# CONCENTRATIONS OF COPPER, CADMIUM, COBALT, MANGANESE, NICKEL, AND LEAD IN THE MUSCLES OF FRESHWATER FISHES, Crassius crassius, Aspius vorax and Barbus luteus COLLETED FROM ALHAMMAR MARSH (SOUTH OF IRAQ).

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### **ABSTRACT**

To assess the significance of metals in fishes from Al-Hammer marsh (South of Iraq), preliminary data is presented on concentrations of Cu, Cd, Co, Mn, Ni and Pb in tissues of three fresh water fishes (*Crassius crassius, Aspius vorax and Barbus luteus*) collected in 2006-2007 seasonally period. Copper range from Below detection limit (BDL) in *B. luteus* tissues for all sampling seasons to 4.12 (μg/g. dw) in the muscles, for Cd, Co and Ni were range between BDL to 24.49 Cd, 4.86 (μg/g. dw) in all tissues and 88.85 Ni (μg/g. dw) in the *A. vorax* and *B. luteus* muscles respectively. Metal concentrations seemed to be increased through hot periods (Summer and Spring) compared with cold periods (Autumn and Winter), During data analyses, *C. crassius* tend to accumulate more concentration of all study metals than *A. vorax* and *B. luteus*.

# INTRODUCTION

Trace metals are generally released in aquatic environments in different ways and accumulation of these metals is dependent on the concentration of the metal, the type of aquatic animals and the exposure period (Canli *et al.*, 1998). Levels of heavy metals in fish have been widely reported (Romeo *et al.*, 1999, Edwards *et al.*, 2001, Gaspic *et al.*, 2002, Satarug *et al.*, 2003, Kuçuksezgin *et al.*, 2006).

Cadmium has not been found to occur naturally in its pure state and its concentration seems to be directly proportional to zinc and lead concentrations. Use of Cadmium in agriculture and industry has been identified as a major source of wide dispersion into the environment and food.

The major route of exposure to Cd for the non-smoking general population is via food; the contribution from other pathways to total uptake is small (Goyer, 1991). and many chemical elements that are present in aquatic food are essential for human life at low concentrations, but can be toxic at high concentrations while Others such as mercury, cadmium and lead have no known essential function in life and are toxic even at low concentrations when ingested over a long period (Williams and Moore, 2003). Therefore, many consumers regard any presence of these elements in fish as a hazard to health (Oehlenschlager, 2005).

To understanding the relationship in fish between environmental exposure and the resulting concentration of contaminants in fish tissues is necessary, but often lacking, basis for effective use of fish as indicators of chronic environmental contamination (Goyer, 1991). When fish are used as pollution indicators, the underlying objective is protection of the organisms themselves, which requires an understanding the relationships between tissue residues, impacts on the animals and ultimately on populations and community assemblages (Canli and Atli, 2005).

Few studies have been undertaken to assess the concentration of elements in concerned different species of fish collected from Arabian Gulf, Shatt al Arab river and South Iraqi marshes. Due to the fact that fish are considered an essential part of the diet in the region (Abaychi and Al-Saad 1988; Al-Saad *et al.*, 1994; Mustafa *et al.*, 1995; Al-Saad *et al.*, 1996, Al-Saad *et al.*, 1997).

Therefore, an investigation was usual assumption is that contaminant concentrations are positively correlated with contaminant exposure. Their components may alter quantitatively and qualitatively the natural biochemical cycle (Grimanis *et al.*, 1978). Fish which live in polluted waters may accumulate toxic trace elements via their food chains or via water column thus possibly endangering human health. In the Arabian Gulf region, recently vast industrial, agricultural, economic and social developments have taken place, in addition to an increase in population. This may enhance the magnitude of environmental pollution year by year.

Fish species usually accumulate small quantities from heavy metals, but predatory fishes sometimes accumulate greater quantities than the rest of aquatic organisms (Canli and Atli, 2005). Hallebach (1985) demonstrates the fact that the heavy metals first of all penetrate through the mucous membrane of the branchia, from where they spread after some days and accumulate in the kidneys and the liver.

Over the last few decades, there has been growing interest in determining heavy metal levels in the marine environment and attention was drawn to the measurement of contamination levels in public food supplies, particularly fish (Dietz *et al.*, 1996; AMAP, 1997).

