Investigation of heavy metals accumulation in the sediment and body of carp fish in Aras River

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Abstract

Heavy metals are considered as the most dangerous water contaminants because of their possibility of bioaccumulation and toxic effects. This study tried to investigate the bioavailability of heavy metals in terms of Ni, Zn, Cu, Fe, Hg, Cd, and Pb in the sediment during dry seasons in Aras River basin located in Ardabil Province, north-west of Iran. Also the metal concentration in the skin and flesh carp was measured during all four seasons in 2010 in Aras River. Sediments were collected from five stations during summer but fish sampling was carried out seasonally in five fixed stations. The results of this study indicated that there was a meaningful and positive correlation between the existence of high levels of bioavailable metals and their concentration in fish body. Among the measured metals, Fe is highly bioavailable and the highest level of Fe in the sediment was in the ST4 (93.4mg/l). This could be due to high accumulation of this element in fish body. Also, maximum concentration of Fe in fish body was in summer (1.87mg/l) as well.

Keywords: Heavy metals, Bioavailability, Bioaccumulation, Carp, Aras River

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Introduction

Industrial development accompanied by and consumption population growth imposed by heavy pollution loads to natural resources (Nasrabadi et al. ,2009; Baghvand et al., 2010). Trace elements, especially the so-called heavy metals, are amongst the most common environmental pollutants, and their occurrence in waters and biota indicate the existence of natural or anthropogenic sources (Nabi Bidhendi et al., 2007; Mehrdadi et al., 2009). The main natural sources of metals into the aquatic system are the weathering of soils, and also from anthropogenic rocks activities, whereby industrial and urban wastes are discharged into water bodies (Pardo et al., 1990; Boughriet et al., 1992; Klavins and Apsite, 2000; Yu et al., 2001). Because of the importance of sediments to the overall quality of aquatic systems, sediment analysis is often included in environmental assessment studies (Horsfall and Spiff 2002; Jain et al., 2005; Li et al., 2006; Adekola and Eletta, 2007). Also, the examination of bioavailability of metals in sediment is as important as in the body of fish. Paying more attention to the portion of metals attached loosely to the sediment environment make it possible to have a more realistic view of the existing metallic pollution potential which may be resulted in bio-accessibility, availability bioaccumulation and (Nasrabadi et al., 2010b).

Depending on environmental, physical, chemical, and biological conditions, heavy metals in soil or water can be available for food web to various degrees (Siegel, 2004). Heavy metals as one of the environmental pollutants have

different influence on aquatics, including growth reduction, behavior and genetic changes. They can also kill them (Pillay, 2004). Different surfaces of fish body, which are in contact with the environment, can be mediums of transfer, settlement and accumulation of heavy metals. Most of the metal compounds, or their ions are accumulated in fish organs, especially liver, gill, heart, and spleen as well as bones. They not only damage gill and other organs of fish through accumulation in them, but they may also kill fish or change the taste and smell of their fish (Van, 2000; Jalali and Agazadeh, 2007), Metals absorption through food depends on different factors. Some reports indicate that considerable absorption of a metal by fish occurs only when the metal in the food exceeds minimum threshold level (Varedi, 1997). Except copper and zinc which have a weaker tendency to settle in muscles, other heavy metals (iron, nickel, lead, and cadmium) are accumulated within muscles (Stoskopf, 1993). These metals have the capability of being absorbed and accumulated in the body of living creatures. Therefore, their level in fish body should be controlled because their consumption may pose health hazards to humans (Njiru, 2008). The solved metals in the suspended materials are bioavailable because they are moved easily and enter the food web before being deposited in the sediment (Watt et al., 1993). A study on aquatics in Greenland revealed that the concentration of heavy metals in their body was more than the concentration of these metals in the body of animals living in land ecosystems. More importantly, the concentration of Hg, Se,

and Cd increases at the higher levels of food pyramid. This means that these metals are susceptible to bioaccumulation (Dietz et al., 2000). In the studies conducted on sediments and fish body in the Persian Gulf and Oman Sea, it became evident that high levels of cadmium in the liver of some fish in south Oman may be because of Cd bioaccumulation in food chain (De Moran et al., 2004). The results of these studies were also used to examine the relationship between the spread of diseases metal and concentration (Thornton, 1993). If there are heavy metal sources which pollute a river, a depletion of living creatures like Planktons and Nektons may occur in that river which may result in the death of fish (Goyer, 1992). Approximately 12.5 million fish died due to this kind of pollution in the United States, between the years form 1961 and 1975 (Heath, 1987).

