Original Article

Monitoring of Heavy Metals in Water, Sediment and *Phragmites australis* of Aras River along the Iranian-Armenian Border

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ABSTRACT

Background: Aras River is the main source of drinking water supply in northwestern provinces of Iran. The present study aimed to determine the concentration of heavy metals in the river on the border between Iran and Armenia.

Methods: Three samples were taken from the Aras river water, the river bottom sediments and the root of *Phragmites australis*. In water sampling, the concentration of Hg, Mo, Cu, C o, B, Cd, Ni, Zn, Pb, Al, Mn, Cr, and Fe was noticed while in sediment sampling, to measure the concentration of Cu and Mo. In samples taken from the plant root, the concentration of Cu was only analyzed. The water sampling was performed at 11 stations along the river course during four seasons fall, winter, spring and summer 2011.

Results: The highest and lowest concentrations respectively belonged to Al (2600 ppb) and Cd (0.4 ppb). Parameters including B, Cu, Mo and Al were all higher than the standard limits. The results obtained from sediment and root sampling indicated that the concentration of Cu exceeds the standard.

Conclusion: Poor quality of Aras River reveals to the necessity of implementing mitigation measures to improve the water quality of the river.

Keywords: Heavy Metals, Iran, *Phragmites Australis*, Standard.

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INTRODUCTION

Heavy metals are released into the environment by many different activities such as agriculture, mining, industries, and even nuclear processes [1]. Very small amount of some heavy metals such as Cu, Zn, Fe, and Mg are essential for all living organisms, however, excessive amounts of them can face the organism with fatal poisoning [2]. Some plant species are able to absorb high quantities of heavy metals from soil and water. Consuming contaminated plants, the heavy metals are entered into the human body [3].

One of the most common plants growing in margin of water bodies such as lakes, ponds, lagoons, and rivers is *Phragmite*s *australis,* known as common reed. It can be used as an indicator plant in heavy metal pollution assessment studies due to its high heavy-metal-uptake capacity [4]. With planting these plants in contaminated areas, it is possible to not only prevent accumulation of high concentrations of heavy metals, but also, to reduce or even eliminate them from the contaminated sediment, and soil [5, 6]. Considering the importance of pollution caused by heavy metals, numerous studies have yet been done worldwide e.g. in 2010. The concentration of five heavy metals was evaluated in sediment as well as in gill and digestive gland of mussels was examined to consider their potential risks to human health and finally found a seasonal trend of metal bioaccumulation which was higher in winter than in summer [7].

The concentrations of heavy metals Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were investigated in the roots, rhizomes stems and leaves of the aquatic macrophyte *P australis* (common reed). In the corresponding water and sediment samples from the mouth area of the Imera Meridionale River (Sicily, Italy) and there are positive linear relationships between heavy metal concentrations in all plant organs and those in water and sediment [8]. A commonly used macrophyte, Reed (*P australis*), for water purification as a new biosorbent for the removal of Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from aqueous solution. Metal adsorption capacity of reed biomass was improved significantly by water-wash as well as base- and acid-treatment. Even after three cycles of adsorption-elution, the adsorption capacity was regained completely and desorption efficiency of the metals was maintained at around 90% [9]. The performance of selected destruction methods was assessed to determine heavy metal concentrations in reed plants (*P. australis* (Cav.) Trin. ex Steudel). Heavy metal analysis results of reed plants significantly depend upon the destruction procedure, applied [10]. The

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extraordinary ability of *P. australis* in absorption of heavy metals have been proven by many researchers around the world [11-13]. However, heavy metals are a key pollution in Iran as well documented in Anzali Wetland, had the highest level of contamination and therefore, protective plans must be implemented in the polluted area [14].

The current study analyzed concentration of heavy metals Hg, Mo, Cu, Co, B, Cd, Ni, Zn, Pb, Al, Mn, Cr, and Fe in Aras River, in the vicinity of copper mines of the City Agarak, Armenia. The research findings can clearly help determining the health of drinking water consumed by indigenous people in the study area.