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The contamination of freshwater with heavy metals has become a matter of great concern, not only because of the threat to public water supplies, but also their damage caused to the aquatic life (Canli *et al.*, 1998). Contamination with heavy metals may have devastating effects on the ecological balance of the aquatic environment and the diversity of aquatic organisms becomes limited with the extent of contamination (Suziki *et al.*, 1988).

This study aimed to determine the natural occurrence of some metals in selected kinds of fresh water fishes collected from Al-Hammer marsh (southern Iraq).

### MATERIALS AND METHODS

Fish samples were collected from Al-Hammer marsh area (southern Iraq) from location as shown in fig. (1) during the period 2006-2007 by "Gill nets". Metals analysis was performed on the 63 um fraction of the fish muscles, which has been separated by sieving after drying and grinding. The determination of metals in fish samples was done according to the following procedure described by Sturgeon *et al.*, (1982). Concentrated of hydrochloric acid (HCl) and nitric acid (HNO<sup>3</sup>) 1:1 was added to each sample and evaporated to near dryness on the hotplate at 80°C, then mixture of concentrated percloric acid HClO4 and HF (1:1) was added. After heating to near dryness, 20ml of 0.5 HCl were added and cooled for 10 mins. The extraction was decanted into 25 ml plastic volumetric flask. Finally the volume of samples were stored for analysis using a Pye-Unicam Atomic Absorption.

# **RESULTS AND DISCUSSION**

The mean concentrations of six metals studied (Copper, Cadmium, Cobelt, Manganise, Nickel and lead) in three fresh water fish muscles (*C. crassius, A. vorax* and *Barbus luteus*) have been illustrated in Figs. (2, 3, 4, 5). The values of metals showed relative variation among different fish species during different seasons, a substantial variability was noted for some metals such as nickel, Cadmium and lead in some study species (*A. vorax* and *B. luteus*).

Gaspic *et al.*, (2002) mentioned that the distribution patterns of the studied metals exhibited similar trend, since their concentrations increased during hot periods (Spring and summer seasons. Figs. 4, 5), compared with those in cold periods (Autumn And winter seasons) Figs.(2, 3). Fish tissues from *A.vorax* were detected in all samples for study metals at Autumn season (Fig. 2), but in the same time some metals are below the limits of detection in each cases such as Cd, Co, Ni, at Autumn, winter, spring and summer respectively, while it is true for muscle in case of lead.

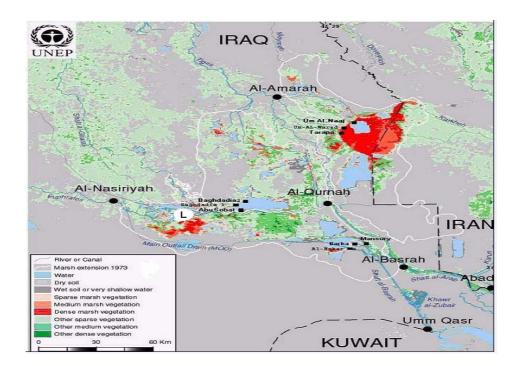


Fig. (1) showed collection station through Al-Hammer marsh (southern Iraqi marshes)

High Cd (at winter) and Pb (at summer) levels in fish muscles indicate that may be contamination has occurred as pointed by (Parsons, 1999). It is clear from the obtained results that nickel showed it's highest values in *C.crassius* tissues during all seasons, but fig. (2) showed that copper, Cadmium, Cobalt and nickel concentrations are below the limits of detection in many cases, the data was summarized the statistical analyses for present results (using Spss statistical program.).

Few data about metal concentrations in Al-Hammer marsh have been reported dealing with general biota especially fish tissues, Al-Khafaji (2005) has been determined the concentrations of six study metals in some *C. luteus* tissues (Gill, liver, mules and kidney) these concentrations were: 0.0-6.1 (as μg/g dw) in the tissues which is agree with present results. While metal concentrations in eleven aquatic plants from Al-Hammer marsh were: Cd:0.0 -5.23/Mn;1.20-3.10/Ni:0.86-10.53/ Pb: 0.09-0.86 μg/g dw (Al-Saad *et al.*, 1994). Mustafa *et al.* (1995) were determined the seasonal variations of some metals in aquatic vascular plants of Al-Hammer marsh, the results were: Cd:nd-1.74/Mn:1.20-4.00/Ni:0.0 -6.73/Pb:0.08-2.84.