The study was aimed to consider metallic pollution caused by elements Zn, Cu, Fe, Pb, Ni, Cd, and Hg in skin and flesh of carp and sediments of Aras River within a specific area in Ardabil province. The amount of the heavy metals in fish body from Aras River can be used as an index for this purpose.

Material and methods

Study area

Aras River, one of the largest rivers in northern Iran with an approximate length of 1072 km, is the common boundary between Iran, Azerbaijan and Armenia in a 470 km distance, and finally reaches to the Caspian Sea. Originating from Binaguldaq Mountains in Turkey, Aras River lies within a water catchment of around

100220 km². The average maximum flow within the study area is 1100 m³/sec at Aras Dam and 2600 m³/sec at Mogan Dam. However, the mentioned values may descend to 32 and 180 m³/sec in arid seasons (Bagirove, 2005). This river supplies potable water to tens of cities and villages, irrigation water to thousands of hectares of irrigation land, water to fish husbandry projects and water to numerous industrial units (Nasrabadi et al., 2009). Accordingly, the river water quality is exposed to a potential threat caused by agricultural, industrial, and residential land uses. Recently, rapid growth of industrial and agricultural activities within the Aras River basin in Iran, Armenia, and Azerbaijan has been adversely affected the river ecosystem. An approximate length of 60 km of the River is located within Ardabil province where a sophisticated irrigation network for agriculture as well industrial complex (Parsabad Mogan) is developed.

In order to allocate the sampling stations, parameters such as geology, topography and access road limitations, as well as anthropogenic pollution sources discharges were taken into account. Accordingly, five stations as S1 (entrance to Ardabil province near Milmogan Dam), S2 (after Darrehrud-Aras junction), S3 Gurrichai-Aras (after junction), **S**4 Parsabad (downstream of Moqan Industrial Complex) and S5 (Iran-Armenia mutual boundary) were selected for fish and sediment sampling campaign (Fig. 1). The seasonal sampling of fishes in Aras River was carried out in five different stations in 2010 using electro- shocker or gillnet. To obtain practical results, all fish were selected with same size and weight so that they were 26-27 cm long and weighed 280-300 g. The specimens were coded and fixed in different plastic containers with 10% formalin and were kept in iceboxes for a short time until they were transferred to the laboratory (Dulka, 1976, APHA, 1992). As a whole, 20 specimens were utilized in this study. In order to prepare the fish specimens, the skin and muscles were separated using scalpel and mixed. Then, they were dried at 103 °C using oven and were sent to laboratory to measure heavy metals (Moopam, 1999). Zn, Cu, Fe, Pb, and Cd concentration was determined by atomic

absorption spectrometry (AAS) (Otto, 1998), whereas Ni and Hg concentration was evaluated using inductively couples plasma- Atomic emission spectrometry (ICE-AES) (APHA, 1992). 10 g of sediment samples was digested by 20 ml of the extractant made by the mixture of 149.2 g of triethanolamine, 19.6 diethylen triamine pentaacetic acid(DTPA), 14.7 CaCl₂ and 200 ml of distilled water with the final volume of 1 liter. The final pH was fixed on 7.3 by the use of normal HCl (APHA, 1992). After a 2 hours shaking period and filtration process, the metallic concentrations were determined mentioned above for fish samples (USEPA, 1997, EPA method, 3050).