MATERIAL AND METHODS

Study Area

The study area is located in East Azerbaijan Province, northwestern Iran, along the border between Iran and Armenia. From hydrological point of view, the study area includes the watershed of Aras River originating from Turkey, Armenia, and Iran. The study area lies between the latitudes 38°-15′- 39°-25′N, and the longitudes 44°-00′ -46°-20′ E (Fig. 1).

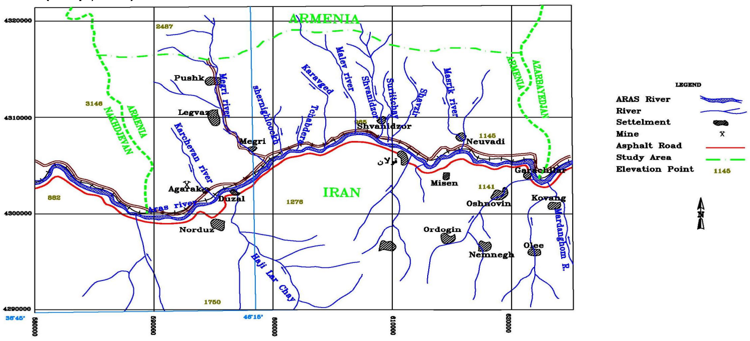

Figure 1. Situation of the study area.

Monitoring Network

Considering the hydrological characteristics of the study area as well as its major industrial, and agricultural activities, a monitoring network was designed to check water and sediment quality of Aras River throughout the study area. In addition to water sampling, due to sedimentation possibility of heavy metals in riverbed, river sediment was sampled at four stations (S2, S4, S6, and S11), as well. Water samples were taken from 11 stations along the river during fall, winter, spring and summer 2011 (Table 1).All steps of the research methodology including sampling, fixation, storage, and measurements were conducted based on the procedure recommended by standard method 3500. The indices applied in this research include WHO drinking water standard, EPA drinking water standard, national drinking water standard (Iran), and river water quality index [15]. Among available water quality, classification methods can be pointed out to the French classification criteria (water quality index). The Krenkel and Novotny Quality Index include four different levels as follows:

Level A1: Water resource is free of pollutant or contamination and is suitable for any type of use.

Level B1: Quality of water resource is slightly less than level A1. However, it fits most of the standards presented for beneficial use.

Level 2: Quality of water resource is "acceptable" for agricultural and industrial purposes for potable water consumption after extensive treatment. The water quality is also suitable for livestock water use. Fish can survive in such a quality of water resources; however, their reproductive rate will be affected. In case of no prolonged exposure, it can be used for swimming, as well.

Level 3: The quality of water resources ranges from "average" to "relatively good" or "poor". It is hard to use the water for irrigation, industrial use, and swimming. The water can be used for fishery purposes while at scarcity. However, long-term use of the water can be dangerous for fish.

Beyond the categories: water quality is lower than the level 3. It is not suitable for most beneficial uses. The water quality is considered dangerous to both environment and public health.

Table 1. Specification of sampling point.

Station	N	E	Sampling from sediment	Location
S1	39.08	45.40	-	Before entrance point of the study area
S2	38.84	46.15	✓	Entrance point of the study area
S3	38.86	46.21	-	The main drainage of Agarak Copper Mine, at the beginning point of the Iran-Armenia border
S4	38.86	46.23	✓	Before joining Aras River to Hajilarchay River (on Aras River)
S5	38.86	46.24	-	Before joining Hajilarchay River to Aras River (on Hajilarchay River)
S6	38.87	46.25	✓	After joining Aras River to Hajilarchay River (on Aras River)
S7	38.89	46.26	-	Before joining Aras River to Megri River (on Megri River)
S8	38.90	46.28	-	After joining Aras River to Megri River (on Aras River)
S9	38.89	46.41	-	After discharging some rivers into downstream of Sedaghat Police Station
S10	38.88	46.45	-	Before joining Aras River to Masrik River (on Aras River)
S11	38.87	46.53	✓	After joining Aras River to Masrik River (on Aras River) at downstream of Garachilar Village

Sampling was done regularly during four seasons of fall, summer, winter, and spring.

