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Heavy metals (Zn, Pb, Cd and Cr) in fish, water and sediments sampled form Southern Caspian Sea, Iran

Saleh Tabari[1], Seyed Soheil Saeedi Saravi[2], Gholamali A Bandany[3], Atena Dehghan[4] and Mohammad Shokrzadeh[5]

Abstract

Environmental pollution is a worldwide problem, heavy metals belonging to the most important pollutants. The progress of industries has led to increased emission of pollutants into ecosystems. Southern Caspian Sea coast is one of the most important aquasystems at the eastern south of Caspian Sea, which receives effluents discharges from heavily industrialized and highly populated settlements. Metals tend to accumulate in water and move up through the food chain. So, studies to ascertain the level of heavy metals in environment and determine potentially hazardous levels for human are necessary. In this investigation, concentration of four heavy metals (zinc [Zn], chromium (Cr), cadmium, [Cd] and lead [Pb]) in three species of most-consumed fishes, water and sediments have been determined. Samples were collected from 10 stations along the Southern coast of Caspian Sea, in spring 2008. Heavy metal concentrations were measured by graphite furnace atomic absorption spectrometry. Then, the data were analyzed by means of one-way analysis of variance (ANOVA) statistical analysis. The results showed that the highest concentration of heavy metals in water and fish and sediment samples were related to Pb and Zn. The minimal and maximal concentrations of these metals in fishes, water and sediments were 53.67−2360.67 and 50.36−2497.25 for Pb and Zn, respectively. However, the observed heavy metals concentrations in fish, water and sediments were below the recommended limits. The investigation showed elevating levels of heavy metals in environment. Thus, a serious notification to industrial and manmade pollution, which can lead to ecosystem and food chain contamination, is necessary.

Keywords

Caspian Sea, fish, heavy metals, sediment, water

Introduction

Environmental pollution and its hazards are the most important problems of societies and living creatures. On the other hand, increased population with the development of technology and production can cause a lack of attention to environmental safety (Saeedu Saravi et al., 2009). Industrialization leads to the pollution of ecosystems. Therefore, recognition of pollutants and prevention of their environmental dispersion are one of the necessities in this field. Therefore, we must determine the pollution sources, their environmental effects and prevention methods; also, filtration of industrial waste water and education of instructions for environmental protection is vital works to control and protect against pollutants.

[1] Central Forrum, Mazandaran University of Medical Sciences, Sari, Iran
[2] Faculty of Pharmacy, Mazandaran University of Medical Sciences, Mazandaran Pharmaceutical Research Center, Sari, Iran
[3] Inland Aquatics Stocks Research Center-Gorgan (IASRC), Iran
[4] Department of Food Science and Technology, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran
[5] Department of Toxicology-Pharmacology, Faculty of Pharmacy, Manzandaran University of Medical Sciences, Sari, Iran

Corresponding author:
M Shokrzadeh, Department of Toxicology-Pharmacology, Faculty of Pharmacy, Molecular Cell Biology Center, Mazandaran University of Medical Sciences, Sari, Iran
Email: M_ali_shokrzadeh@yahoo.com

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; Shokrzadeh et al., 2009b); also, this has increased the concerns about the accumulation of metals in sediments, biota and ultimately humans (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 (Zn), and iron (Chan et al., 1999). In future, seafood will be an even more important source of food protein than they are today and the safety for human consumption of products from aquaculture is of public health interest (WHO, 1999). Fish from estuaries and coastal waters associated with industrial and sewage discharges have been found to be contaminated with heavy metals (Chan et al., 1999; Gibbs and Miskiewicz, 1995; Tariq et al., 1993). Metal residues problems in the fish flesh are serious, as reflect by the high metal concentrations recorded in the water and sediments (Wong et al., 2001). On the other hand, heavy metals are critical in this regard because of their easy uptake into the food chain and because of bioaccumulation processes (Beijer and Jernelöv, 1986; Diagomanolin et al., 2004). Metals tend to accumulate in water (Daka et al., 2003; Förstner and Wittmann, 1979) but may be released under certain physicochemical conditions, moving up through the food chain (Bryan and Langston, 1992; Shokrzadeh et al., 2008a; Shokrzadeh et al., 2009b). It is of vital importance, hence studies are conducted to ascertain the level of concentrations of these metals in environment (Biney, 1991; Okoye, 1991) and determine potentially hazardous levels for human. Several studies were done to measure and determine the effects of heavy metals and trace elements on ecosystem and human. The studies showed that decreased content of antioxidative elements, such as Zn, selenium (Se) and manganase (Mn) and increased content of some elements including cupper (Cu), cobalt (Co) and arsenic (As), which probably elevate the oxidative stress, can cause some inflammatory diseases and cardiac functional disorders (Ala et al., 2009; Barandier et al., 1999; De-Lorgeril et al., 2001; Salehifar et al., 2008, Shokrzadeh et al., 2009a; Topuzoglu et al., 2003). On the other hand, lead (Pb) toxicity can lead to growth retardation, neuronal defects and anemia in children. Also, hepatotoxicity, nephrotoxicity and neurotoxicity can be occurred following Pb chronic toxicity (Shokrzadeh and Saeedi Saravi, 2008b). Cadmium (Cd) was reported to be associated with prostatic cancer, osteomalacia, inhalation toxicity and nephrotoxicity. In addition, chromium (Cr) was shown to be associated with some disorders, such as nasal septa defect (Shokrzadeh and Saeedi Saravi, 2008b).

