Assessment of pollution with some heavy metals in water, sediments and *Barbus xanthopterus* fish of the Tigris River–Iraq

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Abstract

In this study, four sampling stations were selected on the Tigris River (Baghdad region) in order to determine concentrations, seasonal variation and pollution intensity assessment of heavy metals (Cd, Zn and Mn) in water, sediments and *Barbus xanthpterus* fish in this river. The study results showed that the mean concentration of dissolved heavy metals (cadmium, zinc and manganese) were 0.004 ppm, 0.023 ppm and 0.007 ppm, respectively. Whereas, their concentrations in sediments were 1.38 ppm, 86 ppm and 231.4 ppm respectively. Irregular seasonal variation for concentrations of these metals in both sediments and water. The mean concentration of these metals in tissues of fish muscles were 0.0043 ppm, 0.0023 ppm and 0.03 ppm for cadmium, zinc, and manganese respectively, while the mean concentration of these metals for tissues of intestine was 0.01 ppm, 0.0023 ppm and 0.029 ppm, respectively, whereas for tissues of gills the mean concentration of these metals was 0.0121 ppm, 0.0026 ppm and 0.087 ppm, respectively. The results of present study showed the metals concentration in tissues of muscles, intestine and gill higher than water and less than it level in sediments. According to Geo-accumulation index, Contamination factor, Enrichment index and potential ecological risk index used in this study the results explained that Cd was more the metals and existing increased in average from background value and caused high risk to aquatic environment, while the use of Pollution load index and Contamination degree to identify to pollution severity by total heavy metals and explained the station one and two were unpolluted to slightly polluted, whereas the station three and four were polluted by studied heavy metals.

Keywords: heavy metals, Tigris River, sediments, fish, sediments pollution indices.

تقييم التلوث ببعض العناصر الثقيلة في مياه ورواسب وسمك الكَطان في نهر دجله في مدينة بغداد

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الخلاصة:

تم في هذه الدراسة اختيار أربع محطات لأخذ العينات في نهر دجلة عند مدينة بغداد من اجل التعرف على التراكيز والتغيرات الفصلية وتقييم شدة التلوث بالعناصر الثقيلة (الكادميوم والزنك والمنغنيز) في كل من مياه ورواسب وسمك الكَطان (*Barbus xanthopterus*) الموجودة في هذا النهر. بينت نتائج الدراسة الحالية بأن المعدل السنوي لتركيز المعادن الثقيلة الذائبة (الكادميوم والزنك والمنغنيز) كان : 0,004 جزء من المليون و 0,023 جزء من المليون و0,007 جزء من المليون على التوالي. أما معدل تراكيزها في الرواسب فكان : 1,38 جزء من المليون و86 جزء من المليون و231,4 جزء من المليون، على التوالي. أظهرت تراكيز

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المعادن المدروسة تغيرات فصلية غير منتظمة في كل من الماء والرواسب. أما في أنسجة عضلات الأسماك فقد كان معدل التراكيز هو 0,0043 جزء من المليون و 0,0023 جزء من المليون و 0,03 جزء من المليون لكل من الكادميوم والزنك والمنغنيز على التوالي . و كان معدل تراكيز هذه المعادن في أنسجة الأمعاء هو 0,01 جزء من المليون و 0,0023 جزء من المليون و 0,029 جزء من المليون على التوالي. أما في أنسجة الغلاصم فقد كان معدل تراكيزها 0,0121 جزء من المليون و 0,0026 جزء من المليون و 0,087 جزء من المليون على التوالي. أوضحت نتائج الدراسة إن تركيز المعادن في أنسجة كل من عضلات وأمعاء وغلاصم الأسماك كان أعلى مما هو في الماء الا أنه أقل من تراكيزها في الرواسب.اعتمادا على كل من مؤشرات التراكم الأرضي ومعامل التلوث ومعامل الاغناء والخطر البيئي المحتمل المستخدمة في هذه الدراسة أوضحت النتائج بان معدل الكادميوم زاد عن قيمته المرجعية ويشكل خطرا على البيئة المائية، بينما أوضحت نتائج مؤشرات كل من حمل التلوث ودرجة التلوث المستخدمة لتحديد شدة التلوث بمجموع المعادن المدروسة إن المحطتين الأولى والثانية كانت غير ملوثة إلى ملوثة قليلا بمجموع المعادن الثقيلة ، بينما اعتبرت المحطتين الثالثة والرابعة ملوثة بمجموع المعادن الثقيلة المدروسة.

