Concentration of Selenium and Mercury in six species of fishes from Shatt Al-Arab River, Iraq

Article · September 2019

DOI: 10.21276/ijaq.2012.9.2.6

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Concentration of Selenium and Mercury in six species of fishes from Shatt Al-Arab River, Iraq

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Abstract

The present study deal with determination of Se:Hg ratio in six fish species collected from Shatt Al-Arab river during the period June 2010 to Augest 2010. Muscles of the most important six commercial species of fish *C. Carpio*, *B. luteus*, *L. abu, T. zilli, B. sharpeyi and T. ilisha* have been analyzed after wet digestion with a mixture of concentrated acids ($HClO_4$ / HNO_3).The obtained results show that *L. abu* species having the highest Se:Hg ratio, while *B. luteus* species having the lowest Se:Hg ratio. Tissues analysis (skin, gills, kidney, liver, muscles) of *B. sharpeyi* reveals that skin accumulates the highest Se:Hg ratio levels, while muscles contained the lowest Se:Hg ratio. The values obtained are compared with literature data and selenium contents in fish muscle.

Key words: Selenium, Mercury, Fish, Shatt Al-Arab River, Iraq.

Introduction

The aquatic environment has been polluted by effluent wastes containing trace metals from human activities. These inputs arise from various treated or untreated municipal and industrial wastes, agricultural runoff as well as inputs from the atmosphere. Selenium plays an important role in human nutrition, since more and more investigators realize the essentiality of this trace element for human health (Levander, 1982). The interest in daily intake of selenium has resulted not only because of the pathological conditions which induce from deficiency or toxicological reasons, but especially also for the beneficial effects of this element in prevention of various types of cancer (Comstock *et al.,* 1992) and cardiovascular diseases (Singh *et al*., 1991). Selenium has an interesting affinity to bind with mercury, blocking the mercury from binding to other substances, such as brain tissue. The ability of Selenium compounds to decrease the toxic action of mercury has been established in all investigated species of mammals, birds and fish (Culvin–Franess, 1991). Selenium is also an important nutrient for fish. If mercury is depleting selenium, the selenium is not available for creating enzymes that are crucial for cellular function. Thus, it is important to maintain enough free selenium to support selenium-dependent enzyme synthesis and activity (Raymond - Ralston 2004). Fish are a high source of dietary selenium, and cooked fish does not affect or prevent the absorption of selenium when eaten (Fox *et al.*, 2004).Selenium contamination in drain water and surface water is a serious problem to fish and wildlife resources and it has been identified as an environmental contaminant in industrialized areas (Mierzykowski *et al*., 1997).

National dietary intake of selenium by rainbow trout is approximately 0.07 µg Se/g (Hilton *et al*., 1980) .While selenium may cause death to human in deficient amounts (Eisler, 1985). Fish consuming diets with 10 to 33 µg Se/g have experienced toxic effects (Besser *et al*., 1993) .Excessive amounts may be lethal, cause reproductive abnormalities or failure, result in tissue damage, retard growth, or eliminate entire fish communities (Lemly, 1996).

The objective of this study is to analyzed selenium: mercury ratio in the muscles of six species of fish collected from Shatt Al-Arab River, to establish natural background levels of these elements in the study area; hence, no analytical work seems to have been undertaken on the selenium: mercury ratio of Shatt Al-Arab fish.

Materials and Methods

Apparatus

A Shimadzu flame atomic absorption spectrophotometer model (AA-630-12). A pyeunicam hallow cathode lamps of selenium and mercury were used as a sources operated at Se (169.1 nm), Hg (253 nm). The systems of hydride generation and cold vapor used has been described in detail elsewhere (Hussain, 2006), (Awad *et al.*, 2010).