Gorgan coast is located from 36°50' to 37° North and 53°30' to 53°50' East in the northern part of Iran and southeastern of Caspian Sea in the Golestan province (Figure 1). The coast is one of the most important ecosystems in the north of Iran, and receives different inputs from an industrial layout in addition to wastes from a high-density settlement. Presence of heavy metals in Caspian Sea poses a risk for food contamination and heavy metals and trace elements can cause hazards on ecosystem and human health. Therefore, the concentrations of heavy metals (Cr, Cd, Zn and Pb) in water, sediments and three species of most consumed fishes (*Cyprinus carpio, Mugila auratus* and *Rutilus frisikutum*) have been determined at 10 sampling stations along the Southern coast of Caspian Sea, in spring 2008.

Materials and methods

Location of 10 sampling stations established along 4 regions (Gomishan wetland, Eastern beach, Western beach and Gorgan coast) are determined in Table 1 and Figure 2. The sampling stations were chosen based on an experimental scheme design following ecological settings and human activities in the area. These regions are main fishing centers of Golestan province; and also, a variety of industries and touristic centers are concentrated in these regions. Following the large volume of population and industries located there, the four regions were selected to measure the heavy metals concentrations in fish, water and sediment samples during February 2008 to May 2008.

Fish sampling

In this study, 78 fish samples were collected using a cast net from the fishing stations (Gomishan wetland, Eastern beach, Western beach and Gorgan coast), Caspian Sea (Iran). The fish caught were placed in ice-cooled boxes for transportation to the laboratory where they were frozen until further processed.

Water sampling

The water samples at surface, bottom (20-m depth) and median depth (10-m) of water along Gorgan coast, Caspian Sea (Iran), were collected for three

Figure 1. Map location of Gorgan, Golestan province, Iran

Table 1. List of sampling stations

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

specific times (8 a.m., 12 noon and 4 p.m.) in spring after the rains, using the Eckman bottom sampler (ASTM, 1990; Jamabo and Chinda, 2010) and 1-L polyethylene acid-washed containers.

Sediment sampling

The top 20 cm of the bottom sediment samples were collected for three specific times from each sampling station in spring, using the Eckman bottom sampler (ASTM, 1990; Jamabo and Chinda, 2010) and kept in glass bottles (1 kg).

Subsequently, the three water samples (1 L) from surface, bottom and median depth were mixed separately and wet digested. Also, the sediment samples (1 kg) were mixed and wet digested. The fishes were dissected and 25 g of whole body was ash-dried and digested using 0.1 N HCl following the method of the American Society for Testing and Materials (ASTM, 1990).

The concentrations of Zn, Cr, Cd and Pb in water and sediment samples, and Cr, Cd and Pb in fish samples were assessed using graphite furnace Atomic Absorption Spectroscopy (AAS; Chemtech, Eng and

