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THE FOLLOW UP OF MERCURY LEVELS IN SIX FISH SPECIES: A CASE STUDY SHATT AL-ARAB RIVER, IRAQ

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ABSTRACT

The present work is an attempt to study the mercury levels in six fish species from Shatt Al-Arab River were determined by cold vapor atomic absorption spectrometry, provide values that are lower than the most literature data. We found significant species differences, with *Cyprins Carpio* having the highest levels and *Barbus sharpeyi* the lowest levels. The results showed statistically significant differences of total mercury concentration were also found among the individually tested tissues (muscle, kidney, liver, skin and gills), since the muscle of the tested fish accumulate the highest amount of mercury. The present study pointed out that at the time of analysis Shatt Al-arab River is still a non –polluted area as the data illustrated.

INTRODUCTION

Shatt Al-Arab River is formed when the Tigris and Euphrates Rivers of Iraq and the Karun river of Iran meet near Basrah in Iraq. Shatt al Arab River continues for approximately 120 Kilometers before interring the Arabian Gulf. The eating of fish in an average of two to three meals each week help to reduce cholesterol, high blood pressure, and hardening of arteries. The research shows that the consuming of fish increases high quality protein with low calories but it is rich in omega-3 fatty acids, which helps to reduce the risk of coronary artery disease. This helps in the treatment of bipolar disorder/depression, and reduces inflammemation in autoimmune diseases (Sivakumar *et al.*, 2007). The sodium concentration in fish is low but it is a good source of potassium. Unfortunately, the high levels of contaminants including mercury observed in many fish due to industrial pollution, which are absorbed by surrounding waters and from foods they eat. Currently, the EPA limit for mercury in fish is 1 ppm, which accounts for 95% of the fish production (HPHN, 2006). The EPA estimates up to 15% of mercury emissions from these utilities fall within 30 miles of a plant, and up to 50% falls within six hundred miles. The mercury bioaccumulates through the food chain and reaches the predator species.

Mercury and its compounds are present longwith the most toxic substances found in the environment (Renner, 1997) and it is exists in a large number of different physical and chemical forms with a wide range of physical, chemical, and eco-toxicological properties that are of fundamental importance to its environmental behavior (Lambertsson *et al.*, 2001). The presence of mercury in fish can affect brain development and damaging the central nervous system. Mercury poisoning symptoms include numbness in hands and feet, general muscle weakness, and vision, hearing, and speech damage. In extreme cases, insanity, paralysis, coma and death follow. The three most important inorganic chemical forms of mercury (elemental mercury – Hg^0, mercurous – Hg_2^{2+} and mercuric – Hg^{2+} ions) are far more soluble and have a strong affinity for many inorganic and organic legends, especially those containing sulfur. Those forms are strongly accumulated in aquatic organisms and also concentrated in aquatic food chains i.e., fish, birds etc. (Ipolyi *et al.*, 2004) Fishes in the surface water serve as bio-indicators of pollutant loads (Teh *et al.*,1997), it is necessary that suitable measures should be taken to provide chemical monitoring of the risks deriving from its consumption.

The major health impacts caused by mercury affect mostly individuals who have a regular fish diet. Human exposure to mercury intoxication through the ingestion of mercury contaminated fish has been well studied (Harada 1995). The FDA has released guidelines for children, women who are pregnant and women who are trying to become pregnant. These guidelines state that not more than 12 oz of low mercury fish should be consumed weekly. "Highest" mercury fish should be avoided and "high" mercury fish should be kept to only three 6-oz servings per month. Most concern has centered on the presence of mercury in fish since seafood is a major source of mercury in non-occupationally exposed populations (Kurland et al., 1960).

Fish and fish products account for most of the organic mercury in food. The average daily intake of mercury from food is in the range 2–20 µg/day, but may be much higher in regions where ambient waters have become contaminated with mercury and where fish constitute a high proportion of the diet (Gorchev 1991). Mercury concentration in fish is influenced by fish age, mercury concentration in water ecosystem, food contamination, chemical, biological and physical process in aquatic environment and seasonal variations (Sarica *et al.*, 2005).

The objective of this study is to determine the mercury concentration levels in the six fish species from Shatt Al-Arab River, no data on mercury levels in the Shatt Al-Arab fish is available,

MATERIALS AND METHODS

Materials

Study Area: In order to study the mercury levels in six fish species from Shatt Al-Arab River, the Basrah Province has been selected as a study area. Geographically, the Province is situated in the southern part of Iraq at the northwestern corner of the Arabian Gulf, within longitude 46° 60′ to 48° 60′ E and from latitude 29° 13′ to 31° 29′ N with a total area of 19,070 km^2 (Fig. 1).