Sample preparation

Six species of fish commonly consumed and present in Basrah were collected during the period June 2010 to August 2010 at various sites on the shore of Shatt Al-Arab as shown in Fig.1. Some fish samples (*B. sharpeyi, C. carpio, B. luteus* and *T. ilisha*) were bought directly from local fish markets. Muscle flesh from the mid-dorsal region of the five species was removed, while for the *Barbus sharpeyi* different part of organs samples were taken for analysis. The samples were first sun dried until completely dry. 0.5 gm of dried sample with 15 ml HNO_3 were placed in a digestion tube fitted with a 40 cm air-cooled condenser. A temperature and time controlled heated digestion as follows: 25 ^oC (4 hrs.); 70 ^oC (3 hrs.) 140 ^oC (6 hrs.). The condenser was removed to reduce the volume to 2 ml. After cooling, 5 ml $HClO_4$ was added, the air condenser replaced and the following temperature-time schedule implemented: 140 ^oC (10 min.), 160 ^oC (10 min.), 180 ^oC (10 min.) and finally 210 ^oC for 1 hr. This gradual increase in temperature is necessary to prevent charring of the material. The digestion block was cooled to 170 ^oC and the air condenser removed to reduce the volume to 1 ml. (Benemariya *et al*., 1991).

Procedures

1. **Selenium determination**

After cooling to room temperature, 1 ml HCl was added, the mixture heated at 100 ^oC for 15 min to convert all selenium compounds to Selenites and then the solution was quantitatively transferred to a standard flask and diluted to 20 ml with 1.5 M HCl. 0.2 ml volume of the sample solution in 1.5 M HCl medium was placed in the reaction vessel and 2 ml of 1 % w/v $NaBH_4$ solution were added. The solution was mixed for 20 sec. and the formed selenium hydride swept by nitrogen gas at a flow rate of 1.2 L / min in to the heated atomization cell, and the transient absorption signal is recorded. Detection limit calculated following the recommendations of IUPAC was 1.6 µg Se /gm dry weight.

2. **Mercury determination**
After cooling to room temperature, 1 ml of digested fish samples was introduced in the reduction vessel; 2 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 to the quarts cell. Detection limit calculated following the recommendations of IUPAC was 0.73 µg Hg /gm dry weight.

Statistical analysis

The statistical analysis was carried out using two-way analysis of variance with unbalanced repeated measurements. Statistical analysis 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

Fish from Shatt Al-Arab which is the longer river in Basrah (180 km) (fig.1) serve as the main source of protein for the population of Basrah city.

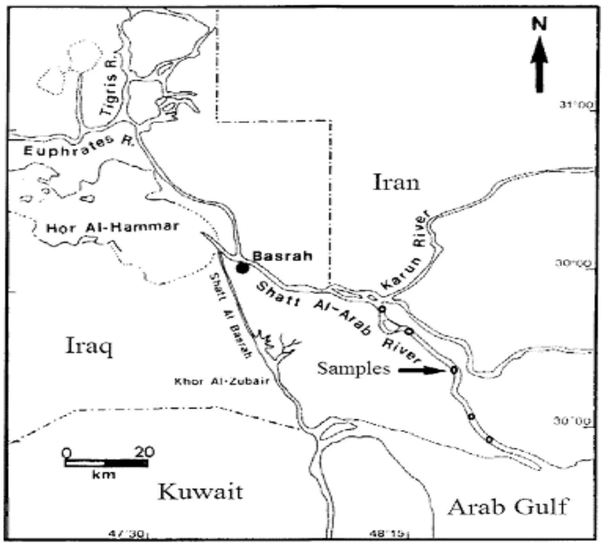

Fig (1) Map showing the study area

Fish can accumulate significant amounts of selenium from both water and food. There are four possible routes for substances such as selenium to enter fish body. One way is by means of the food ingested and another is by means of absorption of the selenium 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. We therefore analyzed selenium levels and the selenium: mercury ratio in Muscles of the most important six commercial species of fish *C. carpio*, *B. luteus*, *L. abu, T. zilli, B. sharpeyi and T. ilisha.* The obtained results in Table 1 show that *Liza abu* species contained the highest levels of selenium (1.10±0.20 µg /gm), while *B. sharpeyi* species contained the lowest levels of selenium (0.19±0.02µg /gm).

Table (1): Concentrations (Mean ± S.D) of selenium (µg /gm, dry weight) in the muscle of different species of fish from Shatt Al-Arab River.