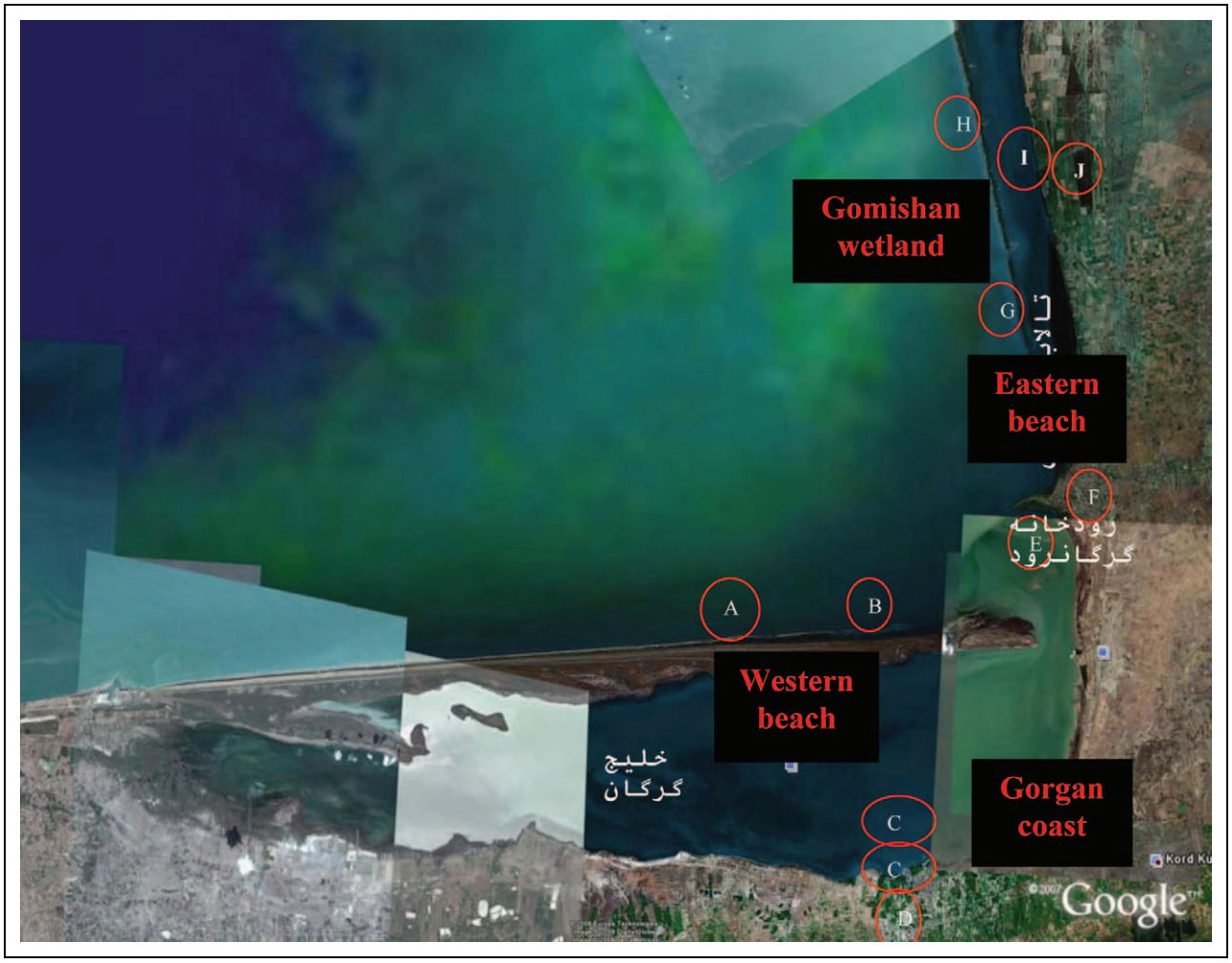

Figure 2. Sampling stations in Gorgan coast, Gomishan wetland, Eastern and Western beach

Alpha-4). Samples were quantified by using standard solutions of the stock solution of soluble salts of the respective metal (Krajca, 1989). Double distilled water (DDW) was used for dilution of the samples.

Statistical analysis

The data related to content of the heavy metals in water, sediment and fish samples were analyzed descriptively by means of one way-ANOVA, followed by Tukey post test ($p < 0.05$). All statistical analysis was done using Prism software ver.3.

Results

Heavy metals in fish samples

The results of the levels of concentration of the heavy metals in the fish samples are presented in Table 2. The highest concentrations of Cd ranged from 46.42 $\pm$ 11.57 to 95.90 $\pm$ 11.80 mcg/kg and were related to *Cyprinus carpio* fishes in the fishing stations. Also, *C. carpio* had the highest levels of these three heavy metals than *Mugila auratus* and *Rutilus frisikutum* ($p < 0.05$). The lowest value of Pb was found in *C. carpio* (78.43 $\pm$ 12.44 mcg/kg), while the highest value was found in *Mugila auratus* (180.08 $\pm$ 73.15 mcg/kg); the mean concentration of Pb in the fishes was significantly higher than that of Cd and Cr levels ($p < 0.05$).