1. Introduction:

In recent years there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the aquatic systems [1]. There are basically three reservoirs of metals in the aquatic environment: water, sediment and biota [2]. Sediments are important sinks for heavy metals and play a significant role in the remobilization of contaminants in aquatic system under favorable conditions and interaction between water and sediments [3]. In a river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities [4]. Fish have ability to collect these metals in concentrations higher than water and sediments due to feed on organic materials in aquatic environment [5]. Fish have been found to be good indicators of heavy metal contamination in aquatic systems, because they occupy different atrophic levels [6, 7]. Sediment represents one of ultimate sinks for heavy metals discharged into aquatic environment [8]. The pollution indexes evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality [9]. In recent years, many assessment methods of heavy metal pollution were used according to the samples characteristics, which include contamination factor and degree of contamination, ecological risk index, enrichment factor, geo- accumulation and pollution load index [10].

2. Study Area

2.1: Description of the study area

The study area (Tigris River within Baghdad city) is located in the Mesopotamia alluvial plain between latitudes 33°14'-33°25' N and longitudes 44°31'-44°17' E.

Tigris River is one of the most important twin rivers in Iraq, sharing with Euphrates River as the main sources for man use, especially for drinking water since they cross the major cities in the country [11].

3. Materials and Methods

Samples of water, sediments and fish *B. xanthopterus* were collected every two months for one year (from October, 2011 to August, 2012) from four stations were chosen at Tigris River in Baghdad city, these were, station 1 (Al-Greaat), station 2 (Al- Atafia), station 3 (Bab-Al-Mudhum), and station 4 (Al-Rashid plant).

Heavy metals extraction from the filtered water of river, sediments was measured with Flameless Atomic Absorption spectrophotometer according to methods were described in [12], while in *B. xanthopterus* by method mentioned in Tsoumbaris [13] and Seady [14].