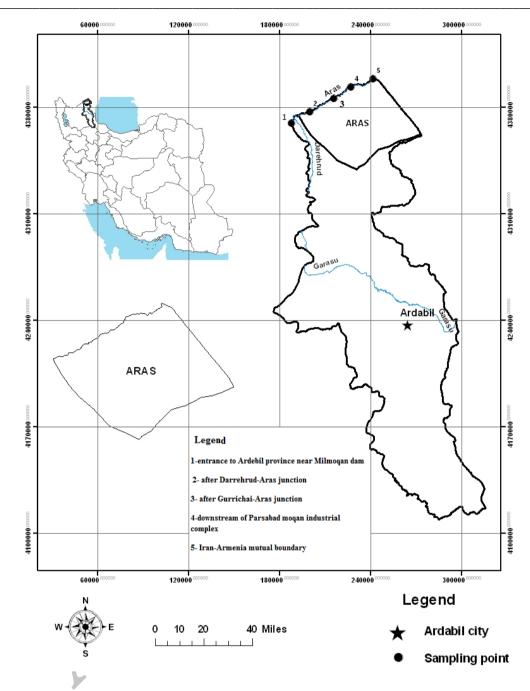


Figure 1: Sampling stations in the study area

Statistical methods

SPSS statistical software was utilized to obtain statistical indices like mean deviation, standard deviation, and correlation between parameters. The Arc View and Arc GIS softwares were used to provide the required maps.

Results

As can be found in Table 1, the bioavailable metals concentrations indicate an ascending trend from the first station towards the last one. In comparison with earth crust, sediment and igneous rocks (Alloway, 1995; Turekian and Wedepohl, 1961) the reported metallic concentration

values, except for Cd, lie within the low risk status. Regarding Cd, the reported values in some stations (S2, S4 and S5) are up to 10 times greater than that of shale which may be considered as a remarkable risk potential. Regarding the results of this study, the maximum quantity belonged to average concentration with 56.42±24.05 mg/kg and the minimum quantity to Cd with average concentration of 0.96 ± 0.47 mg/kg so that the maximum of Fe concentration could be observed in station 4 with 93.4 mg/l. According to the results illustrated in Table 1, the large quantity of iron in Aras River can be attributed to several factors. Iron is the most abundant and the most important metal in the earth's crust and can be dissolved in water after a chain of complex chemical reactions in the rocks and minerals (Klavins and Apsite, 2000). Human activities speed up the entrance of heavy metals into the environment. Although iron is naturally found in water, its presence in water can also be attributed to the acidity of some mines' drainage

ditches (Farm Mine and Songun in Dareroud and Armenia's copper mine), landfills and sewage systems (Aslandouz town at the present study) and industries associated with Fe (Siegel, 2001). The maximum concentration of bioavailable Fe in the skin and flesh of carp was measured in station 4. It can be concluded that the quantity of bioavailable heavy metals is in the highest point in station 5 in comparison with other stations, and copper, zinc, cadmium and lead are in the largest amount in this station. Station 4 is considered to be the drainage basin of 15 industrial units' active wastewater including Moghan's Agro-industrial and livestock Company (near Oltan and Tazekand Ghadim) and Pars- Abad's sugar refinery, dairy farm, and cattle feed center which are among the most important and biggest industrial units in the region. The obtained results related to quantity of bioavailable heavy metals in sediments of Aras River are as following:

Fe>Cu>Ni>Zn>Pb>Cd

Table 1: The quantity of bioavailable metals (mg/l) in sediment of Aras River

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Station	Hg	Pb	Cd	Ni	Zn	Fe	Си
S1	ND	1.02	0.8	1.90	2.16	60.4	5.04
S2	ND	0.40	1.2	1.64	0.92	58.5	7.04
S3	ND	1.16	0.2	1.94	0.72	34.4	3.60
S4	ND	1.60	1.2	2.72	1.68	93.4	13.30
S5	ND	2.30	1.4	2.05	3.28	35.4	20.80
mean	ND	1.29±0.7	0.96±0.47	2.05±0.40	1.75±1.03	56.42±24.05	9.95±7.1

ND: Not Detected

Heavy metals concentration in examined fish during 4 seasons is shown in Table 2. Behavior of Fe, Cu, Ni and Zn concentration along the sampling stations and also through different seasons did not obey a regular pattern, however, the autumn showed no detectable Ni and Cu

concentration in all stations. Considering Fe, Cu, Zn and Ni, the concentration values of spring and summer samples are much more remarkable than those of autumn and winter ones. The sampling station 4 has the highest Fe concentration in both spring and summer seasons.

Regarding Ni, as the most risky metal within the fish body of the study area, the highest concentration is observed in station 3 and in summer (0.6mg/l). Mercury,

Cadmium and lead concentration was too small to be detected by analytical instrument.