The order of the heavy metals concentration in *Cyprinus carpio* in all regions was Pb > Cd > Cr.

Also, the order of the heavy metals concentration in *Mugila auratus* and *Rutilus frisikutum* in all regions was Pb > Cr > Cd.

Heavy metals in water samples

The results of the levels of concentration of heavy metals in the water samples are presented in

Table 2. The concentrations of Pb, Cd and Cr in muscle of the three species of fish

Fish species	Sampling zones	Lead[a]	Cadmium[a]	Chromium[a]
Corpus corpino	Gomishan wetland	141.14 ± 26.35	46.42 ± 11.57	34.29 ± 9.56
	Eastern beach	168.83 ± 69.53	91.93 ± 24.08	42.20 ± 14.29
	Western beach	78.43 ± 12.44	57.24 ± 13.57	24.37 ± 11.01
	Gorgan coast	168.9 ± 38.44	95.90 ± 11.80	50.43 ± 9.43
Mugila auratus	Gomishan wetland	88.52 ± 28.61	24.03 ± 9.96	130.29 ± 31.98
	Eastern beach	88.52 ± 67.15	33.94 ± 11.75	93.91 ± 21.83
	Western beach	69.76 ± 38.53	34.62 ± 11.26	67.71 ± 33.66
	Gorgan coast	53.67 ± 27.47	19.27 ± 7.31	43.90 ± 14.44
Rutilus frisikutum	Gomishan wetland	138.80 ± 32.73	44.62 ± 14.37	66.87 ± 29.90
	Eastern beach	99.15 ± 43.22	31.15 ± 18.92	82.15 ± 58.36
	Western beach	110.43 ± 67.47	20.89 ± 6.65	47.31 ± 24.29
	Gorgan coast	137.06 ± 21.23	58.71 ± 21.26	31.07 ± 10.95

[a] The concentrations are based on mean ± SEM; ppb (mcg/kg).

Table 3. The concentrations of Pb, Cd, Cr and Zn in the water sampled from the four regions (Gomishan wetland, Eastern beach, Western beach and Gorgan coast)

Zinc[a]	Chromium[a]	Cadmium[a]	Lead[a]	Sampling zones
58.23 ± 26.76	91.17 ± 15.85	101.28 ± 19.34	160.26 ± 34.81	Gomishan wetland
50.36 ± 9.63	126.02 ± 26.06	94.65 ± 24.71	164.84 ± 33.05	Eastern beach
120.61 ± 98.31	122.48 ± 50.99	91.24 ± 18.41	158.37 ± 35.58	Western beach
114.83 ± 106.38	115.89 ± 44.86	102.84 ± 26.02	148.60 ± 33.74	Gorgan coast

[a] The concentrations are based on mean ± SEM; ppb (mcg/mL).

Table 3. The results showed that Pb was the highest concentrated heavy metal in sampled water; the mean concentration of Pb in the water samples was significantly higher than that of Zn, Cd and Cr levels ($p < 0.05$). Pb contents in water sampled from Gomishan wetland and Eastern beach (Abu-Hasani station) were 160.26 ppb and 164.84 ppb. The concentration of Zn was highest at Eastern beach and lowest at Gorgan coast. Also, the highest concentrations of Cr ranged from 91.17 ± 15.85 to 126.02 ± 26.06 ppb and were related to Eastern beach.

The order of heavy metals concentration in water samples in all regions was Pb > Cr > Cd > Zn.

Heavy metals in sediment samples

The results of the levels of concentration of heavy metals in the sediments are presented in Table 4. The results showed that Zn was the highest concentrated heavy metals in sampled sediments; the mean concentration of Zn in the sediment samples was significantly higher than that of Pb, Cd and Cr levels ($p < 0.05$). Zn contents in sediments sampled from Makhtoom Qoli station and Abu-Hanifa were 2871.9 ppb and 2690.4 ppb. The concentration of Zn was highest in Gomishan wetland and lowest in Eastern beach. Also, the highest concentrations of Pb ranged from 1960.52 ± 736.32 to 2360.67 ± 632.65 ppb and were related to Gomishan wetland.

The order of the heavy metals concentration in sediments in all regions was Zn > Pb > Cr > Cd.