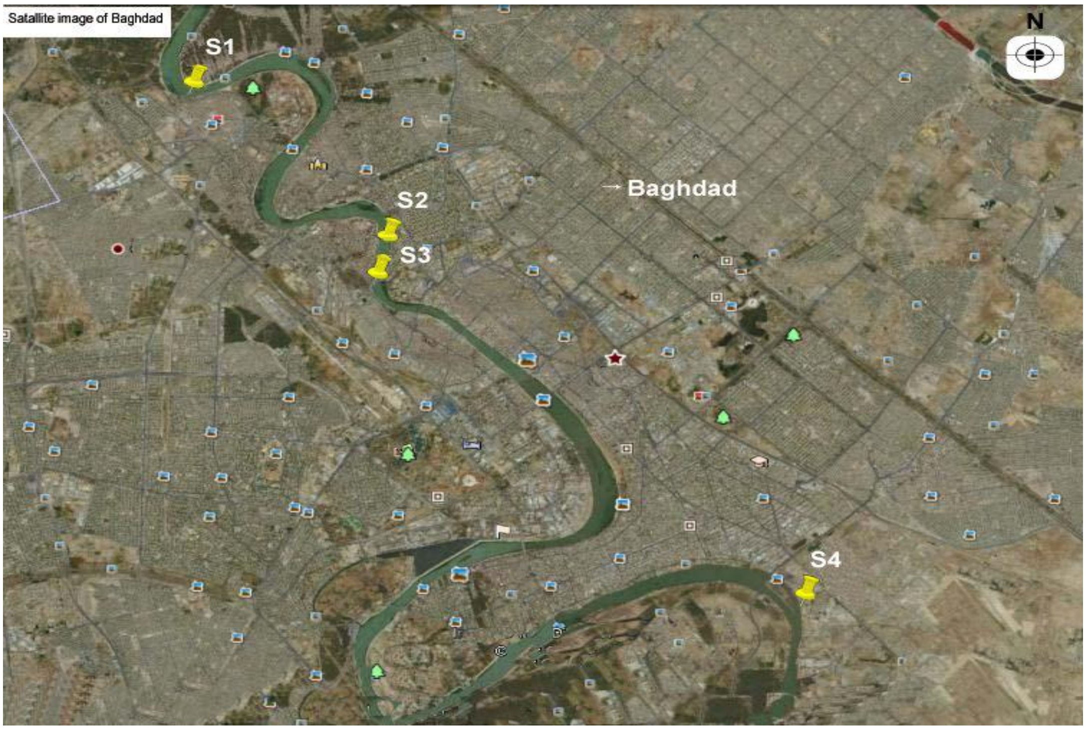

Figure 1-Tigris River in Baghdad city with stations of the study area.

Table 2-Latitudes and longitudes of study stations in Tigris River within Baghdad city

Stations	Latitudes (North)	Longitudes (East)
Al-Greaat area(S.1)	33°23'4.734"N	44°19'59.683"E
Al-Atafia (S.2)	33°21'41.809"N	44°22'18.84"E
Bab-AlMudhum (S.3)	33°20'48.659"N	44°22'11.785"E
Al-Rashid plant (S4)	33°16'59.347"N	44°27'18.692"E

4. The sediments pollution indices

-Geo-accumulation Index (I-geo)

Geo-accumulation index was determined by the following equation according to Müller [15].

$$\textbf{I-geo} = \mathbf{Ln}\ (\mathbf{C_n} / (\mathbf{1.5\ B})_n)$$

Where, C_n = Measured concentration of heavy metal in the Tigris sediment.

B_n= Geochemical background value in average shale of element n. The factor 1.5 is used for the possible variations of the background data due to lithological variations. The geo-accumulation index scale consists of seven grades (0 – 6). These seven descriptive classes are as follows: <0 = practically unpolluted; 0 – 1= unpolluted to slightly polluted, 1 – 2 = moderately polluted; 2 – 3= moderately to strongly polluted; 3 – 4= strongly polluted; 4 – 5 = strongly to very strongly polluted and >5 = very strongly polluted [15]

-The Pollution Load Index (PLI)

The Pollution Load Index (PLI) is obtained as Concentration Factors (CF). This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. With the PLI obtained from each place. Generally pollution load index (PLI) as developed by Tomlinson *et al.* [16] which is as follows:

CF = C metal / C background value

$$\mathbf{PLI} = \sqrt[n]{\mathbf{(CF1xCF2xCF3x\ldots xCFn)}}$$

Where,

CF = contamination factor, n = number of metals

C metal = metal concentration in polluted sediments

C Background value = background value of that metal.

The PLI value of > 1 is polluted, whereas < 1 indicates no pollution [17]. The world average concentration of Zn (95 µg/g), Mn (900 µg/g) and Cd (0.3 µg/g) reported for shale were considered as the background value [18].

-Contamination Factor and Degree of Contamination

The contamination factor C_f and the degree of contamination were used to determine the contamination status of the sediment in the present study. C_f values are suggested for describing the contamination factor [19]. Contamination factor calculated by following equation:

CF = C metal / C background value

Where,

CF = contamination factor,

C metal = metal concentration in polluted sediments

C Background value = background value of that metal.

$C_f < 1$: low contamination factor; $1 \le C_f < 3$: moderate contamination factor; $3 = C_f < 6$: considerable contamination factor; $C_f = 6$: very high contamination factor.

The degree of contamination (C_d) was defined as the sum of all contamination factors. The following terminology was adopted to describe the degree of contamination (C_d values) for the selected metals. $C_d < 6$: low degree of contamination; $6 = C_d < 12$: moderate degree of contamination; $12 = C_d < 24$: considerable degree of contamination; $C_d = 24$: very high degree of contamination indicating serious anthropogenic pollution.