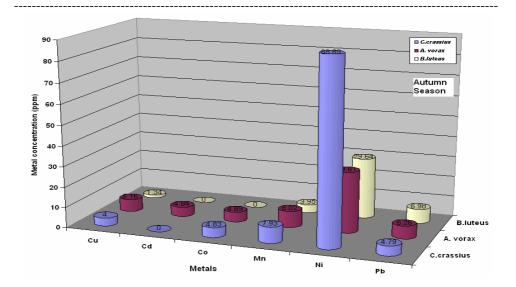


Fig. (2): Concentration of metals in the tissues of (*C. crassius, A. vorax and B. luteus*) collected during autumn season

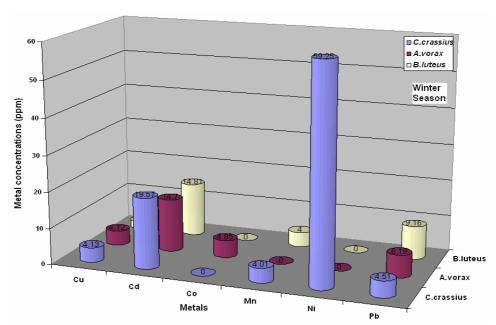


Fig. (3): Showed concentration of metals in the tissues of (*C. crassius, A. vorax and B. luteus*) collected during winter season

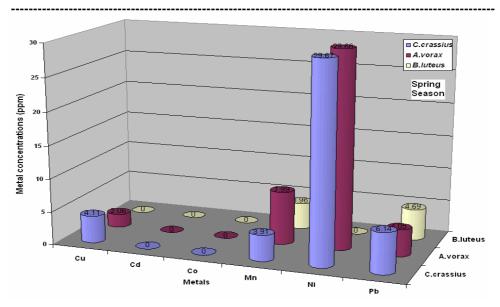


Fig. (4): Showed concentration of metals in the tissues of (*C. crassius*, *A. vorax and B. luteus*) collected during spring season

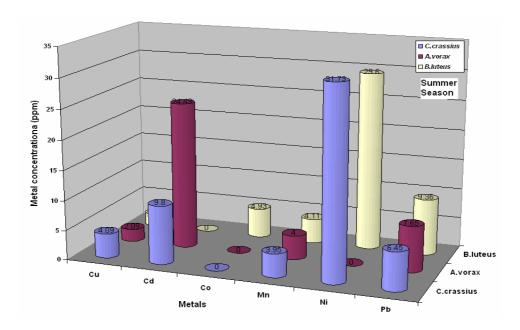


Fig. (5): Showed concentration of metals in the tissues of (*C. crassius*, *A. vorax and B. luteus*) collected during Summer season

The distribution patterns of metals in the water, sediment and biota increased in the hot seasons (spring and summer) and may be attributed to the release of metals from sediments to the overlying water under the effect of both high temperature and fermentation process resulted from decomposition of organic matter (Elewa *et al.*, 2001). Moreover, these increase in water coincided with the decrease in the same metal's values in the sediments and biota. In addition, the values of metals showed an obvious decrease in the water during cold period (winter and autumn) with a correspondent increase in the sediments due to precipitation of heavy metals from water column to the sediments under high pH values and the adsorption of heavy metals onto organic matter and their settlement downward (Goher, 2002).

Because most trace metals tend to accumulate in the different body organs, these metals are dangerous for fish and in turn they lead to serious problems in both man and animals (Marzouk, 1994). Fishes may absorb dissolved elements and trace metals from its feeding diets and surrounding water leading to their accumulation in various tissues in significant amounts and exhibit eliciting toxicological effects at target criteria (McCarthy and Shugart, 1990; Parsons, 1999).

In present study, which are varied mainly due to the different fish habitat and the influence of the surrounding ecosystem. Table (1) showed these differences in the ranges and data statistical analyses. These results are agreed with that reported by Abaychi and Al-Saad (1988), FAO (1996) Zyadah (1997) and Abdel-Baky *et al.* (1998).