Sampling and Measurements

Sampling was done regularly during four seasons of fall, summer, winter, and spring. At the laboratory, HNO_3 was added to the water and sediment samples in order to decrease pH to less than 2 and then, the heavy metals were analyzed using atomic absorption method, according to the Standard Method 3500. In order to examine the intake capacity of the plant root, considering situation of the copper mines in the study area as well as the habitat of *P. australis*, two stations were considered before and after the outlet of industrial wastewater from the copper mines in Armenia. The plant species were monitored in spring as growing period of *P. australis*. During which, a total number of five samples were collected from each station. Using dry ash method, the extract derived from plant digestion was directed towards a flame (a mixture of air and acetylene gas) by a nebulizer and then, transformed into the gas form. The considered element converted into atom can absorb the ray diffused by the hallow-cathode lamp. The absorbed dose was then measured by atomic absorption device.

Statistical Analyses

Statistical analyses were performed for all water, sediment, and plant samples based on variance analysis, and *t*-tests at the confidence level 5%. The results obtained from qualitative tests were first compared with relevant standards and qualitative water indices and then, analyzed with statistical tests (*t*-test) using SPSS 16 (Chicago, IL, USA).

RESULTS

Indices and standards applied in the present study include WHO standard for drinking water [16], EPA water quality standard [17], river water quality index, Australian quality standard for water and soil and sediment, and national drinking water standard (Iran).Table 2, presents a comparison of the measured parameters with relevant standards.

Ascending order of heavy metals in river water is Al > B > Mo> Fe > Cu > Ni >Co> Zn >Mn> Cr>Hg> Pb> Cd.

Table 2. Average of the measured parameters compared to the standard values at 11 stations in four seasons (ISDW: Iranian standard for drinking water (mg/L), ASS: Australian Sediment Standards (mg/kg dry wt)).

Parameter	*P* value	N	ISDW	EPA	WHO	Statistical Result	
				(mg/L)	(mg/L)	t	p
Al(ppm)	2.6	44		0.2	0.2	6.8	0
Hg(ppb)	0.7	44	0.001		0.001	-2.4	0.2
Hg(ppb)	0.7	44		0.002		-12.4	0.4
B(ppb)	321.3	44			0.3	0.7	0.4
Cr(ppb)	2.5	44	0.05		0.05	-107.3	0
Cr(ppb)	2.5	44		0.1		-220.5	0
Cr(ppb)	2.5	44				-107.3	0
Ni(ppb)	10.09	44			0.02	-7.5	0
Zn(ppb)	5.1	44			3	3.7	0
Zn(ppb)	5.1	44		5		0.2	0.7
Zn(ppb)	5.1	44	15			-17.1	0
Zn(ppb)	5.1	44				0.2	0.7
Zn(ppb)	5.1	44				3.7	0
Pb(ppb)	0.6	44	0.05			1.3	0.1
Pb(ppb)	0.6	44		0.015		1.3	0.1
Pb(ppb)	0.6	44			0.01	1.4	0.1
Pb(ppb)	0.6	44				1.3	0.1
Cd(ppb)	0.4	44			0.003	-18.3	0
Cd(ppb)	0.4	44		0.005		-32.6	0
Cd(ppb)	0.4	44	0.01			-68.2	0
Cd(ppb)	0.4	44				-32.6	0
Fe(ppb)	95.2	44		0.3		-30.4	0
Fe(ppb)	95.2	44	1			-134.3	0
Fe(ppb)	95.2	44				-208.6	0
Fe(ppb)	95.2	44				60.1	0
Cu(ppb)	83.6	121	1			-52.3	0
Cu(ppb)	83.6	121				1.9	0.5
Cu(ppb)	83.6	121			2	-109.5	0
Cu(ppb)	83.6	121		1.3		-69.5	0
Cu(mg/kg)	342.6	16				1.3	0.3
Cu(mg/kg)	342.6	16				3.9	0.1
Mo(ppb)	107.8	121			0.07	2.9	0.4
Mn(ppb)	3.9	44	0.5		0.5	-323.2	0
Mn(ppb)	3.9	44		0.05		-30.03	0
Mn(ppb)	3.9	44				-160.3	0
Mn(ppb)	3.9	44				-62.6	0

The concentration of the given heavy metals in water and sediment are presented in Fig. 2 and 3.In order to examine bioaccumulation ability of *P australis*, Cu was selected as an indicator metal due to its high concentration at Station 3, as in riverbed sediments, and Agarak Copper Mine drainage released into the Aras River. Cu concentration was investigated in 2 stations as depicted in Fig. 4.