Enrichment Factor (EF)

The Enrichment Factors (EF) was calculated to evaluate the abundance of metals in sediments. Enrichment Factor (EF) calculated by the comparison of each tested metal concentration with that of a reference metals. Enrichment factors (EF) for mean metal concentration in sediments at all the stations was calculated and used for comparison by using the following equation:

$$EF = \frac{Cn\ (sample) / Cref\ (sample)}{Bn\ (background) / Bref\ (background)}$$

Where:

Cn (sample) = the metals concentration (μg/g) in a sample.

Cref (sample) =the reference metals concentration (μg/g).

Bn (Background) = the metals concentration (μg/g) in reference (background) environment.

Bref (background) = the reference metals concentration (μg/g) in reference background environment. According to Acevedo-Figueroa *et al*. [20] six contamination categories were recognized on the basis of the enrichment factor: <1 indicates no enrichment, 1-2 → minimal enrichment, 2-5 → moderate enrichment, 5-20 → significant Enrichment, 20-40 → very high enrichment and > 40 → extremely high enrichment.

As the Enrichment factor increase, the contributions of the anthropogenic origins also increase [21]. The commonly used reference metals are Mn, Al and Fe [22] thus, Mn was used as the reference metal in this study because it was found most abundant in the sediment and natural in the environment.

Potential Ecological Risk Index (E^i_f)

The potential ecological risk of a given contaminant according to Hakanson [19] and Kucuksezgin *et al*. [23] is,

$$\mathbf{E^i_f = T^i_f \cdot C^i_f}$$

Where,

$\mathbf{T^i_f}$ is the toxic response factor for a given heavy metal,

$\mathbf{C^i_f}$ is the contamination factor.

$\mathbf{T^i_f}$ for Cd and Zn are (30 and 1) respectively [18]. The potential ecological risk of heavy metals is classified into five levels according to the values of $\mathbf{E^i_f}$:< 20 →low, 20-40 → moderate, 40-80 → considerable, 80-160 → high and > 160 →very high.

All statistical analyses were performed using SPSS version 12 for Windows. One-way ANOVA was carried out to assess significant differences between element concentrations in the study area, followed by multiple comparisons using the Duncan's multiple range test. The level of significance was set at $P < 0.05$. The level of significance was set at $P<0.05$.

5. Results and discussion

Heavy metals in water

The present study results showed that highest value of dissolved cadmium concentration was 0.01 ppm measured in Feb., Apr., and Aug. 2012 at station 4, whereas the lowest value 0.0003 ppm was measured in Dec. 2012 at station 4. The average of dissolved Cd concentration during this study was 0.004 ppm (Figure 2, Table 2). The highest value of dissolved zinc concentration (0.1 ppm) has been noted at station 4 in Apr. 2012 while the lowest concentration value (0.0015 ppm) was recorded at station 1 in Dec. 2012 (Figure 3). The annual average was 0.023 ppm (Table 2). Seasonally the highest values of dissolved zinc concentration were recorded during spring months while the lowest values were in winter and autumn months. The results of this study also showed that the highest value of dissolved manganese concentration was 0.022 ppm recorded at station 4 in Aug. 2012 while the lowest value 0.0006 ppm recorded at station 1 in Oct. 2012 (Figure 4). The annual average was

0.007 ppm (Table 2). Seasonally, the highest values of dissolved Cd, Zn and Mn concentration were observed during later stage of winter and summer months whereas the lowest values were in autumn months. In present study the average concentration of dissolved Cd, Zn and Mn were within the safe limits for each Iraqi specification and the world standards limits. There were some spatial variation in concentrations of studied heavy metals among different stations which may due to the distribution of elements which affected by many important spatial factors such as, human population, density along the river banks, hydrological conditions of the bed, discharges by local industries, and sewage discharges [24] .

