Bull Environ Contam Toxicol (2012) 89:419–423
DOI 10.1007/s00128-012-0670-3

Evaluation of Metal Pollution in Fish and Water Collected from Gorgan Coast of the Caspian Sea, Iran

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Received: 14 January 2012 / Accepted: 3 May 2012 / Published online: 5 June 2012

Abstract In this study, concentrations of zinc, chromium, cadmium and lead were determined in water and three species of fish sampled from 10 selected stations along Gorgan coast using atomic absorption spectrophotometery, summer 2009. Mean lead levels in water and fish samples (119.50 ± 22.24 μg/L and 113.80 ± 33.11 μg/kg) were significantly higher than that of cadmium and chromium ($p < 0.05$). *Cyprinus carpio* had highest metals content than *Mugila auratus* and *Rutilus frisikutum*. The evaluated metals values in water collected from Gomishan wetland (Pb, Cd, Cr and Zn values are 145.31 ± 35.32, 120.46 ± 11.44, 96.47 ± 6.05 and 82.02 ± 34.37 μg/L, respectively) were higher than the other sampling sites. The result is consistent with the findings accessed by evaluation of the metals in fish specimens. The metals concentrations in the fish and water samples were below the recommended limits. But, elevating levels of metals in water and fish made a serious concern about ecosystem and food chain contamination.

Keywords Metal · Contamination · Fish · Water · Gorgan coast

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Industrial progress and development of global population have led to an excessive contamination of ecosystems, particularly marine environment, by metals over the last three decades (Franca et al. 2005). Pollution is discharged into rivers and lakes and leaches into the soil and ground water, or is emitted into air as particulate matter (Abernathy et al. 1984; Diagomanolin et al. 2004). This has increased the concerns about the accumulation of metals in sediments, biota and ultimately humans (Gibbs and Miskiewicz 1995). Metals tend to accumulate in water (Förstner and Wittmann 1979; Daka et al. 2003), but may be released under certain physicochemical conditions, moving up through the food chain (Bryan and Langston 1992). It is of vital importance, hence studies are conducted to ascertain the level of concentrations of metals in environment (Biney 1991; Okoye 1991) and determine potentially hazardous levels for human (Shokrzadeh et al. 2008). Fish from estuaries and coastal waters associated with industrial and sewage discharges have been found to be contaminated with heavy metals (Tariq et al. 1993; Gibbs and Miskiewicz 1995).

Fish, as human food, are considered as a good source of protein, polyunsaturated fatty acids (particularly omega-3 fatty acids), calcium, zinc, and iron (Chan et al. 1999). In the future, seafood will even be a more important source of food protein than they are today; and safety of products from aquaculture for human consumption is as public health interest (WHO 1999). Metal residues in the fish flesh are serious, as are reflected by high metal concentrations recorded in water and sediments (Wong et al. 2001).

In this study, we assessed the concentrations of the metals (lead, cadmium, chromium and zinc) in water samples and three species of most consumed fish in Iran (*Cyprinus carpio*, *Mugila auratus* and *Rutilus frisikutum*) from the fishing stations of Gorgan coast, in summer 2009.

Materials and Methods

The area of sample collection is depicted in Fig. 1. Fish specimens and water samples were collected 10 sampling stations were selected along 4 regions (Gomishan wetland, Eastern and Western beach, and Gorgan coast), which were chosen based on ecological settings and human activities in the area. Gorgan coast is located at South-eastern Caspian Sea, and receives different inputs from industrial layout in addition to wastewater from a high density settlement.

The samples were collected from half surface, bottom and median depth of water at the stations on 3 specific times (8:00 a.m., 12:00 a.m. and 4:00 p.m.) using Eckman bottom sampler (ASTM 1990; Shokrzadeh and Saeedi Saravi 2009), and were kept in a 5-1 polyethylene jerrycans previously cleaned with acid (6 M HNO) and rinsed with deionized water. The bottom water samples were also collected, 30 cm above the bottom to avoid disturbance of the sediments. At each station, the pH of water was determined before filtering using a glass electrode. The 3 water samples (1 L) were mixed and wet digested; then, 25 mL of the samples was prepared with HCl 0.1 N, following the method adjusted by American Society for Testing and Materials (ASTM 1990; Tabari et al. 2010).

