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Seasonal Variations in Trace Metals contamination in two species belonging to fish families *Sciaenidae* and *Haemulidae* from the Arabian Sea, Pakistan

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Abstract

Heavy metals contamination in food commodities is a serious threat because of their toxicity, bio-magnification and bioaccumulation in food chain, which has been increasing day by day. In the current study, heavy metal (Cd, Co, Cu, Pb and Ni) analysis was carried out in two different species Parastematus Gibosus, belonging to Heamulidae family and Johnnies Dussumieri belonging to Sciaenidae Family. These species were collected from two different locations i.e. West Wharf and Korangi Creek during Jan to December 2020. For fish samples of Sciaenidae, the concentration of Cd was observed to be 0.21 to 0.40µg g^{-1}, Co was 16.5 to 18.6µg g^{-1}, Cu was 15.2 to 23.5µg g^{-1}, Pb was 4.1 to 9.2µg g^{-1} and Ni was22.5 to 35.3µg g^{-1}. On the other hand, for fish samples of Haemulidae the concentration of Cd found as 0.17 to 0.38µg g^{-1}, Co as 15.4 to 17.5µg g^{-1}, Cu as 14.2 to 17.8µg g^{-1}, Pb as 1.5 to 7.5µg g^{-1} and Ni as 23.5 to 34.8µg g^{-1}. Cd and Pb was found highest in March, Cu in June, Ni in September and Co in December. Month-wise variation in heavy metals (Cd, Cr, Mn, Ni and Pb in the edible tissues of Parastematus Gibosus) for two different coastal areas i.e. Korangi Creek and West Wharf was also studied. For coastal area West Wharf, the concentration of Cr in the edible tissues of Parastematus Gibosusranged from 0.543 to 0.835µg g^{-1}, Cd was 0.35 to 0.80µg g^{-1}, Mn was 0.151 to 0.189µg g^{-1}, Pb was 0.10 to 0.89µg g^{-1} and Ni was0.601 to 0.723µg g^{-1}. On the other hand, for Korangi Creek the concentration of Cr was detected as 0.559 to 0.899µgg^{-1}, Cd was 0.13 to 0.80µg g^{-}1, Mn as 0.158 to 0.168µg g^{-1}, Pbas 0.10 to 0.86µg g^{-1} and Ni as 0.664 to 0.712µg g^{-1}.The results showed a significant difference of seasonal variation of heavy metals concentration in fish samples analyzed. The contamination in fish was higher during the summer season and lowest in winter season, therefore it is advisable to decrease the consumption of fish in summer to avoid the accumulation of heavy metals in human body.

Keywords: Heavy metals, Fish, Seasonal variation, Bio accumulation

Introduction

Seafood especially fish is believed to be a major source of various nutrients, such as protein, amino acids, fiber, vitamins, minerals and n-3-PUFA.Such PUFAs are very helpful in cure of arteriosclerotic and thrombotic disease. These nutrients play vital role in improving metabolic functions of human body. They are also associated with various health benefits such as enhance growth spam, the nervous system, reduction in heart disease and they also have anticancer properties (Liao & Chao, 2009). However, if seafood is contaminated with toxic substances, its consumption can possibly be toxic for human consumption (Afonso, 2013; Castro-Gonzalez, 2008). Heavy metal content in aquatic bodies have arisen due to rapid industrialization. Marine environment closer to industrial activities has been polluted with heavy metals which has emerges as a serious issue(Hajeb, 2009). It is well known fact that heavy metals become toxic at high intake. Organo-metalic derivatives of these metals cause chromosome damage as well as inhibit action of enzymes. It is also reported that toxicity of these metals affect nervous, skeletal, endocrine and renal system.(EFSA, 2010). Heavy metal absorption in fish is taken place through gills, skin and digestive tract; then

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transported to other organs through the blood(Khan, 2012). It has been reported that Korangi Industrial Area stream and SITE stream at Liyari have been contaminated with untreated industrial effluents containing toxic metals. These two stream are one of the major source of toxic substances for Arabian Sea along the coastal area of Karachi, creating hazard to marine environment(Raza R, 2005).

Due to such hazardous effects related to the consumption of heavy metal-contaminated fish, there is a dire need to develop data on commercial fish species potentially at risk of heavy metal contamination. The current study heavy metal (Cd, Co, Cu, Pb and Ni) analysis was carried out in two different species *Parastematus Gibosus* , belonging to *Heamulidae* family and *Johnnies Dussumieri* belonging to *Sciaenidae* Family. These species were collected from two different locations i.e. West Wharf and Korangi Creek during March to December 2020. Trace metals contents in fish muscles will help to understand the influence of anthropogenic activities in the coastal area.