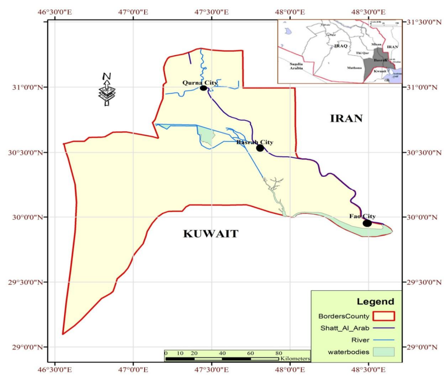

Fig. -1: General location of study area in the (Shatt Al-Arab River) Basrah province and showing sampling stations

Climatically, like most parts of the Arabian Peninsula, a desert-type environment with scanty rainfall and hot dry weather characterizes the climate of Basrah. Summer is very hot, especially in

July and August with mean temperatures of 37.4°C and maximum mean temperatures of 45°C. The average evaporation exceeds 2450 mm/year with average annual rainfall less than 100 mm/year. Shatt al Arab River continues for approximately 120 Kilometers before interring the Arabian Gulf. An estuary of approximately 10,000 to 20,000 square Kilometers surrounds the Shatt Al Arab River it contained sandbars, marshes, lagoons, ox-bow lakes and tidal flats. Billions of cubic meters of water enter this estuary each year much of the water flow is detained in the marshes and an appreciable portion evaporates.

Ancillary Data and Apparatus: The determination of mercury in the fish samples achieved by means of cold mercury vapor atomic absorption spectrometry (CVAAS) using shimadzu atomic absorption spectrophotometer model (AA-630-12) and mercury hallow cathode lamp at (253 nm). Aquartz cell of 12 cm in length and (0.8) cm in diameter with quartz windows, with and out lets ends has been used for measurements.

Methods

Field work and laboratory studies: Fish and sediments were collected from the Shatt Al--Arab River. Muscle flesh samples from the mid –dorsal region of the six species was removed. The samples were first sun dried on the beach sand until nearly dried. Dried samples were stored in a deep freezer until reaching the laboratory, then freeze-dried and ground with agate mortar. Fish samples (1 g dry wt) were digested according to the procedure described by Goldberg et al. (1983) in which concentrated HNO_3 and $HClO_4$ were used in Teflon beakers placed on a hot plate. After digestion, residue was re-dissolved with 2N HNO_3. Only atomic absorption grade acids and double distilled deionized water were used throughout this work. Blank values were negligible. Standard addition methods were employed whenever necessary to overcome matrix effects. To check the possible loss of Mercury during sample processing, quality control samples containing known amounts of Mercury in fish muscles and other organs,

Procedure: Two ml of digested fish samples was introduced in the reduction vessel, 2.0 ml of $SnCl_2$ solution was added and mixed using magnetic stirrer for 2 min. then the mercury vapor forced by nitrogen gas with rate of 0.25 L/min. The atomic absorption signal of mercury was measured at 253.65 nm. The optimum parameters of atomic absorption spectrometer for the determination of mercury were listed in Table-1.

Table -1: Instrumental Parameters

Wave length (nm)	253.65
Band width (nm)	0.3
Lamp current (mA)	6.0
Back ground correction	None
Time of mixing (sec.)	60
Flow rate of carrier gas (L/min)	0.25
Conc. Of $SnCl_2$(%)	25
Volume of $SnCl_2$ (ml)	2.0
Temperature (ºC)	80
Volume of sample (ml)	2.0

The cold vapor system used has been described in detail elsewhere (Ali, 2006). Detection limit calculated following the recommen-dations of IUPAC was 0.73ng Hg /gm dry weight.

Statistical analysis: All results were analysed statistically using two-way analysis of variance with unbalanced repeated measurements. Statistical between individual time points was made by using Revised Least Significant Difference (RLSD) test. The probability level for significance was 5% or less.