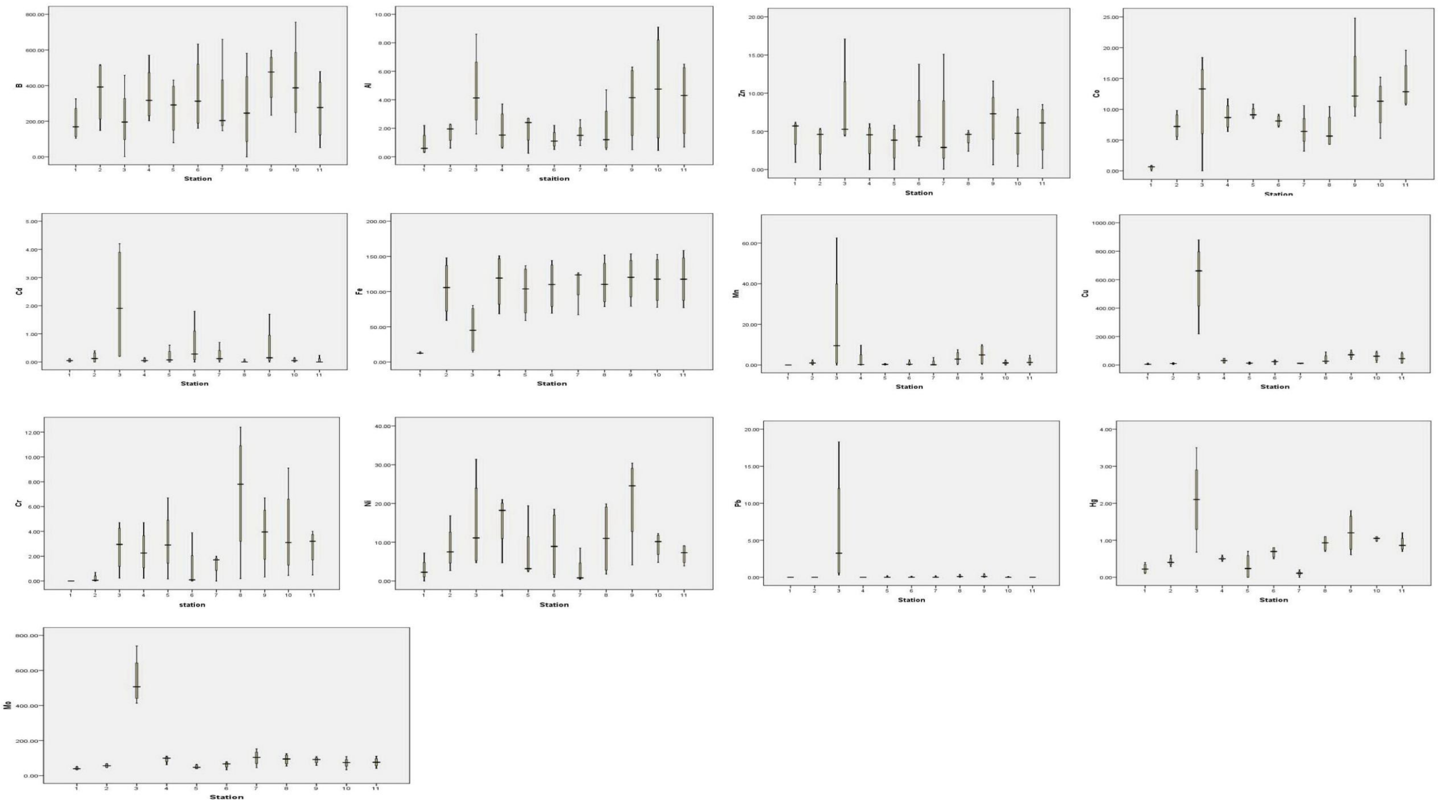

Figure 2. Average Concentration of the heavy metals in Aras River in four seasons.