Furthermore, 78 fish samples, of approximately similar size to minimize the effect of the body weight, were collected manually using a cast net from the sites (Gomishan wetland, Eastern beach, Western beach and Gorgan coast), Caspian sea (Iran), and were cleaned, caught and stored in ice-cooled polyethylene bags for transportation to the laboratory. The fish were dissected and 25 g of dorsal muscle

Fig. 1 Location map of the studied zones showing sampling stations (Gorgan coast, Gomishan wetland, Eastern and Western beach)

GPS coordinates

#A: °36 42' 37" N: °53 52' 4" E , #B: °36 54' 34" N: °53 52' 00" E
#C1: °36 49' 53" N: °54 01' 57" E , #C2: °36 49' 50" N: °54 02' 2" E
#D: °36 54' 34" N: °53 02' 42" E , #E: °36 58' 17" N: °53 59' 49" E
#F: °36 58' 32" N: °53 59' 46" E , #G: °36 46' 24" N: °53 16' 52" E
#H: °36 48' 57" N: °53 51' 32" E , #I: °36 58' 12" N: °53 53' 42" E
#J: °36 57' 25" N: °53 53' 06" E

tissue was ash-dried and digested with HCl 0.1 N (ASTM 1990; Saeedi Saravi et al. 2009; Shokrzadeh and Saeedi Saravi 2010b).

Finally, all samples were analyzed using Atomic Absorption Spectrophotometer (AAS). The flame atomic absorption spectrophotometry was used for analysis of Pb and Cd, while Cr and Zn were measured by graphite atomic absorption spectrometry.

The metal concentrations were expressed in micrograms per kilogram (μg/kg) wet weight. Also, the metal concentrations in the water were expressed as micrograms per liter (μg/L). All data were analyzed descriptively by means of ANOVA, followed by Student t-test ($p < 0.05$). All statistical analyses were done using Prism software ver.3.

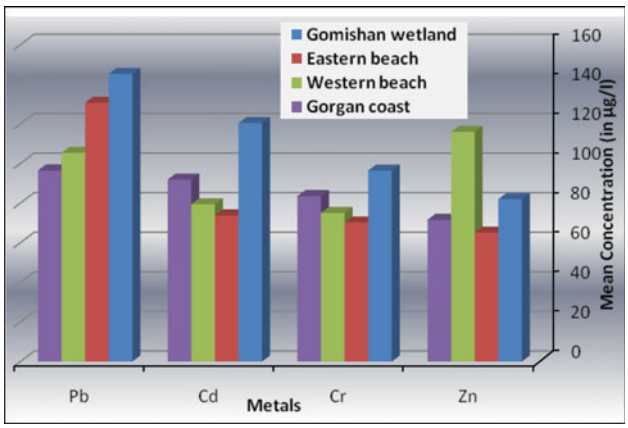

Fig. 2 Geometric mean Pb, Cd, Cr, and Zn concentrations (μg/L) in water from the 4 studied regions, summer 2009

Results and Discussion

The assessed concentrations of the metals in water samples are presented in Table 1. The results showed that mean concentration of lead in the water samples was significantly higher than zinc, cadmium and chromium levels ($p < 0.05$). Pb contents in water sampled from Gomishan wetland and Eastern beach (Abu-Hasani station) were 145.31 ± 35.32 μg/L and 130.71 ± 30.66 μg/L. The highest and lowest concentrations of Zn (116.02 ± 19.07 and 65.14 ± 15.32 μg/L) were found in the samples collected from Western beach and Eastern beach, respectively.

The highest concentrations of chromium ranged from 73.83 ± 24.43 to 120.46 ± 11.44 μg/L, were found in the samples collected from Gomishan wetland. The metals concentrations in water samples decreased according to the rank order of metals Pb > Cd > Zn > Cr (Fig. 2).

The observed concentrations of Cr and Cd in this present work are consistent with the findings of Obire et al. (2003).

Suspension of sediments into the water body may increase the metal concentration in the water. Large amounts of pesticides containing metal compounds are brought via surface runoff from the farms to the river, contributing highly to the agricultural pollution (Rauret et al. 1988; Diagomanolin et al. 2004; Shokrzadeh and Saeedi Saravi 2010a).

Gorgan coast is receiving organic matter in amount exceeding its natural purification capacity due to high population and industrial growth. The wastewater of industries is discharged to the coast and its related rivers directly, without any remediation; only a simple physical screening is being performed. Chemical fertilizers containing Ni and Pb used in agricultural industries of the regions around Gorgan coast are other sources for increased metal contamination (Diagomanolin et al. 2004). The concentration of Pb, Cd, Cr and Zn in water samples in summer are same as the data resulted from an analysis in spring 2008 (Shokrzadeh and Saeedi Saravi 2009). However, the observed metals concentrations in these water samples were below the recommended limits (standard limit for lead and cadmium is about 20-400 μg/L and for zinc and chromium is 100 μg/L, respectively). There should be continuous environmental pollution monitoring to check heavy metals hazard.