RESULTS AND DISCUSSION

Concentrations of mercury in different organs and muscle*:* The freshwater Shatt Al-Arab is the longer river in Basrah (180 km). Fish from this river serve as the main source of protein for the population of Basrah city. Six fish species were selected for monitoring bioaccumulation of total mercury in river ecosystems. There are four possible routes for substances such as mercury to enter fish body. One way is by means of the food ingested and another is by means of absorption of the mercury in its ionic form by the fish through the gills. This can occur probably by simple diffusion and possibly through the pores in the gills. Indications are that metal uptake in the gill tissues may be correlated with mass specific rates, with small fish accumulating metals more rapidly than larger ones. A third possible route is through drinking water while a fourth is by absorption through the skin. The bioaccumulation of mercury was evaluated in selected fish tissues of *Tenaulosa ilisha*. The mercury concentrations in the tested tissues are presented in Table-2.

Table-2: Concentrations of mercury (µg/gm wet weight) in different organs in *Barbus sharpeyi* fish from Shatt Al-Arab river.

Organs	No. of sample	Hg Conc. (Mean±S.D)
Kidney	4	0.076±0.030
Liver	6	0.079±0.025
Muscle	10	0.137±0.053
Skin	7	0.042±0.017
Gills	8	0.056±0.014

Statistically significant differences of mercury concentrations were found among the individually tested tissues with the following exceptions: the skin tissues have statistically insignificant differences compared to the gill. Statistically insignificant differences of the mercury concentrations were also found between liver and kidney. Generally the living environment expressively influences the total mercury content in muscle tissues of fish. Table -2 shows that the highest concentrations of the total mercury were determined in muscle tissues (0.137±0.053µg/gm) of tested fish where mercury is bound to cysteine rich proteins (Boening, 2000; Anonymous, 2002). Also the other authors (Anonymous, 1999, 2002, Dusek *et al.*, 2005) observed high concentrations of the total mercury in muscle tissues of various fish species. Vigh *et al.*, 1996 found the highest mercury concentrations in the kidneys of grass carp .Only the flesh of freshwater fish in England revealed higher values than those in the other tissues (Barak and Mason 1990b). The lowest concentrations of total mercury were found in gills (0.066±0.014µg/gm) and skin (0.052±0.017µg/gm) of tested fish. The mercury content in tested tissues of *Tenaulosa ilisha* decreased in order: muscle >> kidney ≈ liver > skin ≈ gills. Mercury concentrations between fish species *Cyprins Carpio* , *Barbus lutaus, Liza abu, Tilapia zillii,Barbus sharpeyi and Tenaulosa ilisha* were significantly different ($p<0.0001$). Table-3 showed that *Cyprins Carpio* had the highest mercury concentrations (0.160±0.045µg/ gm), followed by *Barbus lutaus* (0.149± 0.075µg/gm)The lowest mercury concentrations were found in the two species *Liza abu* and *Barbus sharpeyi* with mean concentrations of (0.067±0.027µg/gm) and (0.053±0.026µg/gm) respectively. The high mean mercury concentrations observed in *Cyprins Carpio* can be attributed to the widest food web (algae, aquatic plants and terrestrial seeds, larvae and molluse animals). Because of the low range fish age (3-7 years) their age did not influence the content of total mercury in the tested tissues.

Table -3: Concentrations of mercury (µg/gm, wet weight) in the muscle of different species of fish from Shatt Al-Arab river.

Species	No. of sample	Hg Conc. (Mean±S.D)
Liza abu	9	0.067±0.027
Barbus lutaus	11	0.149±0.075
Barbus sharpeyi	10	0.053±0.026
Tenaulosa ilisha	10	0.081±0.032
Cyprins Carpio	10	0.160±0.045
Tilapia zillii	8	0.077±0.036

Concentrations of mercury in fresh water fish and some Tilapia species: In Table-4 literature data for levels of total mercury in fish are presented. Even for the same type of water interspecies comparison has limited value. Consequently our data can only be compared with the scarce values for the same or related *Tilapia* species as shown in Table-5. The total mercury content in the muscle of *Tilapia zillii* from Maryut Lake, Egypt (El Nabawi et al 1987) was 4-times higher compared to the muscle samples from Niger Delta, Egypt (Kakulu and Osibanjo, 1986) and 65-times lower compared to the muscle samples from Wadi El-Raiyan Lake, Egypt (Saleh *et al.*, 1988). Levels of mercury for the Egypt (Nile River) fish samples were identical for those found in the fish samples from Maryut Lake, Egypt (El Nabawi *et al.*, 1987). In the fish samples from Kenya (Lake Nakuru), the total mercury levels obtained by Koeman *et al., (*1972) were significantly lower than those found by Greichus *et al.*, [1978b].