Species	N	Se Conc. (Mean±S.D)
C. Carpio	10	0.86±0.08
B. luteus	11	0.24±0.04
L. abu	9	1.10±0.20
T. zilli	8	0.44±0.05
B. sharpeyi	10	0.19±0.02

Figure 2 shows that there were significant differences ($p<0.001$) in selenium: mercury levels among *C. carpio, B. luteus, L. abu, T. zilli, B. sharpeyi and T. ilisha*, with *L. abu* having the highest Se:Hg levels (12.09) and *B. luteus* the lowest Se:Hg ratio (2.215).

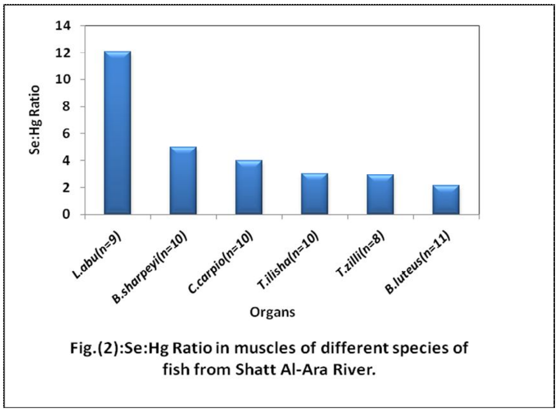

Fig (2) Se-Hg Ratio in muscles of different fish species from Shatt Al-Arab River

Differences found between species may be explained by the levels of selenium in water and the type and amount of food consumed by the fish. Figure 3 illustrates the ratio of Se:Hg in various organs of *B. sharpeyi* species, which were significantly difference ($p<0.01$), The data shows that the skin of *B. sharpeyi* species contained the highest selenium: mercury ratio (8.333) and the lowest ratio was found in muscle (1.752).

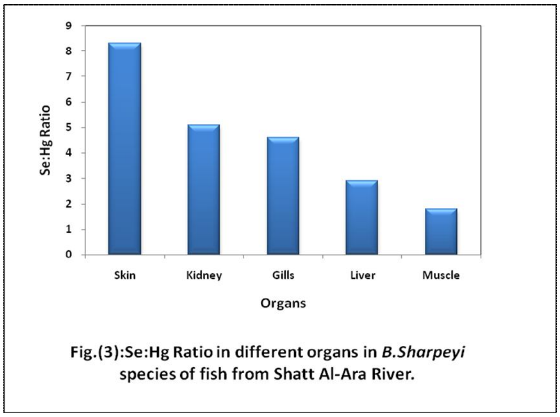

Fig. (3) Se-Hg Ratio in different organs in *B. sharpeyi* from Shatt Al-Arab River.

All the obtained data is reported on a wet (as received) basis; however, results can be converted to a dry mass on the basis of moisture content highlighted in Table 2.

Table (2): Some Characteristics of the sampled fish.

Species	n	Moisture Content (%) (mean±SD)	Fat (%) (mean±SD)	Protein (mean±SD)
C. Carpio	10	76±2	0.5±0.2	14±2
B. luteus	11	75±2	0.4±0.1	19±3
L. abu	9	80±2	0.4±0.2	18±2
T. zilli	8	79±1	0.7±0.2	20±2
B. sharpeyi	10	77±1	0.8±0.2	16±1
T. ilisha	10	76±2	0.5± 0.1	15±2

Concentration of selenium in *Tilapia* species

We have now restricted the literature search to economically important species that are consumed by humans. It is difficult to compare selenium contents of different fish because: (a) species sampled are frequently not identified, or sometimes the common name is used instead of the taxonomic indication, (b) various concentration expressions are used (µg/g fresh weight, dry weight or wet weight) or even not mentioned, (c) different organs or tissues of total fish are sampled, (d) there are different feeding habits and (e) differences can be attributed to various forms of water pollution (and therefore the selenium level of water normally must be taken into account). In Table (3) literature data for levels of selenium 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.