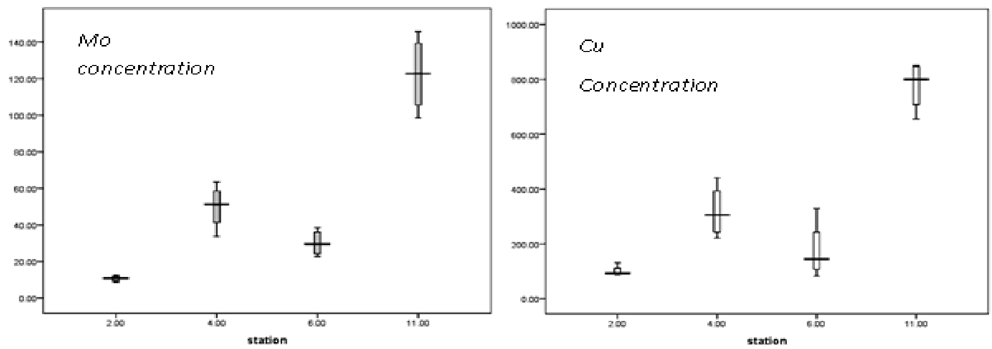

Figure 3. Concentration of the heavy metals in Aras river-bed sediments (mg/kg dry wt).

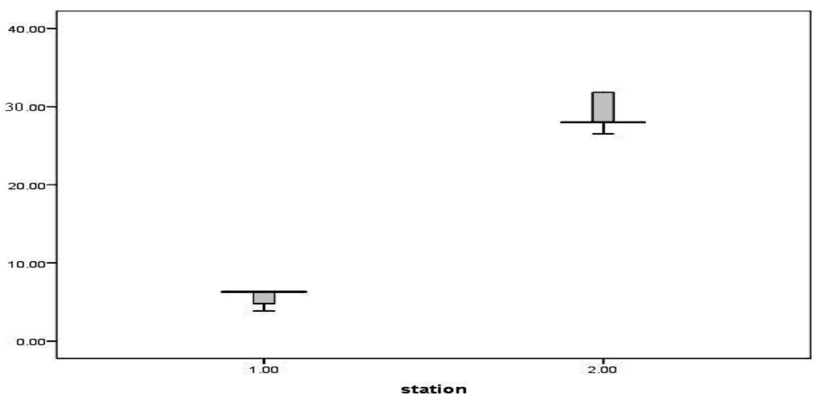

Figure 4. Cu concentration in the root of *Phragmites australis* (ppm).

DISCUSSION

According to the results obtained from Table and Fig 2 Average concentration of Al at different sampling stations of Aras River was equal to 0.2 mg/L, which is higher than standard limits for drinking water presented by WHO, and EPA. Categorized in Class A1, the values of parameters iron, manganese, cadmium, mercury, zinc, lead, and chromium were below the standards of drinking water presented by Iranian drinking water standard, WHO and EPA. Since metal bioaccumulation has not imposed any health hazards to the aquatics, even at high concentrations, therefore, tolerance threshold of aquatics for the metal can be up to 1000 mg/L. Due to the metal bioaccumulation in aquatic bodies, and consumption of seafood such as fish, snails or other mollusks are dangerous to human health.

During winter and autumn, cadmium concentration was higher than drinking water standard limits at Station 3. Reported values for Ni concentration were generally beyond the WHO standard limit for drinking water, which is equal to 20 ppb at all stations and Measured *P*-values were negligible at all stations except for Station 3. Lead is a toxic metal that accumulates in the tissues of human and other creatures. Concentration of zinc at Station 3 in autumn, Station 6 in spring, and Station 7 in summer was higher than the other stations. Reported values for the parameter B exceed the WHO standard limit for drinking water (300 ppb) at all sampling stations except for Station 1. Co was in high concentration at stations downstream of the study area. Very high concentration of copper was reported only at Karchivan tributary.

