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BIOGEOCHEMICAL EVALUATION OF TRACE ELEMENTS IN FISH LIVER CASE STUDY: KHORRAMABAD RIVER BASIN, LORESTAN, IRAN*

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Abstract – Thirteen environmental elements were distinguished in the livers of various species of fish that have been sampled from 15 sites in a restricted area of the KhorramAbad River Basin in Lorestan province (west of Iran). Sites sampled represented agricultural, mining, mixed, and urban/recreation land uses and background conditions. Lithium and silver were not detected at any of the sites. The minimum concentration of trace elements in the fish liver of the above mentioned basin belongs to vanadium and the maximum concentration to iron. Cadmium, selenium, and zinc were selected for a more detailed analysis. Cadmium concentrations in fish liver were highest at mining land use sites, whereas the selenium and zinc concentrations were highest at agricultural land use sites in the KhorramAbad River Basin. A comparison of the study to similar studies in the United States and Iran indicated that the total medium frequency of fish samples for cadmium, selenium and zinc in the KhorramAbad unit was higher than the analyzed fish samples of the Upper Colorado River Basin and Southern beaches of the Caspian Sea study basins.

Keywords – Biogeochemical evaluation, trace elements, fish liver, KhorramAbad River Basin, background conditions

1. INTRODUCTION

The National Water-Quality Assessment (NAWQA) program is a new program of the I. R. Iran. This program is interdisciplinary and integrates chemical, physical, and biological data to assess the water quality at local, regional, and national levels [1]. One component of this integrative assessment is to examine the occurrence and distribution of selected organochlorine compounds and trace elements in fish livers and whole-body fish samples on a basinwide scale. The NAWQA program emphasizes the use of consistent protocol methods for a nationwide approach [2]. The program also strives for consistency of selected target taxa within and among study units. Characterizing the geographic distribution of trace-element constituents with regard to background conditions and sources is one goal of the assessment. The use of biota analyses provides an understanding of the fate, distribution, and potential effects of these constituents. To determine the extent of contamination in an aquatic system by means of the trace elements in fish liver, the natural level (or the background concentration) needs to be established [3]. Measuring concentrations of trace elements in fish liver offers a more complete description (than just one sampling medium) of the occurrence and distribution of trace elements in a catchment area [4].This report presents the results of trace element analyses for fish livers. The fish samples for this study were collected in July 2003.

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2. PURPOSE AND SCOPE

This report (1) identifies the occurrence and distribution of selected trace elements in fish liver at sampled sites; (2) determines the relation of trace elements in fish liver to natural and human factors; and (3) compares the results with similar studies in Iran and the U.S.

3. DESCRIPTION OF STUDY UNIT

Study unit of the KhorramAbad River Basin in the west of Iran is situated in the center of Lorestan province, between 33°, 22′ and 33°, 40′ northern latitudes and 48°, 14′ to 48°, 27′ eastern longitudes. The primary river in the study unit, the KhorramAbad River, originates in the mountain of Chakriz and flows about 11 mi northeast into KhorramAbad city. Its headwater and most of the tributaries originate from the mountains that form the northern boundaries of the study unit. This unit is limited to the Chakriz mountain in the north along the Alashtar road, the Cham Anjir region in the southwest (along side of Khouzestan highway), the Sephid Kouh Mountain in the west and the Kamar Siah Mountain in the east (Fig. 1). The KhorramAbad catchment area is situated in the simple folded zone of the Zagros (west of Iran). Arabia-Eurasia convergence is achieved in the NW of the Zagros by a combination of shortening on NW-SE trending folds and thrusts and by right-lateral strike-slip on the NW-SE trending main recent fault. The geology structure of this province is simple, orderly folded and composed of anticlines ranges that compress together with a usually vertical axial plain and NW-SE trending. The stratigraphic situation of the study unit is very complicated and there are different exposures of folded Zagros depositional units. The Lithostratigraphic units of the region, with familiar and distinctive names include Amiran, Kashkan, Asmari, and Gachsaran formations. The KHRB (Khorram Abad River Basin) study unit has a drainage area of about 115 mi^2 with a cold semiarid climate, varied geology, topography and hydrology. Predominant land use in the KHRB is sparse forest and range land. Within the forest and rangeland setting, other major land uses are mining, urban/recreation, and agriculture. A number of urban/recreation areas are associated with growth resulting from the expansion of energy development in the 1980's.

