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# Heavy metal concentration in dolphinfish (*Coryphaena hippurus* Linnaeus, 1758) from Karachi Harbour, Pakistan

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**Abstract**
In this study, zinc (Zn), copper (Cu), nicel (Ni) and cadmium (Cd) concentrations were determined in muscle of *Coryphaena hippurus* collected from Karachi coast, Pakistan, at autumn inter monsoon, north east monsoon, spring inter monsoon and south west monsoon from October 2010 – September 2011. All samples were analyzed for zinc, copper, nicel and cadmium by AAnalyst 700 Flame Atomic Absorption spectrophotometer. Generally fish showed the accumulation level of Zn (4.13 µg $g^{-1}$), Cu (2.92 µg $g^{-1}$), Ni (0.40 µg $g^{-1}$) and Cd (0.18 µg $g^{-1}$) in muscle respectively. Zn, Cu, Ni and Cd accumulations in muscle tissues of *c. hippurus* caught from Karachi coast Pakistan were not exceeding the limit values. Therefore, all metal accumulations in *c.hippurus* have to be monitored continuously especially in these regions.

**Keywords:** Heavy metal; fish; *C. hippurus*; Karachi; Pakistan

## 1. Introduction
Heavy metals enter the aquatic environment from both natural and anthropogenic sources. The anthropogenic sources include; mining and industrial effluents, domestic discharges, leachates from waste dumps, inputs from agricultural activities and atmospheric sources especially burning of fossil fuels. Incineration of wastes and industrial emissions are, however, the main sources of heavy metal pollution [1].

Fish have an important place in the diet of Pakistan and are a good source of digestible protein vitamins, minerals and polyunsaturated fatty acids (PUFA). However, fish are also source of metals. Some of the metals found in the fish might be essential as they play important role in biological system of the fish as well as in human being, some of them may also be toxic as might cause a serious damage in human health even in trace amount at a certain limit. The term of heavy metals has been replaced in years by a classification scheme that considers their chemistry rather than relative density [2].

Fish may accumulate large amounts of some metals from the water and from their food and then deposit them in the tissue. Therefore it is important to determine the concentration of heavy metals in commercial fish in order to evaluate the possible risk of fish consumption to human health [3].

Large fish such as Swordfish (*Xiphias gladius*), Yellowfin Tunas (*Thunnus al-bacares*), Skipjacks (*Katsuwonus pelamis*) and Common Dolphinfish (*Coryphaena hippurus*), which are at the top of marine food webs, are particularly exposed to high levels of trace elements through their food [4].

Several pollutants such as heavy metals like Cadmium, lead and Mercury are cumulative toxic, stable and not easy biodegradable [5]. Except for occupationally exposed individuals, food is usually the most important source of toxic trace element intake. Amongst food, fish are constantly exposed to heavy metals present in ocean and sea water. Thus, fish have been found to be good bioindicators or biosensor of heavy metal contamination in aquatic systems [6-7].

Karachi is the biggest city of Pakistan and lies within the coordinates of 23º19 N and 24º07' N latitudes and 67º08' E and 68º54' E longitudes. The main sources of pollution in eastern part of Karachi are leather, paints, textile, pharmaceuticals, iron, steel, electrical appliances, refinery, oil, and electroplating industries and sewage water. Karachi is largest city, there are more than 65 categories of industrial plants in the established industrial estates including, textile industries, tanneries, pharmaceuticals, plastic and rubber industries, steel foundries, metallurgical industries, electroplating and metal coating industries, glass, ceramics and tiles

industries, cement industry, soap and detergents, fish processing industries, chemical industries, power plants, fertilizers and pesticides edible oils, automobile cable and conductor manufacturing etc. [8]

The Karachi coastline growing pollution level, which is tied to the increasing of the shipping industry through the Karachi port, is severely contaminating the mangrove, forests and marine life. Industries produce large amount of industrial waste [9]. The city of Karachi, with a population of more than 12 million and one of Pakistan's largest industrial cities, is facing contamination from various pollutants in its coastal areas [10].

The objectives of this study is determine concentrations of heavy metal (Zn, Cu, Ni and Cd) in dolphinfish *C. hippurus* (Linnaeus, 1758) caught between October 2010 and September 2011.

## 2. Materials and Methods

*C. hippurus* (Linnaeus, 1758) fish samples were collected during seasons (autumn inter monsoon, north east monsoon, spring inter monsoon and south west monsoon) from Karachi Fish Harbour. Fish samples were immediately transported to the laboratory, thawed and rinsed in distilled water to remove foreign particles. Fresh length (cm) and weight (g) were measured. Fish were tagged for identification and then freeze until time for analysis. After biometric measurements, approximately 2 g of the epaxial muscle on the dorsal surface of the fish from each sample were dissected washed with distilled water, dried in filter paper, weighted, packed in polyethylene bags and kept at -20 °C until analysis. AAnalyst 700 Atomic Absorption Spectrophotometer was used in present study in Centralized Science Laboratory, University of Karachi. The absorption wavelengths (λ) used for the determination of various metals are as follows: Zn: 213.90 nm, Cu: 324.70 nm, Ni: 232.00 nm and Cd: 228.80 nm. Due to the lack of a reference standard material, accuracy of the analysis and the effect of the matrices in the media were controlled with the standard addition method. All studied elements were tested with standard addition method for 3 randomly selected samples. The samples taken from the muscles tissues were dried first and cut into pieces as small as possible. 3-20 mg portions were taken from the dried samples, placed into Teflon cylindrical vessels and digested with 3 mL of $H_2O_2$/$HNO_3$ (1:2 v/v) at 250 ºC. The organic part was discarded and the remaining part was diluted with demineralized water to 50 mL in a graduated flask [11].