Materials and Methods

Collection of Samples

Fish samples were purchased from local fishermen operating along southwest coastal area of Karachi i.e. Korangi Creek and Whest Wharf during the month of March to December 2020 on quarterly basis. The weight range of purchased fish was 500-1500g.

Chemicals and Reagents

All reagents were analytical reagent grade. For the analysis of trace metals stock solutions (500ml) were prepared from BDH Spectrosole AA standard (1000ppm). The working standard solutions were obtained after diluting the stock to the required concentration. All glassware was pre-rinsed with 10% HCl followed by deionized water.

Sample Preparation

To ensure homogenization, all fish tissue was passed through the grinder three times. Following

processing, tissue was dried in a convection oven for 24 h at 60^{o}C, ground with a mortar and pestle, placed in a glass jar, tightly capped, and stored in a freezer.

Digestion

5 gram of fish sample was taken into digestion tube (Tecator-2006). 10 mL of concentrated nitric acid (65%) was added and sample was allowed to stand for 24 hours. The tube was then heated for 30 minutes till all NO_2 are removed. The tube was then cooled and 15mL concentrated nitric acid was added to it. The tube was then heated for 30 minutes at 120^{o}C and then 150^{o}C till the digestion was completed. The sample was cooled at room temperature then 2 mL perchloric acid (70%) was added. Digested sample was then diluted to 50 mL by deionized distilled water (Anderson, 1972).

Elemental Analysis of the Samples

Absorption of stock and samples were measured by AAS. Perkin-Elmer model-2380 atomic absorption spectrophotometer (AAS) equipped with air acetylene flame was used for trace metal analysis. Blank run on the acid used were

conducted to incorporate background correction. Operational conditions for trace metals investigated are summarized in Table-1.

Table 1: Operational Conditions forCd, Cr, Mn, Ni and Pb Determinations by AAS

Parameters	Cd	Co	Cu	Pb	Ni
Wave Length (nm)	228.8	240.7	324.8	283.3	232.0
Slit Width (nm)	0.7	0.2	0.5	0.7	0.2
Flow Rate of AC (mL/min)	10 – 14	10 – 14	10 – 14	10 – 14	10 – 14
Flow Rate of Air (mL/min)	40 – 45	40 – 45	40 – 45	40 – 45	40 – 45
AC Pressure (psi)	12	12	12	12	12
Air Pressure (psi)	60 – 80	60 – 80	60 – 80	60 – 80	60 – 80
Fuel Gases	A – AC	A – AC	A – AC	A – AC	A – AC

Analysis of each metal was carried out in triplicate to get representative result and reported in ppm. Precision of the method was determined by Coefficient of Variance (CV).

Results and Discussions

Detection Limits and Calibration Curves

The Calibration curves of Cd, Co, Cu, Fe, Pb, and Mn are shown as Fig-1.