The FAO limit for total mercury in fish products, which is also, adopted by various countries about 0.5µg/gm (FAO, 1983). The WHO (1987, 1989) recommended a permitted value of 0.31µg/gm. In all fish samples analyzed a concentration level of at least thirty times lower was observed. Mercury in fish has been featured in the media frequently and people faced with conflicting information about the risks and benefits of consuming fish. We suggest that state agencies are responsible for protecting the health of their citizens and they should obtain information on fish availability in markets and fish preferences of diverse groups of citizens. The state agency should provide the information to select fish for contaminant levels by providing data on the most commonly eaten fish that will help people to make decisions about risks from fish consumption.

Conclusion

From the above analyses, we can conclude that the findings in present study have profound information about the levels of mercury determined, which is higher in *Cyprins Carpio* than in the other fish species consumed by humans. The muscle tissue had the highest mercury concentrations in comparison with other organism. The levels of mercury in the tested fish species is higher, as far as could be compared below published values for other fish and well below the acceptable limits for mercury in foods and thus unlikely to cause adverse effects to aquatic organisms. Present results help us to understand in the better way for the accumulation of mercury in the selected individual tissues of the fish. This study recommended that there is a need to establish a professional research center, which can coordinated with government sectors and different departments in Basrah University to solve the various pollution problems. It is also necessary to compare the case of Basrah Province with other important cities in other developing countries that are experiencing similar forces of pollution processes. It is hoped that our results of this study can open up new arena of comparative research so that a broad based or full picture can eventually be unfolded to shed light over the pattern and processes of pollution transformation in Iraq under environment change processes.

Table-4: Concentrations of mercury in freshwater fish.

Species	Location	No. of samples	Hg contents (µg/gm)	References
Gadus morrhua	Norway (fjords)	-	0.1-0.4	Stenner and Nickless 1974
Commercial species	SW Spain/Portugal (Atlantic coast)	-	0.79	Stenner and Nickless 1975
Composite	South Africa (Transvaal)	-	0.52	Greichus et al., 1977
Composite	Zimbabwe (McIlwaine Lake)	3	0.23	Greichus et al., 1978a
Twelve species	Finland (Lake Paijanne)	1774	0.05-4. 68	Hattula et al., 1978
Lates niloticus	Nigeria (Niger River)	-	0.67	Ndiokwere 1983
All fish	Nigeria (Niger Delta)	-	0.10	Kakulu and Osibanjo 1986
Salmon sole	Pakistan (coastal waters)	16	0.05±0.02	Jaffar and Ashraf 1988
Forimio niger	Pakistan (coastal waters)	16	0.07±0.02	Jaffar and Ashraf 1988
Paralichthys species (sole)	Argentina (Bahia Blanca estuary)	188	0.85±0.18	Marcovecchio et al., 1988
Finfish	USA (Louisiana)	52	0.4	Ramelow et al., 1989
Four species	Spain (Castellan Coast)	-	0.16-0.84	Hernandes et al., 1990
Rutilus rutilus	Eastern England(Rivers)	338	0.01-0.4	Barak and Mason 1990a
Nine fish species	USA (Savannah River)	-	<0.5	Winger et al., 1990
Serranus species	Italy (Coastal waters)	-	0.09-0.63	Giadano et al., 1991
Commercial species	Czechoslovakia	30	0.01-0.12	Palusova et al., 1991
Common fish	Spain (Granada Coast)	32	0.03-1.21	Navarro et al., 1992
Two species	Burundi (Lake Tanganyika)	100	<0.05	Benemariya et al., 1991
Six species	Iraq (Shatt Al-Arab River)	58	<0.3	Present study

Table-5: Concentrations of mercury in some *Tilapia* species.

Species	Location	No. of samples	Hg contents (µg/gm)	References
Tilapia grahami	Kenya (Lake Nakuru)	10	0.016	Koeman et al., 1972
Tilapia	Kenya (Lake Nakuru)	10	0,22	Greichus et al., 1978b
Tilapia melanopleura	Egypt (Niger Delta)	-	1.33	Ndiokwere 1983
Tilapia zillii	Egypt (Niger Delta)	-	0.013	Kakulu and Osibanjo 1986
Tilapia niloticus	Egypt (Nile River)	5	0.05	El Nabawi et al., 1987
Tilapia zillii	Egypt (Maryut Lake)	4	0.06	
Tilapia niloticus	Egypt (Maryut Lake)	5	0.04	
Tilapia zillii	Egypt (Wadi El-Raiyan Lake)	-	4.00	Saleh et al., 1988
Tilapia zillii	Iraq (Shatt Al-arabRiver)	1	0.077	Present study

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