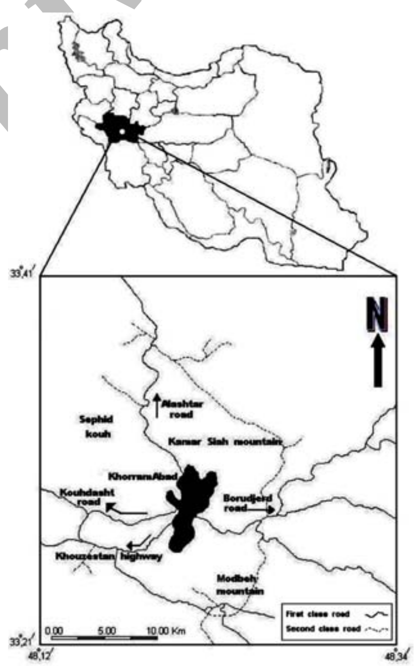

Fig. 1. Geographic coordinates and relational roads to KhorramAbad Basin. Sampling map of KhorramAbad River Basin

4. SAMPLE COLLECTION AND ANALYSIS

The collection and field processing of fish-liver samples for the analysis of trace elements follow the establishment of the Crawford and Luoma protocols [5]. Fish samples were collected at 15 sites throughout the KHRB study unit (Fig. 2; Table 1). Fish collection was done by electrofishing a stream reach that was 450 to 600 ft long at wadeable sites and 1,500 to 3,000 ft long at nonwadeable sites. The fish taxa collected for analyses were selected from a National Target Taxa List (NTTL) that consists mostly of bottom-feeding fish and nonmigrating game fish [6]. The NTTL was established to provide consistency within the NAWQA program. Trace elements in fish liver were analyzed at the Laboratory complex of Islamic Azad University, Science and Research Campus, Tehran [6]. The total digestion method was used for analyzing. In this procedure, liver samples were digested with a mixed-acid solution consisting of HNO_3, $HClO_4$, and HF. This procedure is effective in dissolving organic tissues and their mineral remains such as sulfates, and oxides are only partially dissolved. Previous investigations using a variety of materials support the completeness of the digestion [7]. Results are reported for 13 elements analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy [8, 9]). The minimum reporting limits (MRL) for the total digestion method as well as a statistical summary of mean values, standard deviations, and median values for trace elements in fish liver are given by Timme [10]. The trace element constituents included in fish-liver analyses and the minimum reporting limits are listed in Table 2. Both analytical precision and accuracy are well within acceptable ranges. Results of trace-element analyses for fish liver are listed in Tables 3, 4 and 5. Triplicate samples were collected for fish liver for quality assurance/quality control. The difference between field triplicate samples for fish liver ranged from 10 to 30 percent.