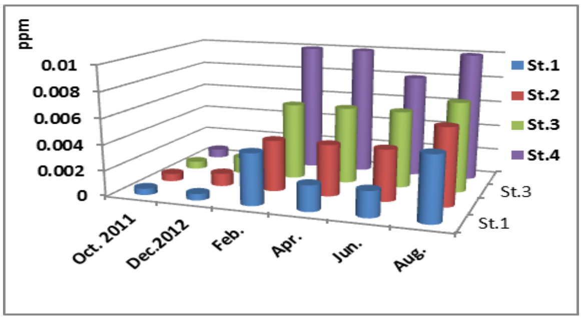

Figure 2- Variation of dissolved Cd in filtered water

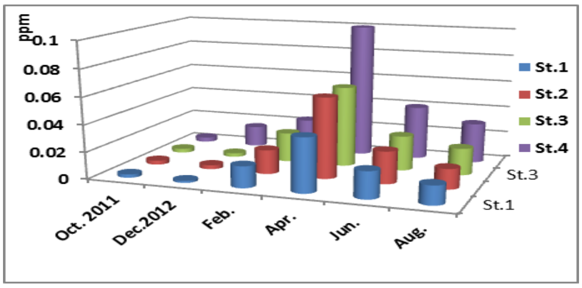

Figure 3- Variation of dissolved Zn in filtered water

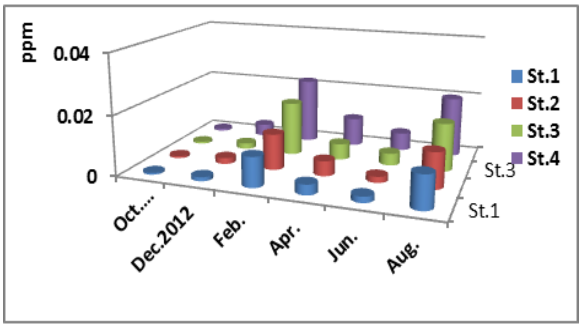

Figure 4- Variation of dissolved Mn in filtered water

Heavy metals in sediments

The study results showed that the highest sediments Cd concentration was 2.5 ppm at station four in Oct. 2011, and the lowest concentration (0.5 ppm) at station one and two in Dec. and Feb. 2012(Figure 5), and the annual mean was 1.38 ppm (Table 3).

Seasonally, the lowest concentrations were observed during winter and spring months, whereas the highest concentrations were in autumn and later stage of summer months. The statistical analysis of the data showed significant differences between months, also there was a significant difference between stations at (P≤0.05). The results of this study for sediments Zn concentrations showed the maximum concentration of Zn (188 ppm) was found at station 4 in Dec. 2012, while the minimum concentration (51.2ppm) was found at station 1 in Jun. 2012 (Figure 6), and annual average was 86 ppm (Table 3).

Seasonally, the highest concentrations have been noted during winter months, whereas the lowest values were recorded during summer and spring months. The results also showed the maximum sediments Mn concentration was 490 ppm recorded at station 4 in Oct. 2011, while the minimum concentration (73.7 ppm) was recorded at station 1 in Apr. 2012 (Figure 7), and annual mean was 231.4 ppm (Table 3). Seasonally, the highest concentrations were recorded during the autumn and later stage of summer months, while the lowest concentrations were found during spring months. Comparing the concentration of metals in sediment between high and low discharges period, it seemed that the concentration is more in low discharge (except for Zn) than high discharge period, and this may be due to the dilution factor related to the high discharge in winter and spring [25]. Almost, lower values of Cd and Mn were recorded during winter and spring, which may be due to the dilution effect during high water discharge. The major source for the metal contamination in rivers is the industrial effluents near this rivers, as well as the transport of small fraction of sediment downstream due to the river velocity contributes to the accumulation of heavy metals in lower parts [26].

