original article

Evaluation of arsenic, lead and cadmium concentrations in fish samples of Zayanderoud districts

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ABSTRACT

Aims: This research was conducted to evaluate the Arsenic (As), Lead (Pb), and Cadmium (Cd) concentrations in fish flesh samples of Bara'an (east of Isfahan) as a contaminated zone. In addition, the obtained result was compared with a control fish group from behind dam area (west of Isfahan).
Material and Methods: In this cross sectional study, 21 fish samples were collected from both the areas and heavy metals concentration was measured by flame Atomic absorption spectrometric method (PERKIN Elmer model 2380).
Results: The mean amount of As were 2.97 ± 1.51 and 2.87 ± 0.3 mg/kg in the behind dam and the Bara'an areas, respectively. The mean amount of Pb were 0.66 ± 0.37 and 0.32 ± 0.17 mg/kg in the behind dam and the Bara'an areas, respectively. The mean concentration of Cd were 3.7 ± 4.11 and 86.64 ± 32.4 mg/kg in the behind dam and the Bara'an areas, respectively. The *t*-test showed no significant differences between the mean concentrations of As in both groups (2.97 Vs 2.87) ($P = 0.78$). The mean concentrations of Pb in the Bara'an area was significantly less than the behind dam area (0.32 Vs 0.66) ($P < 0.001$). Instead the mean concentration of Cd in the Bara'an area was significantly more than behind dam area (86.64 Vs 3.7) ($P < 0.001$).
Conclusion: This study confirmed that the fish samples from Zayanderoud at Bara'an and behind dam was contaminated by As, Pb, and Cd. Therefore, we suggest that the heavy metal levels should be monitored regularly.

Key words: Arsenic, cadmium, fish, Isfahan, lead

INTRODUCTION

Annually, million tons of waste chemicals produced in the world, which is of hazardous nature, create environmental and social concern in the 21th century.[1] The solid waste leachate is the source of one of heavy metals. Heavy metals are nonbiodegradable and their concentration may be increased in food chains. Therefore, heavy metal can threaten our life.[2] The heavy metals are released to the environment from sources including: Tannery factories, steel companies, battery storages, rubbers, and sewage, which find their way to the rivers and seas.[3]

Acute poisoning of Arsenic (As) may be related to acute paralytic syndrome, cardiovascular collapse, and loss of brain function. The As toxicity can lead to encephalopathy,

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gastrointestinal symptoms, skin pigmentation and dermatitis, peripheral vascular disease, neuropathy, genotoxicity, and cancer. Long-term ingestion of As increases the risk of cancers of the skin, bladder, and lung.[4] The Food and Nutrition Board does not establish a DRI (Dietary Reference Intakes) or tolerable upper intake level (UL) for As dietary. The US Environmental Protection agency reported that the maximum tolerable level for As in drinking water was 10 μg/l.[4] Based on reported results of Australia, Brazil, France, Japan, New Zealand, and Singapore, the Joint FAO/WHO (Food and Drug Administration/World Health Organization) Expert Committee on Food Additives reported that the total and inorganic As concentration in fish was 0.10-62 and 0.001-1.2 mg/kg, respectively.[5] The maximum concentration level of As is 0.2 mg/kg for fish.[6]

More than 80% of Cadmium (Cd) intake is concentrated in the kidneys and liver and result in the symptoms of intoxication.[7] The Cd included B_1 carcinogens and its increscent in human body causes bone disease, respiratory failure, hepatic diseases, renal failure, cardiovascular diseases, and hypertension. Also, Cd can remain in the placenta and prevents absorption of Zn and Cu by the embryo.[8-10] Based on the WHO guidelines, the maximum acceptable concentration of Cd in drinking water is 3 μg/l.[11] The collected data from 19 European and 11 nonEuropean countries showed that the concentration of Cd varied from not detectable to 0.008 mg/kg in Finfish.[12] The maximum concentration level for Cd was 0.1 mg/kg for fish.[6]

The high amount of Lead (Pb) intake was transported to the bone.[13] Pb is an unproven carcinogen and fall in B_2.[14] Pb can have an effect on the central nervous system, reduce IQ in children,[14] replace Calcium in tissues, block many enzymes, and prevent heme synthesis.[15] The data of the Joint FAO/WHO Expert Committee showed that the mean and maximum concentration of Pb were 0.054 and 4.06 mg/kg in all seafood.[12] The maximum concentration level of Pb was 0.5 mg/kg in fish.[6]

Other studies reported that heavy metals can be accumulated in different organs of fish and marine animals and may ultimately affect the human food chain.[16-21] This study was aimed to evaluate the As, Pb, and Cd concentrations in fish samples of Bara'an (east of Isfahan) as a contaminated zone and control fish group from behind dam zone (west of Isfahan).