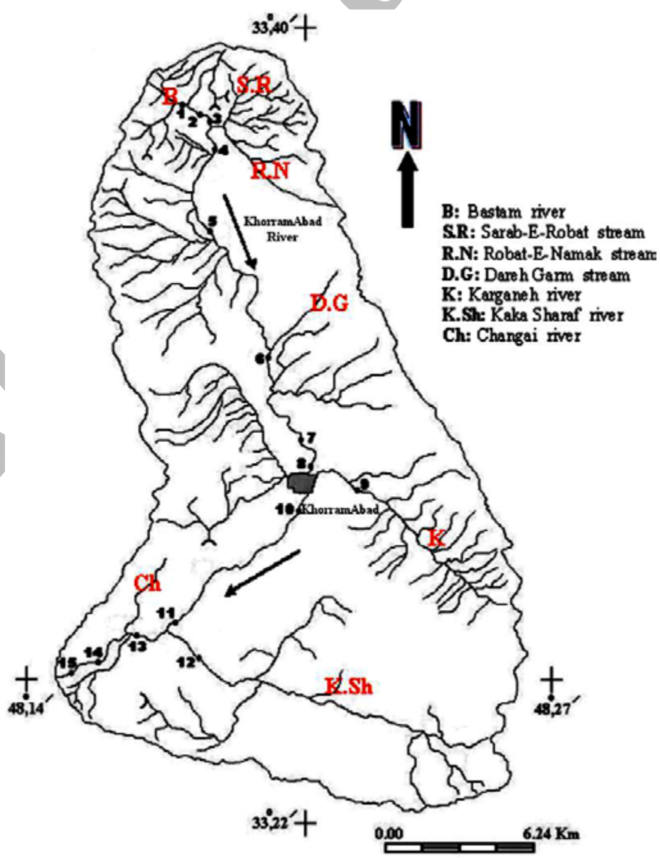

Fig. 2. Location of sites for collection of fish samples in the Khorram Abad River Basin

Table 1. Description of sampling sites in the KhorramAbad River Basin study unit [Triplicate samples were collected at all sites]

Site number (Fig. 1)	Stream	Sample type	Fish sample No.	Species
1	Bastam river	Liver	F_1	Salmon
2	Khorram Abad river	Liver	F_2	Trout
3	Khorram Abad river	Liver	F_3	Salmon
4	Khorram Abad river	Liver	F_4	Salmon
5	Khorram Abad river	Liver	F_5	Mullet
6	Khorram Abad river	Liver	F_6	Salmon
7	Khorram Abad river	Liver	F_7	Salmon
8	Khorram Abad river	Liver	F_8	Salmon
9	Karganeh river	Liver	F_9	Spotted mullet
10	Khorram Abad river	Liver	F_{10}	Spotted mullet
11	Khorram Abad river	Liver	F_{11}	Mullet
12	Kaka Sharaf river	Liver	F_{12}	Salmon
13	Khorram Abad river	Liver	F_{13}	Salmon
14	Khorram Abad river	Liver	F_{14}	Salmon
15	Khorram Abad river	Liver	F_{15}	Mullet

Table 2. Constituents included in the fish-liver Analyses [Values in ppm]

Fish livers Trace elements and major metals (minimum reporting limit)[1]			
Aluminum (1) Antimony (0.1) Arsenic (0.1) Barium (0.1) Beryllium (0.1) Boron (0.2)	Cadmium (0.1) Chromium (0.5) Cobalt (0.1) Copper (0.5) Iron (1) Lead (0.1)	Manganese (0.1) Mercury (0.1) Molybdenum (0.1) Nickel (0.1) Selenium (0.1)	Silver (0.1) Strontium(0.1) Uranium (0.1) Vanadium (0.1) Zinc (0.5)

[1]The minimum reporting limit is the smallest measured concentration of a constituent that may be reliably reported using a given analytical method [10].

Table 3. Concentrations of selected trace elements in fish-liver samples collected from sites in the KhorramAbad River Basin study unit [Values in ppm; -, less than minimum reporting level]