In the present study, the lowest and highest concentrations of cadmium (ranged from 23.19 ± 6.09 to 93.65 ± 21.02 μg/kg) were related to *Rutilus frisikutum* and *Ciprinus carpio*, respectively (Table 2). *C. carpio* had the highest levels of the three metals in comparison with *Mugila auratus* and *Rutilus frisikutum samples* ($p < 0.05$) (Fig. 3). The lowest lead level was found in *M. auratus* (58.37 ± 25.83 μg/kg), while the highest level was

Table 1 concentrations of Zn, Pb, Cd and Cr in the water sampled from the 4 regions, summer 2009

Sampling zones	Lead*	Cadmium*	Chromium*	Zinc*
Gomishan wetland	145.31 ± 35.32**	120.46 ± 11.44**	96.47 ± 6.05**	82.02 ± 34.37**
Eastern beach	130.71 ± 30.66**	73.83 ± 24.43**	70.25 ± 10.75**	65.14 ± 15.32**
Western beach	105.42 ± 4.29**	79.49 ± 19.70**	75.09 ± 10.43**	116.02 ± 19.07**
Gorgan coast	96.55 ± 18.70**	91.97 ± 10.59**	83.59 ± 26.06**	71.61 ± 8.92**

* The concentrations are based on Mean ± SD. (μg/L); Number of water samples (n = 30)

** The data were analyzed using one-way ANOVA and Tukey's post test ($p < 0.05$)

Table 2 concentrations of Pb, Cd and Cr in the fish sampled from Gorgan coast, summer 2009

Fish species	Sampling zones	Lead*	Cadmium*	Cadmium*
Cyprinus carpio	Gomishan wetland	143.01 ± 23.65	48.32 ± 10.47	48.32 ± 10.47
	Eastern beach	167.57 ± 57.33	93.65 ± 21.02	93.65 ± 21.02
	Western beach	79.36 ± 11.57	59.13 ± 10.96	59.13 ± 10.96
	Gorgan coast	169.8 ± 36.38	97.30 ± 8.90	97.30 ± 8.90
Mugila auratus	Gomishan wetland	91.32 ± 28.72	27.08 ± 7.46	27.08 ± 7.46
	Eastern beach	89.63 ± 48.05	36.84 ± 13.73	36.84 ± 13.73
	Western beach	71.36 ± 35.39	37.59 ± 11.98	37.59 ± 11.98
	Gorgan coast	58.37 ± 25.83	23.57 ± 6.67	23.57 ± 6.67
Rutilus frisikutum	Gomishan wetland	141.50 ± 31.54	48.12 ± 12.57	48.12 ± 12.57
	Eastern beach	98.96 ± 31.09	33.95 ± 16.03	33.95 ± 16.03
	Western beach	115.65 ± 48.35	23.19 ± 6.09	23.19 ± 6.09
	Gorgan coast	139.12 ± 19.43	60.71 ± 19.37	60.71 ± 19.37

* The concentrations are based on Mean ± SD. (μg/kg); Number of fish samples (n = 78)