MATERIALS AND METHODS

This cross sectional study was performed in 2010. The 21 living fish samples (carp) were collected from behind dam (control samples) and nearby Bara'an. The fish flesh was analyzed to determine the concentrations of As, Pb, and Cd; other organs were discarded. The fish flesh was maintained in cold box and transferred to laboratory. The samples were maintained in −20°C freezer.

Samples preparation

After fishing, the flesh of the fish was weighed and oven dried at 80°C; then the dried fish flesh was cooled and reweighed in plates containing parafilm. In order to digestion, 0.5 g of dried fish flesh was added into a vessel containing 5 ml of HNO_3, digested at batch system in 150°C oven for 2 h.[22]

Pb and Cd determination

The digested aliquot was poured into a 50 ml tube and 2 ml of nitrate solution was added and oven dried at 375°C for 15-20 min and then at 450°C for 10-20 min after cooling, 1 ml of HNO_3 (1+1) was added and dried by hot plate. The remaining matter was dissolved in 5 ml of HNO_3 (0.5 ml/l) and diluted with H_2O to volume with H_2O.[22]

Arsenic determination

The digested aliquot was poured into a 50 ml tube and 2 ml of nitrate solution was added and oven dried at 375°C for 15-20 min and then at 450°C for 10-20 min. After cooling, 1 ml of HNO_3 (1+1) was added and dried by hot plate. After cooling, the residual matter was dissolved in 2 ml of HCl (8M) and added 0.1 ml of KI (20%) and then kept for 2 min. The Pb, Cd, and As concentrations were determined by atomic absorption spectrophotometer (PERKIN Elmer model 2380). All tests were done in triplicates for both the control and case samples. The accuracy of Pb, Cd, and As was 96%, 100%, and 100%, respectively.[22]

Statistical analyzes

The significant differences between the heavy metals concentration in the case and control samples were examined by *t*-test. The results were considered significant when *P*-value <0.05.

RESULTS

The concentrations of As, Pb, and Cd in the fish samples from behind dam and Bara'an area were studied. The results of the heavy metals concentration in the fish sample from the control and case regions are illustrated in Figures 1 and 2, respectively. As seen in Table 1, The concentrations of As, Pb, and Cd at behind dam and Bara'an area samples were 2.97 ± 1.51 and 2.87 ± 0.3 mg/kg (for As), 0.66 ± 0.37 and 0.32 ± 0.17 mg/kg (for Pb), and 86.64 ± 32.4 and 3.7 ± 4.11 mg/kg (for Cd), respectively.

The *t*-test showed no significant differences between average As concentration in the fish samples from behind dam and Bara'an area ($P = 0.78$), but Pb concentration in Bara'an area was significantly less than behind dam ($P < 0.001$). Also, the concentration of Cd in the fish sample from Bara'an area was significantly more than behind dam ($P < 0.001$).

DISCUSSION

Zayanderoud River originates from the Zardkoohe Bakhtiary mountain and passes through Fereydan, Fereydoonshahr,

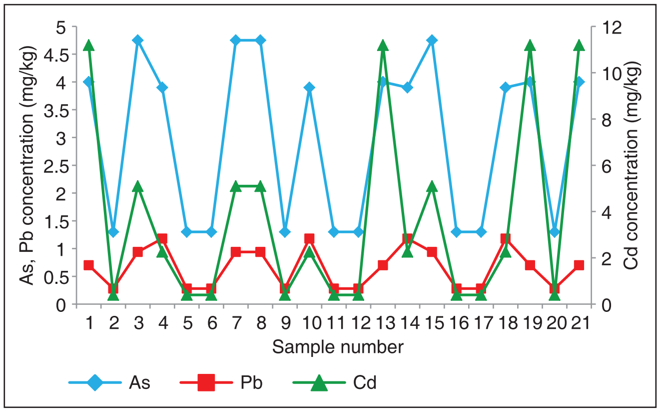

Figure 1: Variation of As, Pb, and Cd concentration in collected fish sample from case region