Few local studies have been done on Arabian Gulf and Shatt Al Arab River, which were concerned determination of metals in water, sediments, and different biota especially fishes as economically source in the region.

Many studies have been done using many species from fishes as bioindicator for pollution monitoring because most of fish tissues can accumulate heavy metals from aquatic environment (Abdul-Hassan and Kareem, 1989; Abdul-Hassan *et al.*, 1989; Ali and Fishar, 2005; Canli and Atli, 2005; Ashraf, 2006; Dalman *et al.*, 2006), due to this reason a few studies have been reported dealing with different fish species collected from area closed to the present study area.

Many studies have been done using many fish species as a bio-indicator for pollution monitoring because most of fish tissues can accumulate heavy metals from aquatic environment (Abdul-Hassan and Kareem, 1989; Abdul-Hassan *et al.*, 1989, Ali and Fishar, 2005: Canli and Atli, 2005; Ashraf, 2006; Dalman *et al.*, 2006). Abaychi and Al-Saad (1988) were determined metal concentrations in some fish species collected from Shatt Al-Arab river (six fresh water species),

Table (1): means and statistical analyses of metal concentrations (as μg/g dw) in the tissues of C. crissius, A. vorax and B. luteus through study seasons.

	Aut	umn			Wint	er	
Metal	Species	Range	Sig.	Metal	Species	Range	Sig.
	C. crassius	3.91-4.45	S.c		C. crassius	4.01-4.22	S.c
Cu	A. vorax	6.06-6.31	S.c	Cu	A. vorax	4.11-4.13	S.c
	B. luteus	1.34-2.11	S.c		B. luteus	2.01-2.09	S.c
	C. crassius	Nd	0		C. crassius	19.56-19.66	S.b
Cd	A. vorax	4.80-5.03	S.c	Cd	A. vorax	14.68-14.71	S.c
	B. luteus	Nd	0		B. luteus	14.37-14.90	S.c
	C. crassius	4.79-4.97	S.a		C. crassius	Nd	0
Co	A. vorax	4.71-4.99	S.c	Co	A. vorax	4.71-5.02	S.b
	B. luteus	Nd	0		B. luteus	Nd	0
	C. crassius	7.81-8.17	S.a		C. crassius	3.89-4.05	S.b
Mn	A. vorax	7.58-8.13	S.a	Mn	A. vorax	Nd	0
	B. luteus	3.91-4.09	S		B. luteus	3.90-4.06	S.b
	C. crassius	88.77-88.90	S.c		C. crassius	59.12-59.33	S.c
Ni	A. vorax	29.42-29.81	S.c	Ni	A. vorax	Nd	0
	B. luteus	29.42-29.79	S.c		B. luteus	Nd	0
	C. crassius	4.10-5.09	S.a		C. crassius	4.10-5.30	S.b
Pb	A. vorax	6.21-6.30	S.b	Pb	A. vorax	5.91-6.50	S.b
	B. luteus	6.56-7.23			B. luteus	8.91-9.40	S.b
	Sp	ring			Sun	nmer	
Metal	Species	Range	Sig.	Metal	Species	Range	Sig.
	C. crassius	4.10-4.15	S.c		C. crassius	4.07-4.21	S.a
Cu	A. vorax	2.00-2.13	S.c	Cu	A. vorax	1.99-2.10	S.a
	B. luteus	Nd	S.c		B. luteus	1.99-2.11	S.a
	C. crassius	Nd	0		C. crassius	9.59-10.00	S.a
Cd	A. vorax	Nd	S.c	Cd	A. vorax	24.48-24.50	S
	B. luteus	Nd	0		B. luteus	Nd	0
	C. crassius	Nd	S.a		C. crassius	Nd	0
Co	A. vorax	Nd	S.c	Co	A. vorax	Nd	0
	B. luteus	Nd	0		B. luteus	4.55-5.10	S.a
	C. crassius	3.88-4.16	S.a		C. crassius	3.92-4.07	S.b
Mn	A. vorax	7.77-8.15	S.a	Mn	A. vorax	3.96-3.99	S.b
	B. luteus	3.90-4.10	S		B. luteus	3.70-4.15	S.b
l	C. crassius	29.51-29.67	S.c		C. crassius	27.31-29.82	S.c
Ni	A. vorax	29.49-29.71	S.c	Ni	A. vorax	Nd	0
	B. luteus	Nd	S.c		B. luteus	29.52-29.74	S.c
	C. crassius	5.91-6.30	S.a		C. crassius	6.23-6.81	S.c
Pb	A. vorax	3.98-4.13	S.b	Pb	A. vorax	7.20-7.99	S.b
	B. luteus	4.50-4.88	Sig.		B. luteus	9.10-9.67	S.b