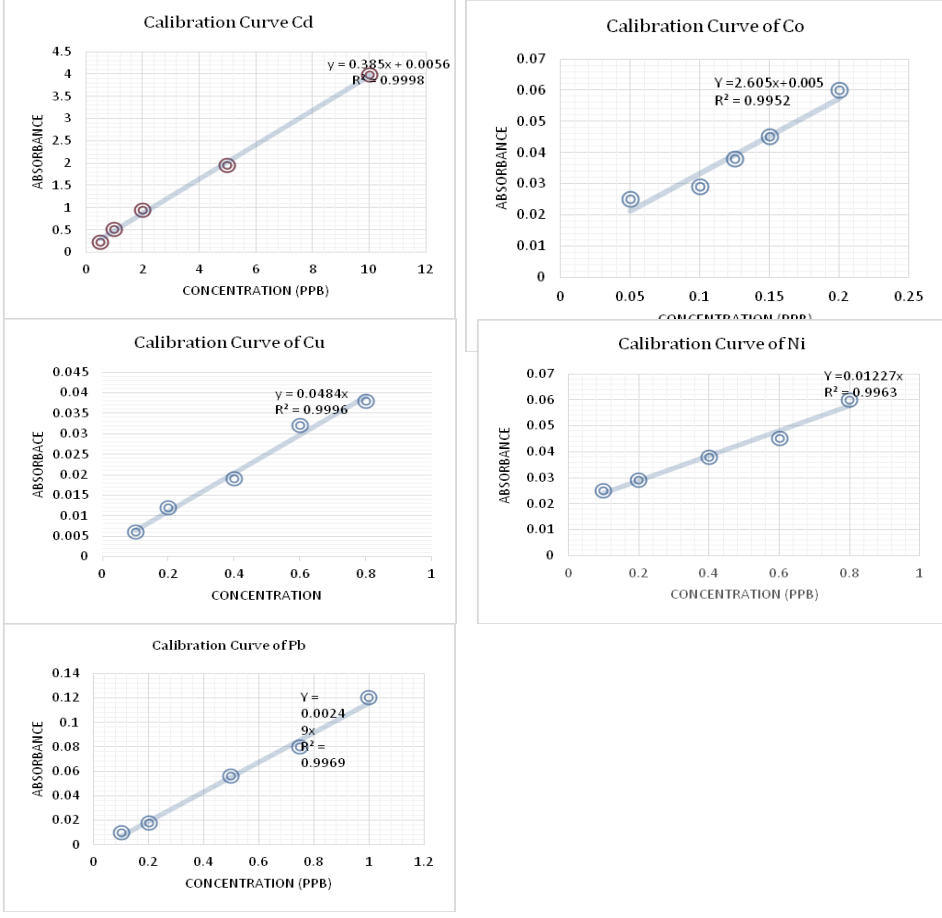

Figure 1: Calibration Curves (Concentration Vs Absorbance) for Cd, Co, Cu, Pb, and Ni

The detection limits of Cd, Cr, Mn, Ni and Pb were estimated and are summarized in Table-2

Table 2: Experimental Conditions for Cd, Cr, Mn, Ni and Pb Determinations by AAS

	Cd	Co	Cu	Pb	Ni
Concentration Range (µg/g)	0 – 10	0.05 – 0.2	0 – 1	0 – 1	0 – 1
Sensitivity (µg/g)	0.025	0.1	0.05	0.5	0.15
Detection Limit (µg/g)	0.025	0.02	0.01	0.05	0.02

The analytical results of heavy metals concentration in fish family *Sciaenidae* and *Haemulidae* are summarized in Table-3 and Table-4 respectively. Occurrence of heavy metals was detected for all samples. The heavy metals concentration in *Scienidae* occurs in descending order of Ni > Cu > Co >Pb> Cd. The concentration of Cd ranged from 0.21 to 0.40µg g^{-1} for fish samples of *Sciaenidae* and 0.17 to 0.38 µg g^{-1} for fish samples of *Haemulidae*. The highest concentration of Cd (0.40µg g^{-1} for *Sciaenidae* and 0.38µg g^{-1} for *Haemulidae*) was detected in March and Cd was found lowest (0.21µg g^{-1} for *Sciaenida*e) in the month of September and 0.17µg g^{-1} for *Haemulidae* in December.

Table 3: Periodical Analysis of Heavy Metal in Sciaenidae

	Cd	Co	Cu	Pb	Ni
March	0.40±0.001	18.3±0.003	21.2±0.04	8.5±0.7	24.0±0.03
June	0.28±0.002	16.5±0.004	23.5±0.04	9.2±0.9	27.2±0.03
September	0.21±0.001	17.6±0.001	19.2±0.04	7.9±0.9	35.3±0.04
December	0.23±0.002	18.6±0.003	15.2±0.03	4.1±0.7	22.5±0.04

Table 4: Periodical Analysis of Heavy Metal in Haemulidae

	Cd	Co	Cu	Pb	Ni
March	0.38±0.001	17.5±0.003	16.1±0.04	7.5±0.7	25.3±0.03
June	0.21±0.002	15.6±0.004	17.8±0.04	6.8±0.9	28.1±0.03
September	0.19±0.002	16.7±0.003	15.9±0.03	3.8±0.7	34.8±0.04
December	0.17±0.002	15.4±0.002	14.2±0.05	1.5±0.8	23.5±0.03

The amount of Co for fish samples of *Sciaenidae* were ranged from 16.5 to 18.6µg $g^{-1}$and 15.4 to 17.5µg g^{-1} for fish samples of *Haemulidae*. The highest concentration of Co 18.6µg g^{-1} for *Sciaenidae* was detected in December and 0.38µg g^{-1} for *Haemulidae* was found in March. Co was found lowest (16.5µg g^{-1} for *Sciaenida*e) in the month of June and 15.4µg g^{-1} for *Haemulidae* in December.