Table (3): Concentrations of selenium in muscles freshwater fish.

Species	n	Se contents (µg/gm)	Country	References
Esox lucius(pike)	14	0.13	Netherlands	Luten *et al*., 1980
Perca flaviatilis(perch)	15	0.24		
Shizostedion lucioperca (pike-perch)	11	0.26		
Salmo trutta(trout)	18	0.25±0.04	Norway	Froslie *et al*.,1985
Lota lota(burbot)	25	0.27±0.05		
Esox lucius(pike)	40	0.21±0.03		
Perca flaviatilis(perch)	145	0.41±0.16		
Esox lucius(pike)	-	0.35-0.44	USA	Cappon &smith, 1981
	-	(<0.20-0.62)	Canada	Speyer, 1980
Freshwater fish	-	0.56	USA	May & McKinney, 1981
	-	0.46	USA	Lowe *et al*.,1985
Anguilla anguilla		0.86	Belgium	Vandelanoote *et al*., 1988
Rutilus rutilus	-	1.25		
Perca flaviatilis		0.75		
L. abu	9	1.10±0.20	Iraq	Prasent study, 2011

In Table (4) concentrations of selenium in the flesh of *Tilapia* were much higher for the Egyptian fish (Saleh *et al*., 1988), probably due to agricultural waste dumping, containing fertilizers with sodium selenite (Na_2SeO_3).

The low levels of selenium found in Burundi (Benemariya *et al*., 1991) fish show that Lake Tanganyika is still a non- polluted area. If all these conditions are fulfilled, sampling the same species at the same point can still result in different figures as a function of time, not only because of the technique of analysis used but because of decreased or increased industrial waste discharges or recently started water treatment, the regulation of this process have been reduced the direct inputs of selenium to the environment. In general, the concentrations of Selenium that accumulate in fish are lower now than at any time for which accurate data exist.

Table (4): Comparison between selenium concentrations in the muscle of *T. zilli* and other species of *Tilapia.*

Species	n	Se contents (µg/gm)	Sample Area	References
T. zilli	-	1.4-5.0	Wadi El-Raijan(Egypt)	Saleh *et al*., 1988
T. niloticus	11	1.5-1.9	LakeTanganyika(Burundi)	Benemariya *et al.,* 1991
T. zilli	8	0.44	Shatt Al-Arab river(Iraq)	Present Study

Conclusion

In conclusion, the Se:Hg ratio is higher in *L. abu* than the other species. Skin of *B. sharpeyi* species contained the highest Se:Hg ratio than the other organs of the same species. Selenium concentration in Shatt Al-Arab fish appears to reflect natural background levels rather than pollution and these data are a first of its kind in the region and could be considered as a baseline study for the future studies.

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تركيز السلينيوم والزئبق في ست أصناف من السمك جمعت من نهر شط العرب – العراق

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الخلاصة

تناولت الدراسة الحالية تقدير نسبة السلينيوم: الزئبق في ستة أصناف من السمك جمعت من نهر شط العرب خلال جدول يمتد من حزيران 2010 الى أب 2010. تم تحليل عضلات هذه الأصناف التجارية الستة المهمة وهي : *T. zilli* و *L. abu* و *B .luteus* و *C. carpio* و *B.* sharpeyi و *T. ilisha*. بعد أن تم هضمها بإستخدام مزيج من حامض النتريك المركز وحامض البركلوريك المركز. أظهرت النتائج المحصلة أن سمكة *L. abu* إحتوت على أعلى نسبة للسلينيوم: زئبق، بينما إحتوت سمكة *B. luteus* على أوطأ نسبة للسلينيوم: زئبق. أظهر تحليل أنسجة سمكة *B. sharpeyi* (الجلد، الخياشم، الكلية، الكبد والعضلات) إحتواء جلد هذه السمكة على أعلى نسبة للسلينيوم: زئبق، بينما إحتوت العضلات على النسبة الأوطأ للسلينيوم: زئبق. قورنت القيم المحصلة مع نتائج دراسات أخرى لمحتوى السلينيوم في عضلات الأسماك.