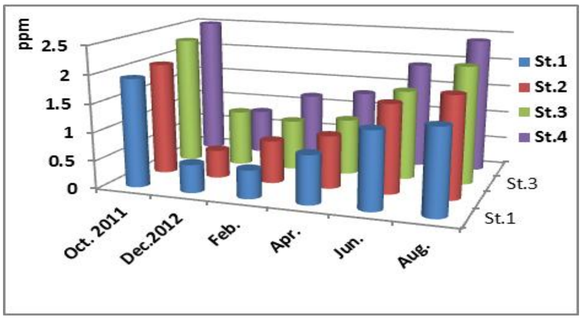

Figure 5- Variation of Cd in Tigris sediments

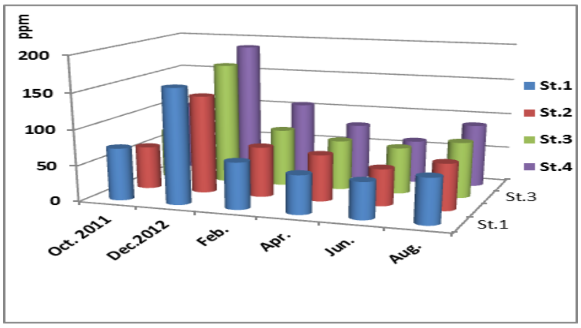

Figure 6- Variation of Zn in Tigris sediments

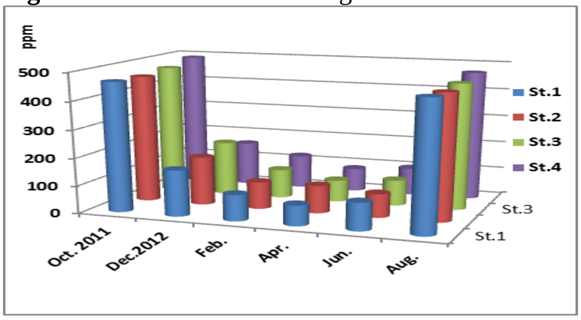

Figure 7- Variation of Mn in Tigris sediments

Heavy metals in *Barbus xanthopterus* fish

The contamination of Cd varied among organs, seasons, and locations. The results of this study showed that maximum concentration of cadmium (0.079 ppm) was recorded in fish gills collected from station 4 in Apr. 2012, while the minimum concentration (0.0001 ppm) was in intestine of fish collected from station 4 in Feb. 2012. The highest annual average of cadmium concentration (0.012 ppm) was recorded in gills, whereas the lowest average (0.004 ppm) was in muscles (Figure 8). The maximum concentration of zinc (0.006 ppm) was observed in intestine of fish collected from station 1 in Oct. 2011, while the minimum concentration of Zn (0.0008 ppm) was also found in intestine of fish collected from station 3 in Dec. 2012. Gills contained the highest annual average of Zn (0.008 ppm), followed by the muscles and intestine were 0.007 ppm (Figure 9). In general order of heavy metals concentrations in various organs of the fish that used in this study can represented as follows: gills > muscles and intestine. The maximum concentration (1 ppm) of manganese was recorded in gills of fish collected from station 1 in Oct. 2011, while the minimum concentration (0.0024 ppm) was found in muscle of fish collected from station 3 in Jun. 2012, and the highest annual average of Mn concentration (0.086 ppm) was observed in gills and the lowest was 0.03 ppm in intestine and muscles (Figure 10). The results of this study showed the metal concentrations in hot and warm seasons were the highest (except for Mn) because chemicals become more soluble by higher temperature, the metabolic rate of aquatic organisms increase, growth rate will also increases with the decomposition of organic matter [27]. However, it was evident from this study that the gills was the site of maximum accumulation for the elements while the muscle was the overall site of least metal accumulation in this species. In fish, gills are considered to be the dominate site for contaminant uptake because of their anatomical and/or physiological properties that maximize absorption efficiency from water [28].

