Physical Sciences

TRACE METAL BUILD UP IN THE MARINE ENVIRONMENT OF SOUTH WEST COAST OF PAKISTAN: EVIDENCE FROM THE EDIBLE FISH MUSCLE

M Jaffar*, M Ashraf, Jaleel Tariq and Khalid Masud

Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

(Received 21 July 1998; accepted 21 February 1999)

Six species of commercially important fish (*Aruis thalassinus*, *Gymnura poecilura, Lutjanus fulviflamma, Nimipterius japonicus, Platycephalus indicus* and *Seriolina nigrofasciata*) captured from the northern coast of the Arabian Sea, Pakistan were analyzed for eleven trace metals (Ag, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn and Hg) and four macronutrients (Na, K, Ca and Mg) using graphite furnace atomic absorption spectrometer to assess the current extent of metal pollution in the coastal waters. In order to evaluate trace metal enrichment in the fish over a time period, a set of elemental data obtained during 1987 for a commercial fish, *Aruis thalassinus*, was compared with the present data. This comparison revealed that almost all trace metals in the presently investigated fish exhibited enrichment compared with 1987 metal levels. The percent enrichment (% E year⁻¹) was found to be maximum for Cr (15.5% year⁻¹), followed by Pb (13.24% year⁻¹). Zinc showed minimum % E year⁻¹ at 5.51%. The study revealed that *Lutjanus fulviflamma* was a good bioaccumulator for As, Cr, Cu, Fe and Zn, and *Platycephalus indicus* for Cd, Mn, Ni, Pb and Mg.

Key words: Coastal water, Marine fish, Trace metals, Arabian sea.

Introduction

3

The heavy trace metal pollution of the marine environment is due largely to the discharge of untreated industrial effluents into the sea. It is a world-wide problem and has created serious health concerns (Gallindo *et al* 1986; Ober *et al* 1987; Pastor *et al* 1988). A rapid growth in population and industrial development has been implicated for the enhancement of metal levels in the marine environment (Lester *et al* 1983; Bagatto and Ali Khan 1987). These metals have the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards (Puel *et al* 1987). In the past fish has been used as an indicator of trace metal stress on aquatic life (Pena and Alberto 1984).

In Pakistan (as in the case of several other countries) the status of the marine environment is not satisfactory in the wake of ever-increasing metal pollution from industrial and municipal sources. The studies conducted during the last few years indicated increasing levels of certain trace metals in the waters of the northern coast of the Arabian sea, Pakistan, resulting in the bio-accumulation of toxic metals in certain marine fish species (Jaffar and Ashraf 1988; Ashraf and Jaffar 1990; Tariq and Jaffar 1991; Ashraf *et al* 1992). The present work was undertaken to study the present day concentration levels of selected trace metals and macro-nutrients in some * Author for correspondence.

commercially important fish species which have been routinely harvested from the waters of Karachi coast for human consumption. The present data was compared with that obtained during 1987 for the fish belonging to the same study area to assess the extent of increase of trace metal levels in fish (Jaffar and Ashraf 1988).

Materials and Methods

A total of 135 fish samples belonging to six species were procured from locations along the coastline of Karachi from local fishermen and fish-catering agencies. Reasonable number of specimens of each fish were collected from each site as per availability, in a narrow weight range (1200-1600 g). The edible muscle of each fish was dissected with a plastic knife, previously washed with distilled water, and dried in folds of tissue paper. The samples were then packed in polythene bags and preserved at 10 °C till analyzed. Precisely weighed 20.0g of muscle sample was digested in 50% (V/V) HNO,, other relevant details are described in earlier papers (Ashraf and Jaffar 1989; Tariq et.al 1993). The sample solutions were used to estimate the concentrations of Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, along with macro-nutrients (Na, K, Ca and Mg) by the graphite furnance atomic absorption technique. The As estimation was carried out following the method of Maria et al (1986), whereas Hg was estimated using the method of Hatch and Ott (1968). A Shimadzu Atomic Absorption Spectrophotometer (Model

 Table 1

 Relevant parameters, average trace metal and macro-nutrient concentrations (µg g⁻¹ wet wt) in the muscle of various fish from Arabian Sea, Pakistan