Sample No.	Cd	Fe	Ni	Pb	Zn	Co	Mn
F_1	-	750	1.3	-	36	5.5	10.2
F_2	3.5	810	2	0.5	17	10.5	6.6
F_3	4	861	17	0.8	86.05	16	4.7
F_4	2	967.5	17	0.4	129.4	8	3.7
F_5	4	228	7.5	0.6	11.85	12	5.7
F_6	2.5	831	13.5	0.5	112.15	0.5	4.2
F_7	2.7	915.5	9	0.5	89.5	1.6	4.5
F_8	3	910	8.5	0.3	94.3	2	6.8
F_9	1	65.5	8	0.6	307	4.5	4
F_{10}	5	125	12.5	0.3	138	9	6
F_{11}	4	103.5	18	0.5	131.15	13.5	4.5
F_{12}	3	610.5	30	0.7	63	17	9.4
F_{13}	4.5	338	16.5	0.8	79.85	19.5	5.2
F_{14}	1.5	939.5	-	1.5	170.8	3	6
F_{15}	3	862.5	17.5	0.4	97.55	3.5	6.6

Table 4. Concentrations of selected toxic trace elements in fish-liver samples collected from sites in the KhorramAbad River Basin study unit [Values in ppm; -, less than minimum reporting level]

Sample No.	V	As	Hg	Se
F_1	0.05	0.3	0.35	51.8
F_2	0.04	0.2	0.25	13.9
F_3	0.04	-	0.14	32.2
F_3	0.03	0.3	-	38.8
F_5	-	0.2	0.3	31.8
F_6	0.02	-	0.2	32.2
F_7	0.02	1.3	0.2	63.2
F_8	0.04	0.8	0.1	6.1
F_9	0.05	0.4	0.13	66.5
F_{10}	0.03	-	-	4.2
F_{11}	0.02	0.2	0.17	3.1
F_{12}	0.01	1.1	0.14	7.2
F_{13}	0.02	1.3	0.13	8.9
F_{14}	0.02	0.7	0.14	11.1
F_{15}	0.03	0.5	0.15	14.2

Table 5. Concentrations of alkaline trace elements in fish-liver samples collected from sites in the KhorramAbad River Basin study unit [Values in ppm; -, less than minimum reporting level]

Sample No.	Li	K	Na
F_1	-	0.08	15.5
F_2	-	0.06	14
F_3	-	0.08	8
F_4	-	0.05	20
F_5	-	0.08	24.5
F_6	-	0.08	1
F_7	-	0.07	1.5
F_8	-	-	2
F_9	-	0.1	4
F_{10}	-	0.08	12
F_{11}	-	0.06	20
F_{12}	-	0.08	0.5
F_{13}	-	0.04	14
F_{14}	-	0.07	5
F_{15}	-	0.05	4

5. TRACE ELEMENTS IN FISH LIVER

Four important attributes of tissue analysis are: (1) to increase the likelihood of detecting contaminants that are undetectable in water and sometimes streambed sediment; (2) to obtain a time-integrated estimate of contaminants in the environment; (3) to indicate bioaccumulation; and (4) to provide the opportunity for integrating tissue concentrations with those in water and sediment to assess contaminant fate, distribution, and effects [11]. The most common taxa present at most of the sampling sites were salmon and mullet (Table 1). Thirteen of the selected trace elements were detected in most sites. Lithium and silver were not detected at any site. The minimum concentration of trace elements in fish liver of the watershed belongs to vanadium, while the maximum belongs to iron. Vanadium is one of the important elements in porphyrins organometallic compounds [11], but its consumption by fish is very low. Poor concentration of mercury and arsenic in fish liver tissue is the consequence of agricultural poisons and drainage waters from marginal farms entering into the surface waters of the study area. Elevated concentrations of Fe, Mn, and Ni trace elements at some sites (4, 12) may be a combination of natural and human factors. Low concentration of alkaline trace elements, Na and K, in analyzed liver samples is the result of low dissolved salts in surface waters and the strong absorption of these major invariable elements on clay mineral surfaces.