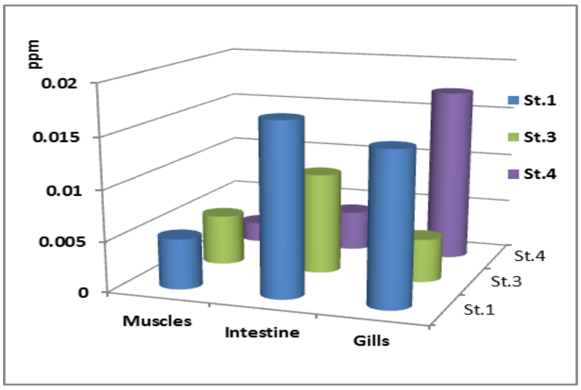

Figure 8- Variation of averages of Cd in *B. xanthopterus* fish

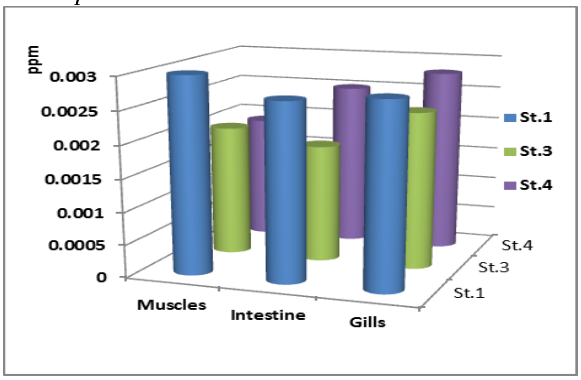

Figure 9- Variation of averages of Zn in *B. xanthopterus* fish

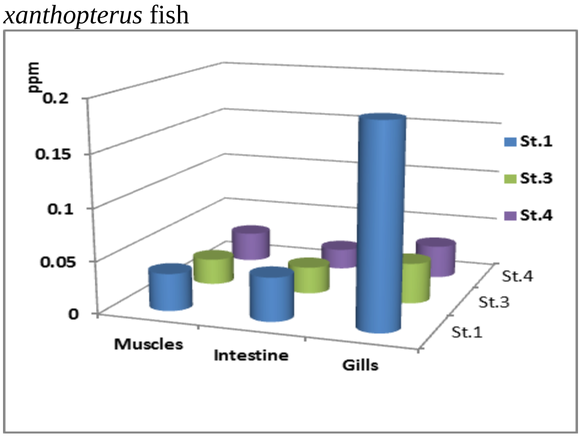

Figure 10- Variation of averages of Mn in *B. xanthopterus* fish

Sediments pollution indices

According to, Geo-accumulation index all stations are unpolluted for Zn and Mn (average I-geo ≤ 0). Station 1 is slightly polluted (0≤ average I-geo ≤ 1) with Cd, while the stations 3, 2 and 4 are moderately polluted with Cd (1≤ average I-geo ≤ 2). I-geo values of studies heavy metals in sediments are shown in (Table 4). The station 1 and 2 can be classified as non-polluted areas where PLI values < 1, while station 3 and 4 had PLI values > 1confirming there were considerable contamination for studied heavy metals according to the classification of Harikmar *et al.* [17]. Maximum value of contamination factor was noticed for cadmium at station four was 5.6, while the minimum value of contamination factor (C_f) was recorded for manganese at station one and two (Table 5).

All stations in present study recorded considerable contamination factor values for cadmium ($3 = C_f < 6$) according to the Hakanson's classification (1980). The station 1, 2 and 3 had low contamination factor values for zinc ($C_f < 1$), while the station 4 recorded a moderate contamination factor for this metal ($1 \leq C_f < 3$). Manganese exhibited low contamination factor for all investigated stations (C_f< 1).

The station 4 recorded the maximum value of degree of contamination while station 1 recorded the lowest degree of contamination as illustrated in Table 4. The station 1 and 2 recorded low degree of contamination (C_d< 6), whereas the rest of stations were moderate degree of contamination ($6 = C_d < 12$).

From these indexes the study area was observed the highest contamination by cadmium and zinc metals than Mn metal due to influence of external discrete sources like industrial activities, agricultural runoff and other anthropogenic inputs. The EF for Zn, remains in the range 2-5 in all stations indicates moderate enrichment (Table 6). The high values of enrichment factor for Cd ranged between 5- 20 that refer to the all studied stations were significant enrichment by these metals. Therefore, the heavy metal pollution of study area was likely to originate from anthropogenic activities. According to potential ecological risk index for heavy metals, contaminations of Cd reach to the high degree of potential ecological risk = 80 - 160 at station 1, 2 and 3 while the station 4 recorded very high degree of potential ecological risk index > 160. The contamination of Zn observed the low degree of potential ecological risk index < 20 at all studied stations as shown in Table 7.