Discussion

The Cr and Cd concentrations in water and sediment samples recorded in this study 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. Sediment is the major depository of metals in some cases, holding more than 99% of total amount of a metal present in the aquatic system (Odiete, 1999). In addition, heavy rain fall leads to farm draining. Large amounts of pesticides containing metal compounds are brought via surface runoff from the farms to the river, contributing highly to the agricultural pollution. Chemical fertilizers containing Ni and Pb are used in agricultural industries of the regions around Gorgan coast. Fungicides are used

Table 4. The concentrations of Pb, Cd, Cr and Zn in the sediments sampled from the four regions (Gomishan wetland, Eastern beach, Western beach and Gorgan coast)

Zinc[a]	Chromium[a]	Cadmium[a]	Lead[a]	Sampling zones
2497.25 ± 509.59	615.62 ± 113.19	135.15 ± 41.25	2360.67 ± 632.65	Gomishan wetland
2239.02 ± 801.75	701 ± 138.79	139.75 ± 30.15	2331 ± 400.79	Eastern beach
2470.75 ± 695.64	703.07 ± 187.49	129.78 ± 25.05	2112.48 ± 288.92	Western beach
2451.4 ± 500.95	726.53 ± 220.96	121.7 ± 42.1	1960.52 ± 736.32	Gorgan coast

[a] The concentrations are based on mean ± SEM; ppb (mcg/mL).

in fish farming in order to prevent epidemic diseases, such as fin erosion. Fungicides and algaecides are used in the paper industry for pulp making, in order to protect papers from mould development; these preparations contain copper compounds (Diagomanolin et al., 2004; Rauret et al., 1988). Gorgan coast is receiving organic matter in amount exceeding its natural purification capacity due to high population and industrial growth. Pb, Cu, Cr and Ni compounds are used as pigments in the painting industry and as anti-fouling agents in marine paints (Diagomanolin et al., 2004; Ramelow et al., 1992). Otherwise, Local industries in Gorgan and Aq-Qala (the cities of Golestan province) use Cr, Cd and Zn compounds in electroplating. In the past, natural purification and dilution were usually sufficient (Saad et al., 1994). Also, the wastewater of these industries is discharged to Gorgan coast and its related rivers directly, without any remediation; only a simple physical screening is being performed. Several sources for the increased metal concentrations appear likely (Diagomanolin et al., 2004).

The results implies that of all the water, sediment and fish species examined, the likelihood of obtaining high Pb dosage from eating fish from the study area is more apparent than that of Cd and Cr. Pb is known to cause serious concern to health, but the contamination of the sea and sea products does not appear to be a matter for serious concern (Clark, 1997). The safe limits for heavy metals in seafood vary from region to region (Ashraf, 2006). The concentrations of Cr, Cd and Pb evaluated in the fish selected from Gorgan coast indicated that consumption of fishes sampled from Caspian Sea may not cause hazardous effects on human health. However, determined values of Pb, Zn and Cd in the water samples were below the recommended standard limits (standard limit for Pb and Zn is about 0.1−0.2 mg/L and for Cd is 0.5 mg/L), but Cr values were higher than tolerable standards (0.05 mg/mL; Joine FAO/WHO food standards programme, 1990; Linneman et al., 1973). On the other hand, Pb and Cd intake from daily food is considered to be 20−400 ppb and 400−500 ppb. So, the measured values of Pb and Cd in the fish samples were lower than standard detected metal concentrations in food (Emami-Khansari et al., 2005; Joine FAO/WHO food standards programme, 1990; Linneman et al., 1973).

The aim of this study was determination of the heavy metals concentration in three species of most consumed fish, water and sediment sampled from Southern coast of Caspian Sea. Then, the heavy metal values were compared with standard limits. The results showed that level of the heavy metal in the evaluated samples are in standard range. However, there should be continuous environmental pollution monitoring to check heavy metals hazard. In order to control heavy metals level in water, sediment and fish (aquaculture) of Caspian Sea, quality control of water of farmlands, quality control of input and output water, and assessment and control of the metals content in water of the sea which was exposed to water contamination, resulted from farmlands and industries have wide importance. Also, heavy metals content of input soils to Caspian Sea, which enter with rain and rivers form local farmlands and industries, should be assayed. Guidance for people and farmers about the instructions for use of pesticides or fertilizers, determination of sedimentation process in Caspian Sea, control of house wastewaters spreading in rivers and crops, establishment of reference laboratories equipped with analytical apparatuses etc are necessary.

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