Generally, trace element concentrations that have been corrected for their background contribution correlate better with measures of human activity or impact such as population density, land use, and toxic release inventory than uncorrected trace element concentrations [12]. In this study, background refers to trace element concentrations of fish liver samples collected from undeveloped areas in the stream sampling site basins. For fish samples, the background concentration is obtained from bottom feeding samples, which usually represent minimal anthropogenic activity during the early stages of reservoir development so that the naturally occurring concentrations could be separated from the anthropogenic sources of trace elements. Natural factors include weathering and subsequent erosion of local soil and bedrock, and atmospheric deposition unaffected by anthropogenic activity [13]. Natural activities can occasionally elevate concentrations greater than the background. Anthropogenic trace element concentrations are calculated for liver samples by subtracting the background concentration from the total trace element concentration. A basin-specific background concentration for cadmium, selenium, and zinc was determined by plotting cumulative frequency curves for the KHRB study unit for data from 15 fish liver samples (Fig. 3). The concentration at the first break point (change in slope) was designated as the background concentration [3]. Because of their concentrations in the study unit and their toxicity to aquatic biota, cadmium, selenium, and zinc were selected for detailed analysis. Cadmium had a determined background concentration of 4ppm (Fig. 3; Table 5). Sites 2 and 5 (sites chosen to represent background conditions) had a lower concentration of zinc than the background concentrations for the basin. Because of the extent of mineralized areas in the KHRB study unit, the concentrations of cadmium, selenium, and zinc could represent natural conditions at some sites. Four sites exceeded background concentrations for the KHRB for cadmium and eleven sites for zinc (Table 3). The site affected by mining, site 10, generally exceeded the background concentrations by orders of magnitude for cadmium. Sites 7 and 9 which are agricultural land-use sites, had about two times the background concentration for selenium. The underlying geology, consisting mainly of Amiran Shale of Paleocene age, and the irrigation return flows upstream, are likely contributing factors to the elevated selenium concentration. Selenium is present naturally in the shale bedrock of the middle and lower reaches of the basin and is present in the surface and ground waters. Elevated concentrations from sites 1 and 7 may be a result of human factors. Individual samples of cadmium were highest in both sampling media at mining land-use sites, whereas selenium was highest in both sampling media at agricultural land-use sites. Zinc was highest in fish liver at agricultural land-use sites. The highest mean concentration of cadmium, selenium and zinc were found in spotted mullet fish-liver samples at sites in the KhorramAbad River Basin (Tables 3, 4). The highest concentration of zinc was in a mullet (spotted) liver sample at site 9, an agricultural land-use site in the KHRB physiographic region, which was the most downstream site in the catchment area. Although site 9 represents agricultural land use, it also had past mining activities in the eastern part of the basin. The high concentration of zinc in the liver samples is due to fish needs for this minor nutritional element, especially in the early days of growth. A medium frequency of selenium in fish samples (spotted mullet) is relatively high, the result of joining industrial and agricultural waste waters to the main waterway of this region. Site 14 represents a mixed land-use site and receives water from a mining affected river just upstream from the sampling site.