The difference in indices results due to the difference in sensitivity of these indices towards the sediment pollutants [29]. These confirmed that Tigris River is facing probable environmental pollution especially with dangerous heavy metal such as Cd which result from increased rate of non-treatment industrial waste which are discharged to Tigris River. The geo-accumulation index, contamination factor and pollution load index of Mn agreed, while the results of Cd exceed with results of study of Rabee *et al*. [30] on Tigris River as well as, this results exceed for Cd from study of Rabee *et al*. [31] on Tigris River and Euphrates River.

Table 2- The minimum (Min), maximum (Max), mean and standard deviation (SD) of concentration of studied heavy metals (ppm) in filter water during (2011-2012) in studied stations

Dissolved heavy metals		**S1**	**S2**	**S3**	**S4**
Cd	**Min**	0.0005	0.0006	0.0006	0.0003
	Max	0.005	0.006	0.007	0.01
	Mean	0.0023 **c**	0.0032 **c**	0.0044 **b**	0.0065 **a**
	SD	±0.0019	±0.0020	±0.0026	±0.0051
Zn	**Min**	0.0015	0.003	0.0028	0.0035
	Max	0.04	0.06	0.06	0.1
	Mean	0.0156 **b**	0.0205 **b**	0.0223 **b**	0.0355 **a**
	SD	±0.0146	±0.0202	±0.02006	±0.0384
Mn	**Min**	0.0006	0.0007	0.0007	0.0008
	Max	0.11	0.012	0.018	0.022
	Mean	0.0047 **c**	0.0056 **c**	0.0076 **b**	0.0104 **a**
	SD	±0.00456	±0.004962	±0.007071	±0.008924

Different letters in same row that indicate different significance

Table 3- The minimum (Min), maximum (Max), mean and standard deviation (SD) of concentration of studied heavy metals (ppm) in river sediments during (2011-2012) in studied stations

Heavy metals in sediments		**S1**	**S2**	**S3**	**S4**
Cd	**Min**	0.5	0.5	0.9	0.8
	Max	1.92	2	2.3	2.5
	Mean	1.1066 **d**	1.2633 **c**	1.4833 **b**	1.6744 **a**
	SD	±0.5625	±0.5845	±0.5893	±0.6731
Zn	**Min**	51.2	51.5	65.2	60.5
	Max	160	137	170	188
	Mean	77.7166 **c**	74.8 **c**	88.8333 **b**	103 a
	SD	±39.1472	±29.5455	±38.1588	±42.1747
Mn	**Min**	73.7	85.6	79	85
	Max	465	460	470	490
	Mean	226.58 **b**	228.28 **b**	241.37 **a**	237.95 **a**
	SD	±174.3019	±167.8385	±172.9666	±177.961

Table 4- Geo-accumulation index (average I-geo values) for studied heavy metals in sediments of Tigris River

Stations	**Average I-geo values**		
	Cd	**Zn**	**Mn**
1	0.89	-0.60	-1.78
2	1.02	-0.64	-1.77
3	1.18	-0.47	-1.75
4	1.31	-0.32	-1.73

Table 5- Contamination factor (C_f), degree of contamination (C_d) and pollution load index (PLI) of sediment samples collected from Tigris River

Stations	**C_f values**			**C_d**	**PLI**
	Cd	**Zn**	**Mn**		
1	3.36	0.81	0.25	4.42	0.88
2	4.2	0.78	0.25	5.23	0.93
3	4.93	0.93	0.26	6.12	1.06
4	5.6	1.08	0.26	6.94	1.16

Table 6- Enrichment factor of heavy metals collected from Tigris River

Stations	**EF values**	
	Cd	**Zn**
1	14.56	3.24
2	16.55	3.10
3	19.04	3.61
4	21.18	4.10

Table 7- Potential ecological risk index for heavy metals collected from Tigris River

Stations	**E^i_f values**	
	Cd	**Zn**
1	100.8	0.81
2	126	0.78
3	147.9	0.93
4	168	1.08

References

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