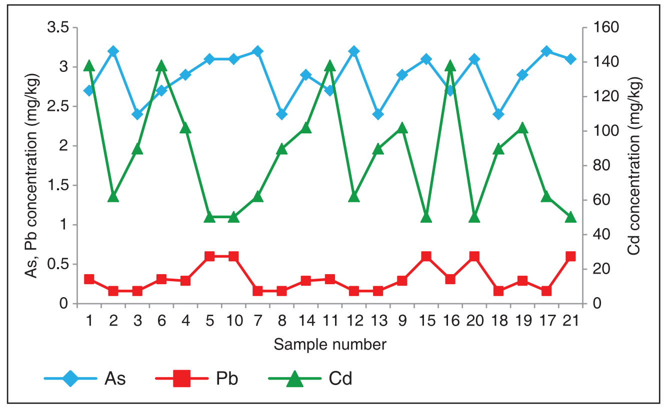

Figure 2: The extent of heavy metals concentration in fish sample from case region

Table 1: The mean of pollutant amounts in the two regions

	Case region		Control region		*P* value
	Mean (SD) mg/kg	Min and max	Mean (SD) mg/kg	Min and max	
Arsenic	2.87 (0.3)	2.4, 3.2	2.97 (1.51)	1.3, 4.75	0.78
Lead	0.32 (0.17)	0.16, 0.6	0.66 (0.37)	0.28, 1.18	<0.001
Cadmium	86.64 (32.04)	50.3, 138.0	3.70 (4.11)	0.4, 11.19	<0.001

and Isfahan, the surface run-off water of these areas (the path of about 360 km), discharged to the Gavkhoony wetland. Zayandehroud River provides water for drinking, agriculture, and for industrial purposes. The river's bed consists of different kinds of sedimentary rocks (like $CaCO_3$), igneous rocks (source of all elements including As, Pb, and Cd), which effects the water quality of the river. Many industries, including steel industries, petrochemical, power plant, rubber, ceramic, tile, and textile factories, are located around the river and their waste water is discharged into the Zayanderoud River. These human activities can lead to heavy metals being released into the Zayanderoud River. Moreover, the Zayanderoud River is habitat of several fish types, which are consumed by the local population.

According to report No. 6952, Institute of Standards and Industrial Research of Iran (ISIRI) set the maximum concentration level for As, Pb, and Cd in fish and fish products as 0.2, 0.5, and 0.1 mg/kg, respectively.[6]

Other studies reported that the concentrations of studied metals (As, Pb, and Cd) in fish muscle were below the maximum concentration level proposed by the FAO, WHO, and European Communities (EC) based on threat to human health.[23-27] In other studies, the concentrations of these heavy metals (As, Pb, and Cd) were less than the daily intake recommended by the international organizations except for As.[23,27,28]

An investigation on heavy metals concentration of three species of most-consumed fish from the Caspian Sea in north of Iran reported that the concentration range of Cd and Pb were 53.67-168.83 and 19.27-95.90 μg/kg, respectively. However, the heavy metals concentrations in fish samples were below the maximum concentration level. The study showed the increasing levels of heavy metals in environment.[26]

In contrast, in some studies, the amount of As, Pb, and Cd were found in higher concentrations than the FAO standards (permissible levels) for fish.[29-34]

These studies showed that many parameters can have an effect on the amount of heavy metals in the water and fish tissue.