The concentration of Cu ranged from 15.2 to 23.5µg g^{-1} for fish samples of *Sciaenidae* and 14.2 to 17.8 µg g^{-1} for fish samples of *Haemulidae*. The highest concentration of Cu (23.5µg g^{-1} for *Sciaenidae*17.8µg g^{-1} for *Haemulidae*) was detected in June. Cu was found lowest (15.2µg g^{-1} for *Sciaenidae* and 14.2µg g^{-1} for *Haemulidae*) was found lowest in the month of December.

The concentration of Pb ranged from 4.1 to 9.2µg g^{-1} for fish samples of *Sciaenidae* and 1.5 to 7.5 µg g^{-1} for fish samples of *Haemulidae*. The highest concentration of Pb18.6µg g^{-1} for *Sciaenidae* was detected in June and 0.38µg g^{-1} for *Haemulidae* was found in March. Pb (4.1µg g^{-1} for *Sciaenidae* and 1.5µg g^{-1} for *Haemulidae*) was found lowest in the month of December.

The concentration of Ni ranged from 22.5 to 35.3 µg g^{-1} for fish samples of *Sciaenidae* and 23.5 to 34.8 µg g^{-1} for fish samples of *Haemulidae*. The highest

concentration of Ni (35.3µg g^{-1} for *Sciaenidae* and 22.5µg g^{-1} for *Haemulidae*) was detected in September and Ni (34.8µg g^{-1} for *Sciaenidae* and 23.5µg g^{-1} for *Haemulidae*) was found lowest in the month of December.

The findings of the present study were higher than the results reported earlier (Raza, 2003; Solangi, 2002; Tabinda, 2012; Tariq, 1993). An irregular pattern of concentration of each metal in both fish sample was observed throughout the year. A higher concentration of each metal in both of the fish samples was detected. The obvious reason for the high concentration of the fish with these toxic trace metals is may be the untreated industrial effluents; are being dumped into the sea continuously through industrial streams. Karachi has two planned industrial areas viz. Korangi Industrial Area (KIA) with about 2000 industrial units and Sindh Industrial Trading Estate (SITE) with more than 500 industries(Beg, 1978; Driver, 1987). The two streams coming from these industrial areas bring these toxic metals to sea which then accumulated in the edible tissues of various fish. The results showed a significant difference of seasonal variation of heavy metals concentration in seawater and sediment. The contamination in fish was higher during the summer season due to increase of temperature, and lowest in winter season. However, this study found no significant correlation between the concentration of heavy metals in the environment and fish.

Month-wise variation in heavy metals (Cd, Cr, Mn, Ni and Pb) concentration in two different coastal areas i.e. Korangi Creek and West Wharf was also studied through heavy metal analysis in *Parastematus Gibosus* and the results are summarized in Table-5 and Table-6.

The concentration of Co in the edible tissues of *Parastematus Gibosus* was ranged from 0.35 to 0. 80µgg^{-1} for West Wharf and 0.13 to 0.80 µg g^{-1} for Korangi Creek. The highest concentration of Coin the edible tissues of *Parastematus Gibosus* of both area has been found June-July and lowest in the month of Oct-Nov for West Wharf and for Korangi Creek in Feb-Mar.

For coastal area West Wharf, the concentration of Cr in the edible tissues of *Parastematus Gibosus* ranged from 0.543 to 0.835µg g^{-1}, Mn was 0.151 to 0.189µg g^{-1}, Pb was 0.10 to 0.89µg g^{-1} and Ni was0.601 to 0.723µg g^{-1}. On the other hand, for Korangi Creek the concentration of Cr was detected as 0.559 to 0.899µg g^{-1}, Mn as 0.158 to 0.168µg g^{-1}, Pb as 0.10 to 0.86µg g^{-1} and Ni as 0.664 to 0.712µg g^{-1}. The results showed a significant difference of seasonal variation of heavy metals concentration in seawater and sediment which then accumulated into fish tissues. The contamination in fish was higher during the summer season and lowest in winter season.