For all heavy concentrations of metal in *C. hippurus*, within muscle tissues among seasons were determined by making analyses of variance (ANOVA) using Tukey's HDS post-hoc comparison method. The results were evaluated on the basic of homogenous groups with a significance level of ($p<0.05$). The elements which were common in the muscle tissue of *C. hippurus* are assessed by means of Pearson's correlation coefficients. Data collection and statistical calculations were performed by SPSS software (Ver.18).

## 3. Results and Discussion

Length and weight (min-max) of *C. hippurus* found in our sample was 67 – 74 cm and 2900–3900 g. Seasonal and average distribution of metal (Zn, Cu, Ni and Cd) concentrations are given in Table 1.

Accumulation of metals in muscles was observed to follow the order of Zn > Cu > Ni > Cd. Accumulation of metals in muscles at autumn inter monsoon, northeast monsoon, spring inter monsoon and south-west inter monsoon were observed to follow the order of Zn > Cu > Ni > Cd. (Table 1).

The overall order of heavy metal concentration in seasons of *C. hippurus* was follows: Spring intermonsoon, South-west intermonsoon, north east monsoon, autumn inter monsoon for Zn; South-west intermonsoon, springintermonsoon, autumn intermonsoon, northeast monsoon for Cu; South-west intermonsoon, , north east monsoon, spring intermonsoon, autumn inter monsoon for Ni; Spring intermoonsoon, South-west intermonsoon, autumn inter monsoon, northeast monsoon for Cd.

Zn values are lower than reported data from literature [12-16]. Ni values are lower than reported data from literature [17]. Cu accumulation of muscle in lower than Biswas et al [12] and Cu accumulation of muscle in higher than Bhupander et al [13]; Bashir et al [14]; Khoshnood et al [17]; Bhupander et al [13]; Tabinda et al [18]; Asmah and Biney [16]. Cd values are lower than reported data from literature [15] while Cd values are higher than reported data from some studies of the literature [14, 17-18] (Table 2).

**Table 1:** Heavy metal concentrations in *C. hippurus* (μg $g^{-1}$)

| Seasons | | Zn | Cu | Ni | Cd |
|---|---|---|---|---|---|
| Autumn inter monsoon | Minimum | 2.66 | 1.49 | 0.01 | 0.01 |
| | Maximum | 5.43 | 4.17 | 0.43 | 0.28 |
| | Mean | 3.50 | 2.53 | 0.25 | 0.16 |
| | Std. Error of Mean | 1.03 | 0.91 | 0.16 | 0.09 |
| North east monsoon | Minimum | 2.18 | 2.10 | 0.03 | 0.01 |
| | Maximum | 4.56 | 4.23 | 0.82 | 0.26 |
| | Mean | 3.86 | 2.36 | 0.48 | 0.13 |
| | Std. Error of Mean | 1.06 | 0.92 | 0.26 | 0.01 |
| Spring inter monsoon | Minimum | 3.08 | 2.41 | 0.06 | 0.04 |
| | Maximum | 8.86 | 6.77 | 0.77 | 0.44 |
| | Mean | 4.86 | 3.09 | 0.37 | 0.23 |
| | Std. Error of Mean | 2.23 | 0.75 | 0.26 | 0.14 |
| South west monsoon | Minimum | 2.36 | 1.41 | 0.02 | 0.06 |
| | Maximum | 6.22 | 6.77 | 0.88 | 0.32 |
| | Mean | 4.31 | 3.71 | 0.52 | 0.18 |
| | Std. Error of Mean | 1.72 | 1.58 | 0.29 | 0.09 |
| All Seasons | Minimum | 2.36 | 1.41 | 0.01 | 0.01 |
| | Maximum | 8.86 | 6.77 | 0.88 | 0.44 |
| | Mean | 4.13 | 2.92 | 0.40 | 0.16 |
| | Std. Error of Mean | 1.57 | 1.15 | 0.25 | 0.11 |

In fresh tuna samples, Hg showed the highest concentrations, followed by Pb, Cd, Hg and Cd were detected in all samples analyzed with concentrations ranging from 0.04 to 1.79 µg $g^{-1}$ wet wt and from 0.01 to 0.14 µg $g^{-1}$ wet wt respectively, while Pb was encountered in 40 samples analyzed with levels varying between 0.02 and 0.16 µg $g^{-1}$ wet wt [19].