A significant increase in copper concentration was reported at stations downstream of the study area. Due to sediment/water interaction in Aras River, there is a possibility to release copper from the sediment and enter into the river water. Compared to WHO drinking water standards for molybdenum (70 ppb), the measured values were generally high that represents unacceptable conditions of the river. The metal concentration was very high in Karchivan tributary (Station 3). There is also a relative increase in the concentration of molybdenum at downstream stations due to flowing contaminated tributaries into Aras River as well as leakage from tailing dams of Agarak Copper Mine.

As the obtained results suggest, mercury concentration at Station 3 and downstream of the study area including Stations 8-11, was high. Because of joining contaminated tributaries containing high level of mercury, the metal concentration has recently been increased in Aras River. The copper analysis results at sediment indicated that the metal values were higher than Australian standard limit for drinking water quality at Station 4 (after joining the tributary Karchivan to the River Aras) and Station 11 (after joining the tributaries from Armenia). Copper concentration was decreased at Station 6 due to joining Hajilar River, which has desirable water quality. Unfortunately, there is no standard to compare with concentration of molybdenum, however, the metal changing trend was found consistent with changes in copper. Therefore, it was concluded that by increasing water pH through adding carbonate (in Karchivan Branch), the metals Cu, and Mo deposit in the river sediment.

This represents poor quality of Aras River where mitigation measures should urgently be implemented.

According to ANOVA results, there was a significant difference at a confidence level of 95% between Cu content of *P. australis* at Stations 1, and 2. This is mainly because of the effluent of copper mines at the entrance of Aras River, which causes abnormal copper accumulation in the roots of *P. australis*. Cu concentration in plant samples of Station 2 (30.6ppm) is significantly higher than that of at Station 1 (5.9 ppm). Long-term effects of these pollutants on *P. australis*, continuity of copper uptake by the plant species, and resistance against pollutants reveal good absorption capability of the plant. Accordingly, it could be used as a bioindicator to reduce pollution in aquatic environments. Water, plant, and sediment test results revealed that pollution load of Aras River is increased after flowing some tributaries (particularly Karchivan) into the river. Very high concentration of the forenamed pollutants would foreclose survival possibility of all types of organisms and restrict any kind of water use for drinking water or agricultural purposes in the study area. Fig. 4 depicts concentration of copper accumulated by the roots of *P. australis.* The development of some new industries in the case study had a meaningful role in increasing of heavy metals as well documented already [18]. The heavy metal pollution was reported in aquatic ecosystems in Iran especially in lentic freshwater ecosystems like wetland [19], so to preserve the environment of the pollution is seriously recommended.

CONCLUSION

The highest and lowest concentrations of 2600 ppb and 0.4 ppb belonged to Al, and Cd, respectively. Furthermore, parameters of B (based on WHO), Cu (class A1 and Australian sediment quality guidelines), Mo (based on WHO standard), and Al (based on EPA and WHO) were all higher than the standard limits. This represents poor quality of Aras River in the study area and reveals the necessity of implementing mitigation measures. Discharge of wastewater resulting from copper mine excavation is an important source polluting the Aras River. Increased concentration of heavy metals in the study area can cause kidney, blood, liver, intestine, and brain diseases. In addition, cyclic organic compounds and some heavy metals can cause different kinds of cancer. Considering increased industrial activities in the region, the mentioned risks and diseases are expected to get worse due to increased heavy metal contamination, which can be transferred downstream by the river flow. In overall, water, plant, and sediment test results revealed that pollution load of Aras River is increased after flowing some tributaries (particularly Karchivan) into the river. Very high concentration of pollutants would foreclose survival possibility of all types of organisms and restrict any kind of water use for drinking water or agricultural purposes in the study area. The importance of Aras River for supplying agricultural and potable water consumptions, it is necessary to control the river pollution.

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