Table 5: Periodical Analysis of Heavy Metal in *Parastematus Gibosus* (Korangi Creek)

Months	Cd(µg g^{-1})	Cr(µg g^{-1})	Mn(µg g^{-1})	Ni(µg g^{-1})	Pb(µg g^{-1})
Dec-Jan	0.36±0.002	0.543±0.002	0.151±0.05	0.601±0.8	0.10±0.03
Feb-Mar	0.40±0.002	0.654±0.004	172±0.04	0.689±0.9	0.51±0.03
Apr-May	0.65±0.001	0.746±0.003	0.189±0.04	0.712±0.7	0.68±0.03
Jun-July	0.80±0.002	0.835±0.004	0.190±0.04	0.723±0.9	0.89±0.03
Aug-Sept	0.60±0.002	0.743±0.003	0.168±0.03	0.689±0.7	0.78±0.04
Oct-Nov	0.35±0.002	0.567±0.002	0.154±0.05	0.612±0.8	0.72±0.03

Table 6: Periodical Analysis of Heavy Metal in *Parastematus Gibosus* (West Wharf)

Months	Cd(µg g^{-1})	Cr(µg g^{-1})	Mn(µg g^{-1})	Ni(µg g^{-1})	Pb(µg g^{-1})
Dec-Jan	0.14±0.001	0.632±0.003	0.158±0.04	0.678±0.7	0.51±0.03
Feb-Mar	0.13±0.002	0.745±0.004	0.160±0.04	0.689±0.9	0.10±0.03
Apr-May	0.42±0.002	0.832±0.002	0.166±0.05	0.701±0.8	0.46±0.03
Jun-July	0.80±0.002	0.899±0.004	0.168±0.04	0.689±0.9	0.86±0.03
Aug-Sept	0.60±0.002	0.645±0.003	0.158±0.03	0.712±0.7	0.81±0.04
Oct-Nov	0.55±0.002	0.559±0.002	0.160±0.05	0.664±0.8	0.72±0.03

The graphical representation of the heavy metals (Cd, Cr, Mn, Ni and Pb) concentration in two different coastal areas i.e. Korangi Creek and West Wharf demonstrated through figure-2 and figure-3 indicate variation in concentration of heavy metals analyzed. The results showed a significant difference of seasonal variation of heavy metals concentration in seawater and sediment which then accumulated into fish tissues. The contamination in fish was higher during the summer season and lowest in winter season. This indicate that two streams Korangi Industrial Area (KIA) and Sindh Industrial Trading Estate (SITE) coming from these industrial areas bring varied amount of heavy metals to sea which then accumulated in the edible tissues of various fish. The concentration difference in various season is may be due to the operational routine of the industries which somehow decreased in the winter session, hence decreased industrial effluents in the two steams. Therefore, it is advisable to decrease in the consumption of fish in summer to avoid the accumulation of heavy metals in human body.

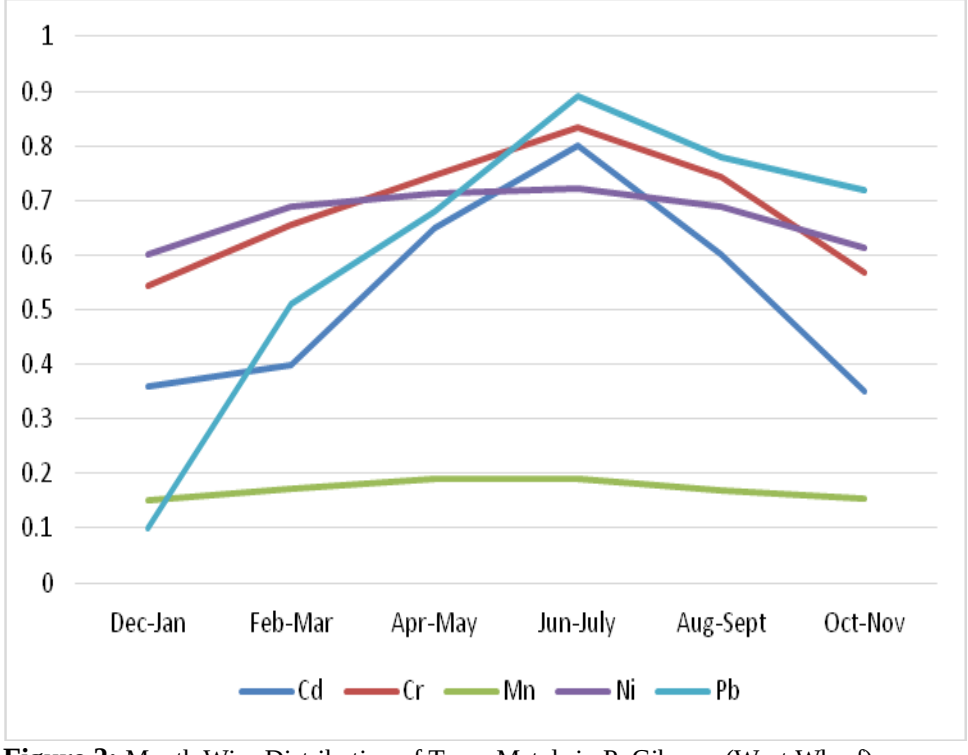

Figure 2: Month Wise Distribution of Trace Metals in P. Gibosus (West Wharf)