**Table 2:** Comparison of concentration found in fish tissues from previous studies

| Locations/Limits | Fish | Metal and concentrations (µg $g^{-1}$) | | | | Studies |
|---|---|---|---|---|---|---|
| | | Zn | Cu | Ni | Cd | |
| **Kalpakkam** | *S. longiceps* | 23.69 | 3.21 | - | - | Biswas *et al* [12] |
| **Bay of Bengal** | *R. kanagurta* | 16 | 2.20 | - | - | Bhupander *et al* [13] |
| **Kapar** | *A.thalassinus* | 20.54 | 1.21 | - | 0.06 | Bashir *et al* [14] |
| | *J.belangeri* | 18.27 | 0.66 | - | 0.06 | |
| **Mersing** | *A.thalassinus* | 30.21 | 1.56 | - | 0.03 | |
| | *J.belangeri* | 13.12 | 0.95 | - | 0.04 | |
| **Persion Gulf** | *S.sindensis* | - | 1.43 | 0.45 | 0.03 | Khoshnood *et al* [17] |
| **Kalpakkam region St 1** | *R. kanagurta* | 13.76 | - | - | 0.87 | Saravanamurugan *et al* [15] |
| **Kalpakkam region St 2** | | 22.87 | - | - | 1.12 | |
| **Keti Bunder Thatta** | *S. sindensis* | 1.22 | 0.01 | - | 0.03 | Tabinda *et al* [18] |
| **Ghana** | *K.pelamis* | 46.1 | 2.28 | - | - | Asmah and Biney [16] |
| **Port of Abidjan** | *K.pelamis* | - | - | - | 14.94 | Koffi *et al* [22] |
| **Karachi fish Harbour,** | *C.hippurus* | 4.13 | 2.92 | 0.40 | 0.18 | This study |
| International Limits | | 50 | 30 | - | 1.00 | WHO [23] |
| | | 40 | 10-100 | - | 0.50 | FAO [24] |

Emami Khansari et al. [20] reported a Cd concentration range of 0005-0.072 µg $g^{-1}$ wet wt, while Tüzen and Soylak [21] exhibited a mean value of 0.08 µg $g^{-1}$ wet wt for canned tuna purchased from popular supermarkets in Turkey.

Respectively there is no difference ($p > 0.05$) between the seasons accumulation of Zn, Cu, Ni and Cd all season (Table 1). In the present study, Table 3 showed that there is no high correlation between all metals. Negative correlations were found between cadmium-nicel, nicel-zinc.

**Table 3:** Pearson correlation coefficients of *C. hippurus*

| Metal | Zn | Cu | Ni | Cd |
|---|---|---|---|---|
| **Zn** | 1.000 | | | |
| **Cu** | 0.008 | 1.000 | | |
| **Ni** | -0.066 | 0.178 | 1.000 | |
| **Cd** | 0.154 | 0.292 | -0.176 | 1.000 |

Concentrations of Zn, Ni, Cu and Cd found in per capita daily fish consumption is calculated to evaluate potential health risk to Pakistani people. Average daily fish consumption in Pakistan is 33 g per capita [25]. PTWI (Provisional Permissible Tolerable Weekly Intake) values (PTWI for 60 kg adult person (lg/week/60 kg body weight)) of Zn, Ni, Cu and Cd was calculated as 7000, 3500, 35 and 7, respectively in lg/week/60kgs body weight [26].

The heavy metal accumulation in muscles of *C. hippurus* was found to be below nationally and internationally stipulated values and do not pose a serious health risk (Table 4).

**Table 4:** Estimated daily and weekly intakes for the economically significant fish species consumed by adults in Pakistan

| Metal | PTWI | PTWI* | PTDI[a] | *C. hippurus* EWI[b] (EDI)[c] |
|---|---|---|---|---|
| Zn | 7000[a] | 420000 | 60000 | 136.29 (19.47) |
| Cu | 3500[a] | 210000 | 30000 | 96.36 (13.77) |
| Ni | 35[a] | 2100 | 300 | 13.20 (1.89) |
| Cd | 7[a] | 420 | 60 | 5.28 (0.75) |

* Provisional Permissible Tolerable Weekly Intake (PTWI) in l g/week/kgs body weight.

[a] PTDI, permissible tolerable daily intake (lg/day/60 kgs body weight).

[b] EWI, estimated weekly intake in lg/week/60 kgs body weight.

[c] EDI, estimated daily intake in lg/day/60 kgs body weight.

Zn, Cu, Ni and Cd accumulation is lower than international limits in the muscle, while Mn accumulation is higher [23-24].

The results of this study show that Zn, Cu, Ni and Cd accumulations of C. *hippurus* caught from Karachi coast were generally below the international limits. Therefore, Cd bioaccumulations in *C. hippurus* have to be monitored continuously in this region. The present study shows that precautions are needed to be taken in order to obviate metal pollution in future. Otherwise, these pollutants can be hazardous for the fish populations's health and human consuming them.

The authors declare that they have no conflict of interest.

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