S= Significant, a=P<0.001, b=P>0.01, C=P>0.005

the concentration range for Cd was 0.00-0.02, for Co=0.20-0.80, for Cu=3.9-10.3, for Mn=1.2-7.3, for Ni=0.0=4.3, and for Pb=0.16-0.82 (as  $\mu$ g/g dw). While concentration ranges of these metals in fourteen marine fish species were collected from Arabian Gulf, the ranges were for Cd= 0.1-0.28, for Co=0.4-1.5, for Cu=3.1-16.4, for Mn=0.0-6.9, for Ni= 0.0-6.8 and for Pb=0.02-0.50 (as  $\mu$ g/g dw).

The ranges of Cd=0.50,0.03, for Cu=37,1.57, for Mn= 7.9, 1.79, for Ni= 39.3, 2.27 and for Pb=5.9,0.06 as as  $\mu$ g/g dw in the tissues of shrimps and Liza subviridus fish respectively (Al-Saad and Al-Imarah, in press) which are agree with present study.

Trace metals enter the aquatic environment of southern Iraq from both natural and anthropogenic sources (Abaychi and Al-Saad, 1988). Natural sources include storm dust fall, erosion or crusted weathering and dead and decomposition of the biota in the water, whereas the anthropogenic sources include sewage wastes, industrial effluent, automobile effluent, petroleum and fertilizer industry effluent. The accumulation of these metals in the fish muscles depend on the concentration of these metals, exposure time, physiological conditions of theses organism and environmental factors (Al-Saad et al., 1996). These different in concentration may related also to the food habitat of these fish which played the dominant role. There are few data available on the concentrations of trace metals in different tissues of fish from Shatt Al-Arab and its estuary and other area of the Arabian Gulf which could used together with values from world wide and heavily polluted site for comparative purpose. All the concentrations of trace metals obtained in these fish in the present study are much lower than those reported at heavily polluted site (Table 2).

Table (2): Trace metal concentrations in muscle of fish ( $\mu g/g$  dry weight) from Iraqi and NW Arabian Gulf in comparison with word wide average concentration and polluted site

location	Cd	Co	Cr	Fe	Mn	Ni	Pb	V	Zn	Source
Shatt Al-Arab	0.10	0.60	4.50	60.5	7.30	1	0.46	1.00	13.0	Abaychi and Douabul (1988)
Arabian Gulf	0.05	1.20	0.80	55.2	6.90	4.80	0.50	4.60	10.7	Abaychi and Douabul (1988)
Khor Al- Zubair	0.90	-	-	51.5	1.70	6.00	3.90	5.40	16.3	Al-Edanee et al. (1991)
Kuwait	0.35	0.04	0.14	12.5	0.52	-	0.27	0.07	20.0	Fowler <i>et al.</i> ,(1993)
Shatt Al-Arab estuary	ND	0.30	ND	43.9	1.40	4.16	0.33	1.73	2.93	Al-Saad et al.,(1997)
Shatt Al-Arab	ND	0.11	1	1	0.09	0.36	0.05	0.22	5.70	Al-Khafaji (2005)
Kuwait	0.35	0.04	0.14	12.5	0.52	-	0.27	0.07	20.0	Fowler <i>et al.</i> ,(1993)
Al-Hamme marsh	0- 24.49	0- 4.86	-	195- 411	3.75- 5.00	48- 88.85	4.1- 9.67	-	-	Present work
World wide	0.10	0.20	0.10	50.0	10.0	1.00	3.00	1.00	80.0	Bryan (1978)
Polluted region	0.92	-	8.90	-	3.90	7.80	20.1	-	517.8	Dallinger and Kautzky (1985)

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