Table 2: The results of heavy metals evaluation in flesh of fishes (mg/l) in Aras River within Ardabil Province (2010)

Season	station	Нg	Pb	Zn	Fe	Cd	Си	Ni
	ST1	ND	ND	0.1	0.42	ND	0.23	0.1
0,0	ST2	ND	ND	0.29	0.62	ND	0.1	ND
spring	ST3	ND	ND	0.88	0.15	ND	0.38	ND
ds	ST4	ND	ND	0.16	0.94	ND	0.1	0.1
	ST5	ND	ND	0.14	0.17	ND	0.39	0.1
	ST1	ND	ND	0.25	1.47	ND	0.12	0.25
er	ST2	ND	ND	0.67	1.37	ND	0.24	0.23
summer	ST3	ND	ND	0.23	0.87	ND	0.16	0.6
ms	ST4	ND	ND	0.52	1.87	ND	0.1	0.21
	ST5	ND	ND	0.23	1.2	ND	0.1	0.4
	ST1	ND	ND	ND	0.27	ND	ND	ND
ш	ST2	ND	ND	0.28	0.17	ND	ND	ND
Autumn	ST3	ND	ND	ND	0.15	ND	ND	ND
Aut	ST4	ND	ND	0.22	ND	ND	ND	ND
,	ST5	ND	ND	ND	ND	ND	ND	ND
	ST1	ND	ND	0.1	0.28	ND	ND	ND
.	ST2	ND	ND	ND	ND	ND	0.53	ND
Winter	ST3	ND	ND	ND	ND	ND	ND	0.37
Wi	ST4	ND	ND	ND	ND	ND	ND	ND
	ST5	ND	ND	ND	ND	ND	ND	ND
Total Mean		ND	ND	0.31±0.23	0.71±0.57	ND	0.22±0.14	0.26±0.16

ND: Not Detected

The concentration of copper in flesh of the fish in Aras River was 0.22 ± 0.14 mg/kg and the maximum value was 0.53 mg/kg in station 2 during winter. Fe has the highest concentration in fish in comparison with other elements with average concentration of 0.71 ± 0.57 mg/kg and the maximum value was 1.87 mg/kg in station 4 during summer. Nickel average concentration in flesh and skin of fish is 0.26 ± 0.16 mg/kg and it was higher than the acceptable level (EPA) only in three cases (0.37, 0.40, 0.60) mg/kg, respectively in station3(In winter), station5, station3(In summer)with the

maximum value of 0.60 observed in station 3 during summer. It is noteworthy to be mentioned that the permissible level of nickel in fish is 0.3 (Schlodtfeldt and Aldermna, 1995), while nickel's maximum permissible level of concentration in freshwater is 0.730 mg/l (Clark, 1992). In this study, the maximum zinc concentration was 0.88 mg/kg and average concentration was 0.31 mg/kg. Therefore, there is no pollution problem considering current standards. All zinc measurements indicate that there was no zinc in fish flesh (Farabi et al., 2009). According to results

of statistical analysis obtained various stations within different seasons, there was no significant difference (p>0.05). The concentration of zinc in the body of Caspian Sea fish, other freshwater fishes, and salmon is 20.6 ± 6.8 ppm 2.0 (Patin. 1982), and 0.5 ppm, respectively (Gardiner and Mance, 1984). Furthermore, it has been proved that the concentration of zinc in fish body depends on its concentration in water and the length of exposure time (Heckman, 1990). WHO has identified that the average cadmium concentration in seafood is 50 ppb while it is 15.3 ppb in meat and chicken (WHO, 1993). The results provided in Table 3 reveal that there is positive and significant correlation between Fe in sediment and fish (p=0.05).

Table 3: The results relating to the correlation between bioavailable heavy metals in sediment and fish

	Fe(sed)	Cu(sed)	Zn(sed0	Cd(sed)	Ni(sed)	Pb(sed)
Fe(Fish)	0.969**	0.017	-0.225	0.424	0.554	-0.252
Cu(Fish)	-0.856	0.179	0.352	-0.389	-0.218	0.539
Zn(Fish)	-0.494	-0.529	-0.677	-0.832	-0.236	-0.238
Cd(Fish)	a •	a •	a •	а •	a •	. a
Ni(Fish)	0.000	0.000	0.000	0.000	0.000	0.000