We only analyze *fish flesh*, while the metals in other organs like liver, muscles, glands, and skin may be varied. The trace elements analysis in the muscle, gills, and liver tissues of some fish species showed that the concentration of Cd varied between 0.59 and 0.001 μg/g.[23] In addition, Malhat reported that high concentration of metal was accumulated in the muscle of *Cyprinuscarpio* and *Carassiuscarassius* fishes rather than in the liver or gills.[29] But, one study showed that the Cd concentration was higher in the liver, kidney, gill, and gonad tissues.[27]

Other investigations showed that metal concentrations were differently distributed among different *fish species*.[24,34] It may be due to the food chain and the age of the fish.[35]

Also, *feeding habits* is an important factor. Benthic carnivorous and euryphagous (feeding on a large variety of food) fishes had higher metals concentrations rather than phytoplankton and herbivorous fish.[34] Zrncic *et al.* analyzed the heavy metal concentration in fish muscle tissue collected from Croatian part of the Danube River according to feeding habits. The Pb concentration varied from 0.015 μg/kg of planktivorous dry weight to 0.039 μg/kg of herbivorous dry weight, and Cd concentration fluctuated from 0.013 μg/kg of herbivorous dry weight to 0.018 μg/kg of piscivorous dry weight, and As concentration varied from 0.018 μg/kg of planktivorous dry weight to 0.039 μg/kg of omnivorous dry weight.[36] This variation may be due to differences in habitat, swimming behavior, and metabolic activity.[34]

A positive relationship was found between *fish size* and metal concentration in most cases.[34] In the present study, the average length of the fish samples was 20 cm and reflects the fish age.

The heavy metals accumulation in the fish body may be due to the *depth of water.* Some studies reported that heavy metals concentrations in tissue of fishes in river bottom and lower water level layer were higher than fishes in upper and middle water level.[34,35] The Carp fish (studied fish) usually live in upper water level.

Seasonal variations of heavy metals concentrations in liver of fish, sediment, and water were reported.[37,38] Ramos-Rosas *et al.* reported that higher concentrations of Pb were detected during dry season and Cd during wet season.[39] In the present study, the fish samples were collected at summer in both the zones.

The difference between Cd and Pb concentrations of fish tissues and *its parasite* was statistically significant. The Cd and Pb concentration was higher in parasites (the small living creatures with fish) than the other parts of fish. Furthermore, significant differences are detected in the heavy metal accumulations between the parasitized and unparasitized fish tissues in Cd and Pb concentrations.[30]

The studies demonstrates that majority of the metal emissions are deposited *near* the pollution source, and only moderate amounts of the heavy metal contaminants transported to long distances.[40]

Our results can be explained in another way. The plant growing and marine animals can absorb heavy metals and cleaning the aqueous environment. In contrast, some kinds of plants and marine animals can release the heavy metals to the aqueous environment and can lead to increment of their concentration (e.g., Cd). For example, a native oyster's species in the Persian Gulf has the absorption ability of heavy metals such as Cd and can act as a biological degradation.[41]

Some of the artificial activities and natural resources (e.g., catchment erosion) releases the heavy metals to the environment.[42]

The high concentration of Cd in the studied samples may be a result due to summer sampling and the low water level. Also, the dam closure due to drought water deprivation for about 12 months resulted in the riverbed being enriched with different heavy metals and the consequent flow of the Zayandehroud River resulted with heavy metal increment. In contrast, utilization of the Zayandehroud River for agricultural activities and the usage of fertilizers/pesticides causes heavy metals concentration in summer.[43] Discharge of sewage sludge from wastewater treatment plant to the Zayandehroud River and plants growing leads to Cd absorption by the plants and consequently increscent in fish tissue.[44]

According to the results of this study, application of some new, simple, and cheap methods for contamination reduction of heavy metals in the Zayanderoud River seems to be necessary. Some methods were used for removal of heavy metals including sawdust (ligno cellulose), phytoremediation (an ecologic method) and vital creatures' plants, algae, fungi, and bacteria.[45] Also, sand, calcareous and noncalcareous soil, and organic compounds can be used for absorption of heavy metals.[46]

The results of a study in 2006 showed that the Zayandehroud River contamination has increased, which may be due to drought, less rainfall, gradual decrease of river water level, and some policies.[47]

The present study has suffered from the sampling type (only fish tissue) due to high accumulation of heavy metals in the liver.

In conclusion, discharge of domestic wastewater and agricultural activities into the Zayanderoud River, may increase the heavy metals concentration of fish tissues. Therefore, we suggest that the heavy metals concentration should be regularly monitored.

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