by the transfer factor. Obviously, the human health risk associated with fish consumption cannot be neglected and the sources of some heavy metals such as As in fish should be controlled. The discrepancy of total *THQ* for fish inhabiting Köyceğiz Lagoon System may be primarily attributed to the distinct contribution of As. Although it is known that heavy metal in fish can represent a threat for human health; the result showed no evidence of an unacceptable non-cancer risk for local population. However, Horiguchi *et al.* (2004) suggested that the ingested dose of heavy metals is not equal to the effective absorbed pollutant dose because a fraction of the ingested heavy metals may be excreted, whereas the rest is accumulated in body tissues and could affect the human health. Considering that the annual production of mullet in Köyceğiz Lagoon System is approximately 200 tons/year, the high *THQ* value of As found in the present study suggests that it can represent a potential concern for human health.

CONCLUSIONS

The paper presents interesting and original results on environmental and health risk assessment of heavy metals on Köyceğiz Lagoon System and explains the potential regional impacts of these heavy metals in details. On the basis of investigations carried on eight stations located throughout the watershed, heavy metal concentrations in sediment, water and fish tissues were measured. Potential environmental and health risk was evaluated and the possible sources of heavy metal pollution were analyzed. The heavy metal concentrations in the sediment were higher than water except for Cd. In fish tissue the highest Zn, Cu, As and Cd concentration were determined on muscle while the highest Hg, Pb and Cr were determined in liver. Analysis of the potential ecological risk of sediment heavy

metal concentrations showed that some area (Yuvarlakçay River and Sultaniye area on winter; Estuary area and Sultaniye on spring) presented considerable ecological risk. Conspicuously the potential ecological risk index for a single regulator (E_{ir}) for Cd represented a considerable risk in all sites on winter. The estimated *THQ* value was higher than 1 further suggesting potential health risk for local people by consumption of fish. Although a *THQ* involving a single heavy metal could be considered not significant, it may experience a certain degree of adverse health effect because the total *THQ* was accounted for 60% by As. To conclude, this study suggested a potential health risk for the local inhabitants by consumption of contaminated fish especially in term of As

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**مقدار فلزات سنگین در آب، رسوبات، و ماهی (*Mugil cephalus*) سامانه
تالاب Köyceğiz در ترکیه: روش هایی برای ارزیابی خطرات زیست محیطی و
بهداشتی**

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چکیده

در این پژوهش، غلظت فلزات سنگین (شامل Hg، Cd، Cu، As، Cr، Pb و Zn) در آب، رسوبات و ماهی (*Mugil cephalus*) در مناطق مختلف سامانه تالاب Köyceğiz بررسی شد. تجزیه و تحلیل خطرات زیست محیطی بالقوه غلظت فلزات سنگین در رسوبات، موکداً حاکی از



خطرات زیست محیطی چشمگیر در دو محل در اطراف تالاب و در فصل های زمستان و بهار بود. برخه ضریب انتقال برای Hg, As, Cu, Cr و Zn در ماهی مزبور بیشتر از ۱ بود و به این معنا، این فلزات در ماهی ها از آب تالاب و تحت فرایند زیست انباشتی (bioaccumulation) باقی می مانند. تعیین "برخه خطر هدف" (Target Hazard Quotient, THQ) در بافت ماهی حاکی از بی خطر بودن آن برای مردم محلی بود ولی یک خطر محتمل از نظر THQ کل وجود دارد زیرا مقدار بیشینه THQ مربوط به As چنین اشاره دارد که مردم محلی ممکن است تا حدودی دچار مشکلات بهداشتی شوند.