Discussion

In this study, metallic pollution caused by elements Zn, Cu, Fe, Pb, Ni, Cd, and Hg in sediment and carp fish of Aras River within a specific area in Ardabil province located in north of Iran was considered. The concentration of metals Ni, Cu, Zn, and Fe in fish showed a direct relationship with river water discharge and the amount of precipitation. Enhanced soil erosion, bed load dissolution, and run-offs may play a vital role in remarkable augmentation of metallic ions concentration in water, sediment and fish. Furthermore. excessive use of pesticides and fertilizers which contain a variety of metallic ions

(mainly Fe and Cu) in spring and summer may also result in an increase in the metals concentration. Regarding Fe and Cu, abnormally high concentrations would be attributed to anthropogenic sources and in the case of this study such sources may be introduced as Fe, Curich run-offs irrigated from Moqan plain agricultural lands fed by various pesticides through hot seasons. The results of the current study indicate that the concentration of some metals like iron and zinc in cyprinid is higher in the summer, which can be attributed to the reduction in the water yield of the river during this season, increase in metals concentration, and finally accelerated metal absorption. When the volume of water in the river decreases, the amount ofthe suspended materials also decreases. One consequence of this change is the slowdown in the speed by which dissolved metals can suspended transferred to materials (Saeedi et al., 2005).

A research conducted in 2001 identified that fertilizers containing heavy metals cause water and fish contamination. Fe in *Tilapia nilotica* in Naser Lake, in Egypt, has identified to have a high concentration of Fe (6.45 mg/g). Previous experiments in lake had revealed that iron concentration in the same species of fish was 56 -104 ppb which are regarded to be the lowest concentration. Increase in the concentration of studied elements in fish can be the result of high levels of pollutants in the lake originating largely from agricultural sewage discharges containing fertilizers (Nageeb, 2001). According to statistics published by Jihade-Keshavarzi Organization 2008-2009, the area under cultivation in Pars- Abad had been 51206 ha with the agricultural output amounting to 448855 tons. This amount of agricultural output requires 70000 liter of toxins like herbicides, fungicides, and insecticides as well as fertilizers. These figures reveal the danger imposed on aquatics by heavy metals finding their ways to Aras River from agricultural sources of pollution. The considerable reduction in the amount of pesticides and fertilizers used on agricultural lands as well as loss of industrial shut-downs through winter will cause relatively lower

concentrations in comparison with other Additionally, lower seasons. temperatures will reduce the affinity of metals for being dissolved in liquid phase (Drever, 1997). The investigation of heavy metals in this study indicates that the amount of measured parameters, except Ni, is appropriate for consuming river fishes according to Iran and world standards and there is no danger concerning the accumulation of heavy metals in the body of studied fish. Ni may be found abundantly in lots of cereals, nuts and soybeans (Merian, 1991). The potential risk of Ni exposure to the sediment environment of the study area is assigned to juice, dairy products, edible oil and sugar cane factories as well as soybean croplands, which are located within the Sub-basin of Aras River in the study area. Furthermore, the municipal wastewater may also carry significant loads of Ni (Vega, 1998). As shown in Tables 1 and 2, Fe has the highest concentration in both sediment and fish body. Inspired by the results, it was revealed that Fe is available for living creatures to a considerable degree. The table reported correlation coefficients indicates that there is a positive and significant correlation between the bioavailability of Fe and its accumulation in skin and flesh of fish (p=0.05). This is in line with the reports that claim considerable metal absorption by fish happens only when the amount of metals in the food exceeds the threshold level minimum (Varedi, 1997).On the other hand, because of the wastewater discharged from industrial units and agricultural fields into the river, station four is one of environmentally most hazardous place in the region. Fish is exposed considerable amounts of bioavailable therefore absorb more comparatively. The investigation iron's effect on aquatics is important because of its indirect toxic effects are largely limited to sedimentation of Ferric hydroxide on gills. Ferric hydroxide sedimentation on gills prevents the exchange of oxygen. Sedimentation on eggs too may lead to embryo suffocation and death by blocking the access of embryo to oxygen through Korion membrane (Snieszko and Axelrod, 1976).

As summary, the concentration of bioavailable heavy metals in the sediment of Aras River is more than the quantity reported in the sediment of Shadegan pool (1> mg/kg) (Hosseini, 2011). Respected increasing development of human activities in neighboring countries around Aras River and industrial, urban, and agricultural sewage and wastewater disposal into this river in recent years, it is likely that water consumers like people, animals and water products including fish will be poisoned. So making sure of fish health is a prerequisite of using the water of this river for human consumption.

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