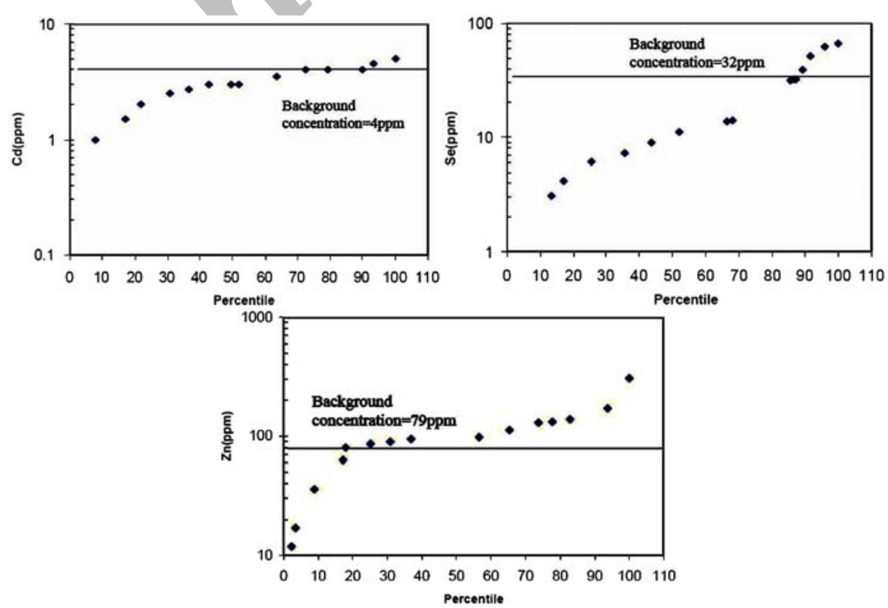

Fig. 3. Cumulative frequency curves used to determine the background concentration of cadmium, selenium and zinc

6. DISCUSSION AND RESULTS

The quantification of potential contaminants in biological tissues can be an important part of water-quality assessment programs. Trace element concentrations for fish tissue can be used to estimate the proportion of contaminants in stream bed sediments that are biologically available. Again, because of the continuous nutrition of recent sediments and waters by fish, trace elements concentration for fish tissue (especially fish liver) directly reflects a potential source. The determination of contaminants in fish tissue can be used to provide information about (1) direct threats to human health and ecosystem integrity and (2) the occurrence and distribution of potential contaminants in the environment.

A major limitation to tissue analysis is that a single species is not available at all sites in a large basin (such as trout). In spite of the problem, comparisons among different species may not be questionable because accumulation rates among species rarely differ in high ranges, especially for bottom-feeding fish that ingest the latest streambed sediments. Thus comparison of selected trace-element concentrations in fish liver among the different taxa at the sampling sites indicated that trace element bioconcentration may not be species dependent. According to some opinions, migration and mobility of fish add to variability when comparing trace element concentrations at sites to land use. I believe that the mobility of nonmigrating fish in big sampling sites is not an important factor in comparison with the ingestion rate from the bottom sediments. On the other hand, the size and age of the analyzed fish may be important for the ingestion rate, but not for trace element bioconcentration [14] as bioconcentration is source dependent. In my opinion, only the migration of some migrating fish (such as salmon) caught in a particular site may be misleading to conclude that elevated concentrations reflect trace elements inputs from that site. All samples, even salmon which we sampled, were nonmigrating. Salmon and mullet were the only taxa that were collected in more than of 60% of the physiographic basin; therefore, these taxa were used for biogeochemical comparisons between the two physiographic provinces. A comparison of the present study to other studies in the United States and Iran indicated that the total medium frequency of fish samples for cadmium, selenium and zinc in the study unit was higher than the analyzed fish samples of the Upper Colorado River Basin (UCOL) [4] and Southern beaches of the Caspian Sea (SBCS) [15] study basins (Table 6). Regional similarities in fish sample concentrations occurred more often than regional differences among the study units. More relations were observed between two study units, KHRB and UCOL, rather than among all three study units. All three study units have agricultural, mining, urban/rural, and recreation land use. The highest concentrations for zinc and selenium in fish liver samples for two study units, KHRB and UCOL, were at sites affected by agricultural activities and for cadmium were at sites affected by mining, whereas the highest concentrations for cadmium, selenium, and zinc in fish samples for SBCS were at sites affected by mixed land use.

Table 6. Background concentrations for selected trace elements in fish liver
[All values in ppm. Fifteen fish samples were analyzed and used to compute background concentrations for this study]

Trace Element	Shaham (1999)[1]	Deacon & Verlin (1995-96)[2]	KhorramAbad Basin
Cadmium	0.70	3	4
Selenium	1.30	22.10	32
Zinc	190	52	79

[1]Background concentrations established for Southern Caspian Sea fish samples [15].
[2]Geochemical data for fish samples in the Upper Colorado River Basin, Colorado (UCOL) [4].

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