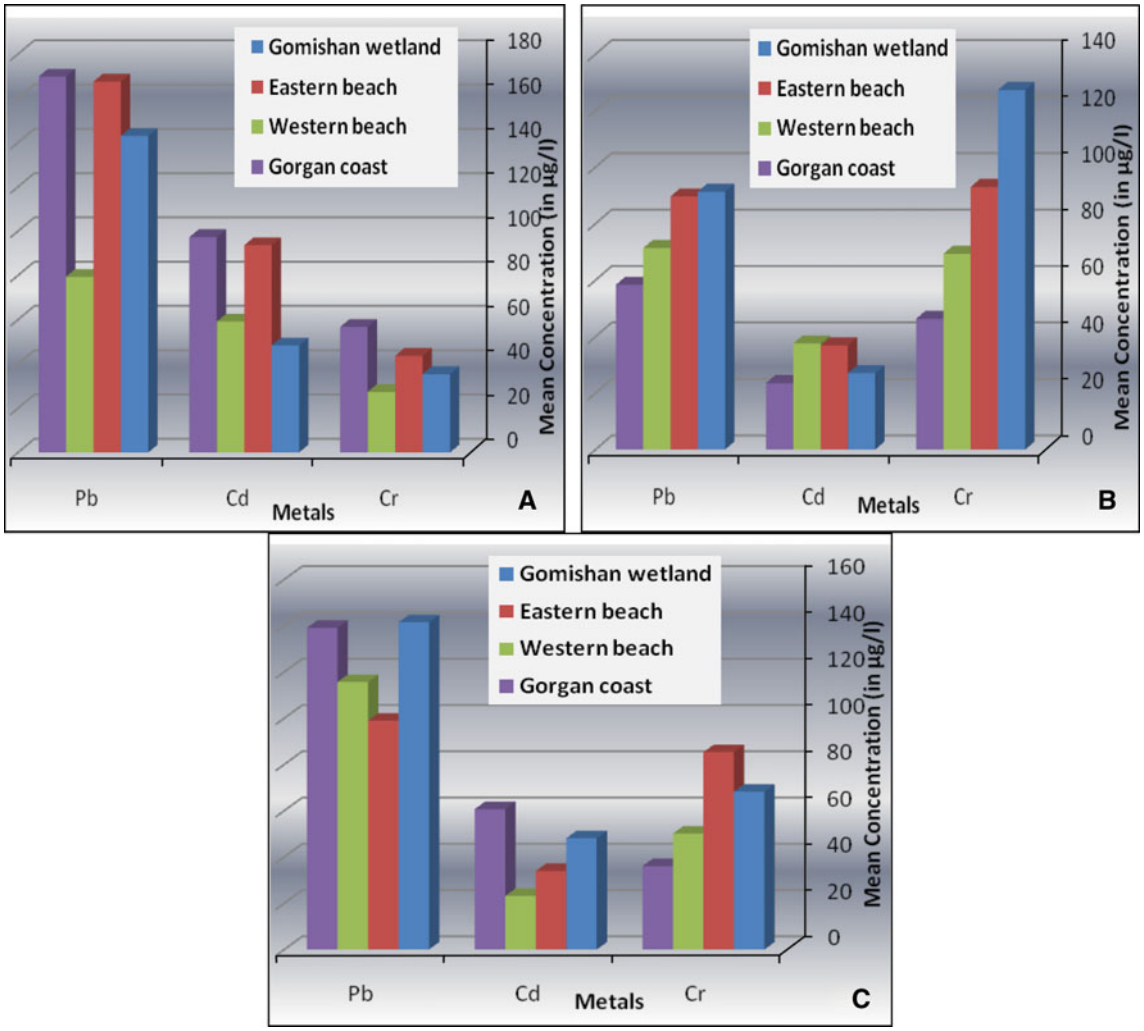

Fig. 3 Geometric mean Pb, Cd, Cr, and Zn concentrations (μg/L) in the fish collected from the 4 studied regions, summer 2009. Diagrams **a**, **b**, and **c** refer to *Cyprinus carpio*, *Mugila auratus*, and *Rutilus frisikutum* fish

observed in *C. carpio* (167.57 ± 57.33 μg/kg). The mean concentration of lead in the fish samples was significantly higher than that of cadmium and chromium levels ($p < 0.05$). The metals concentrations in the selected fish samples, similar to the results consequence from metals in water samples, decreased according to the rank order of metals Pb > Cd > Cr (Fig. 3). Findings resulted from a study performed in spring 2008 showed that Cr residual levels in fish samples were higher than that of Cd (Shokrzadeh and Saeedi Saravi 2010b).

The results imply that of the water, the likelihood of obtaining high lead dosage is more apparent than that of cadmium and chromium. The observed metals levels were lower than standard limits adjusted for safety of water and fish (standard limit for lead is about 100–200 μg/kg and for cadmium and chromium is 50 and 500 μg/kg, respectively). The concentrations of chromium, cadmium and lead found in the fish from Gorgan coast indicated that the fish are suitable for human consumption. But following development of scientific knowledge, determination of more precise limits is necessary to improve public health. Thus, the assessed metals levels may be higher the proceeding standard levels. As a result, guidance of farmers to use pesticides or fertilizers, control of house wastewaters spreading in rivers and crops, establishment of reference laboratories, etc. should be performed (Tabari et al. 2010).

The aim of this study was to determinate the metals concentration in three species of most consumed fish and water collected from Southern coast of Caspian Sea. The findings of this study showed that level of the metal in the evaluated samples within the standard limits set by various authorities. Finally, we recommend that a long-term continuous monitoring to check metals pollution, in order to control of metals in water, and fish (aquaculture), control and assessment of the metals content in water of Caspian Sea which was supplied by water used in agriculture, industries, quality of water of farmlands. Also, quality control of input and output water into Caspian Sea has widely importance. In addition, guidance of people and farmers about the instructions for use of pesticides or fertilizers, and control of house wastewaters spreading in rivers and crops are necessary.

Acknowledgment The valuable help of Research commission of Iran Organization of Environment in preparation of this manuscript is gratefully acknowledged.

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