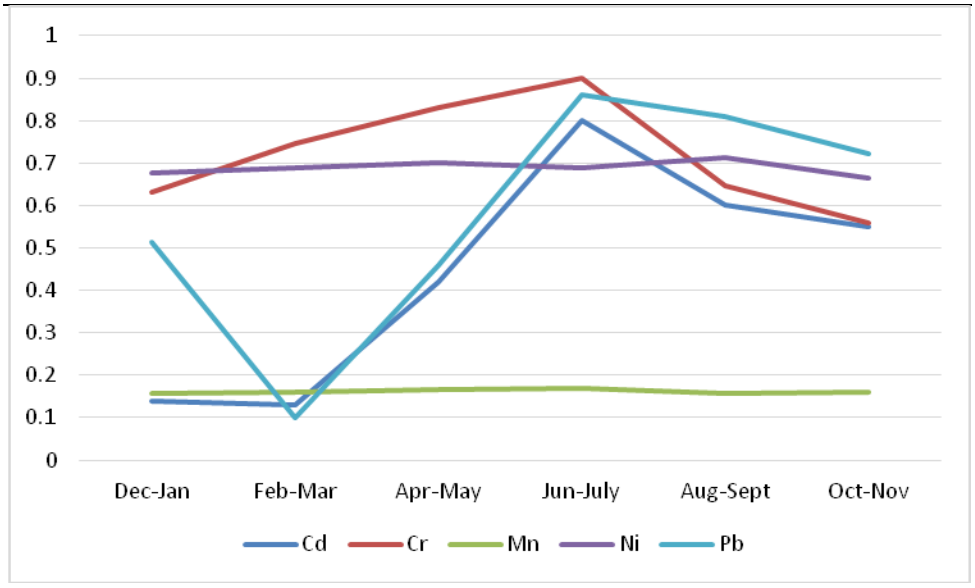

Figure 3: Month Wise Distribution of Trace Metals in P. Gibosus (Korangi Creek)

Conclusion

The current study heavy metal (Cd, Co, Cu, Pb and Ni) analysis was carried out in two different species *Parastematus Gibosus*, belonging to ***Heamulidae*** family and *Johnnies Dussumieri*belonging to ***Sciaenidae*** Family. These species were collected from two different locations i.e. West Wharf and Korangi Creek during March to December 2020. The results of present study revealed elevated concentrations of heavy metals in commonly consumed fish. Heavy metals concentrations were found in descending order of Ni > Cu > Co >Pb> Cd for the sample analyzed for both of the species. Among the heavy metal detected for fish samples of *Sciaenidae,* Cd ranged from 0.21 to 0.40µg g^{-1}, Co ranged from 16.5 to 18.6µg g^{-1}, Cu was ranged from 15.2 to 23.5µg g^{-1}, Pb was ranged from 4.1 to 9.2µg g^{-1} and Ni ranged from 22.5 to 35.3 µg g^{-1}.Among the heavy metal detected Cd ranged from 0.17 to 0.38 µg g^{-1}, Co ranged from15.4 to 17.5 µg g^{-1}, Cu ranged from14.2 to 17.8 µg g^{-1}, Pb ranged from1.5 to 7.5 µg g^{-1} and Ni ranged from 23.5 to 34.8 µg g^{-1} for fish samples of *Haemulidae*. The highest concentration of Cd and Pb was found in March, Cu in June, Ni in September and Co in December. The results showed a significant difference of seasonal variation of heavy metals concentration in fish samples analyzed. The contamination in fish was higher during the summer season due to increase of temperature, and lowest in winter season therefore it is advisable to decrease in the consumption of fish in summer to avoid the accumulation of heavy metals in human body. Detoxification of industrial effluents may also be controlled, which carry toxic heavy metals to the sea, toxifying the Arabian Sea.

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