Species n (Site)	Level	Wt (g)	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg	Na	К	Ca	Mg
Aruis thalassinus	X	1600	0.05	0.78	0.04	0.18	0.32	2.61	0.10	0.04	0.07	2.82	0.13	508	238	189	284
23 (S2, S3, S4, S5)	± SD	250	0.02	0.22	0.02	0.06	0.10	0.74	0.03	0.02	0.02	0.96	0.03	83	49	45	55
Gymnura poecilura	X	1250	0.05	1.07	0.04	0.20	0.31	1.61	0.11	0.05	0.27	2.80	0.11	661	239	199	385
0(\$1, \$2, \$4, \$5)	± SD	300	0.02	0.21	0.02	0.04	0.10	0.41	0.08	0.02	0.06	0.83	0.04	89	67	49	67
utjanus fuloviflamm	a X	1175	0.19	1.53	0.03	0.26	0.38	3.71	0.11	0.06	0.19	3.21	0.04	640	181	268	459
1 (\$2, \$2, \$3, \$4, \$6	5) ± SD	290	0.04	0.31	0.02	0.10	0.09	0.38	0.03	0.02	0.04	0.83	0.02	110	63	37	89
Nemipterius japonicu	s X	1430	0.04	0.02	0.04	0.11	0.23	1.21	0.14	0.05	0.18	1.72	0.10	650	223	329	315
19 (S2, S3, S4, S5, S6	$(5) \pm SD$	235	0.02	0.01	0.02	0.03	0.05	0.42	0.05	0.02	0.05	0.45	0.02	132	72	35	72
Platycephalus indicu	s X	1508	0.10	0.27	0.11	0.05	0.19	3.41	0.27	0.05	0.36	2.30	0.12	585	274	360	576
28 (S1,S2,S3,S4,S5,S	6)± SD	197	0.03	0.11	0.03	0.02	0.04	1.21	0.09	0.02	0.10	0.65	0.05	98	66	64	73
Seriolina nigrofascia	ta X	1453	0.20	0.32	0.12	0.09	0.23	2.72	0.28	0.17	0.03	2.11	0.15	400	365	369	503
24 (\$2,\$3,\$4,\$5,\$6)	± SD	279	0.03	0.12	0.04	0.02	0.05	0.69	0.05	0.05	0.01	0.65	0.04	152	70	73	82
Ainimum			0.04	0.02	0.03	0.05	0.19	1.21	0.10	0.04	0.03	1.72	0.04	400	181	189	284
Maximum			0.20	1.53	0.11	0.26	0.38	3.71	0.28	0.17	0.36	3.21	0.15	661	365	369	576

Table 2

Comparative concentrations (µg g⁻¹ wet wt) and enrichment parameters for various metals in *Aruis thalassinus*

	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
*1999	0.05	0.78	0.04	0.18	0.32	2.61	0.10	0.04	0.07	2.82	0.13
**1987	-	0.53	0.02	0.09	0.24	2.01	0.07	0.03	0.04	2.12	0.08
E.R.	-	1.47	1.60	1.93	1.34	1.30	1.39	1.34	1.79	1.33	1.56
%Enrich-		47	60	93	34	30	39	34	79	33	56

* Present study; ** Jaffar et al 1988.

AA-670), in automatic background compensation mode, equipped with a hydride generator and graphite furnance, was used for the analyses. The same instrument, with the same auxiliary facilities, was used in the earlier study. The reagents used were of guaranteed spectroscopic purity (>99.9%). Standard reference samples acquired from National Institute of Health, were analyzed by the same procedure and run in parallel to check the accuracy of the results, which for all the metals analyzed ranged between ± 1.00 and 1.50%.

Results and Discussion

Concentration data for the metals and macro-nutrients are given in Table 1. The sites of fish capture are shown in Fig. 1. Table 2 summarizes comparative concentration of the metals in *Aruis thalassinus* for the present and earlier study. The same Table also lists enhancement ratios and percent

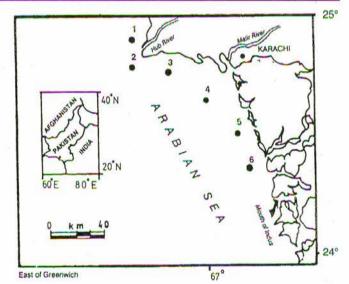


Fig 1. Location of the sampling

enhancement per year parameters.

The metals and macro-nutrients showed an overall large variation with regard to species and the location of the catch. It was anticipated that individual variability played a major role in the uptake of metals by these fish belonging to the same habitat. The industrial metals (Fe, Cu, Cr and Zn) were at higher levels in these fish compared with the other metals, and hence it could be inferred that fish were under an anthropogenic pollution stress, as was evidenced in earlier studies (FAO Report 1986; Tariq *et al* 1993). The results of

Trace Metals in Fish

S.No.	Kind of fishes	Cd	Cu	Pb	Zn	Hg	Area of catch (reference)
1.	Whiting, haddock, herring	0.06-0.12	0.32-1.6	0.5-1.0	1.7-14.7	Ξ.	Firth of Clyde, U K(Holden, et al 1972)
2.	Grouper species	0.01-0.09	0.23-1.15	0.05-0.73	3.17-4.0	×	Bahamas Islands (Taylor et al 1973)
3.	Flounder perch, shark	0.05-0.06	0.25-2.1	<u>.</u>	4.6-13.5	1 a	Tasmania, Australia (Eustace 1974)
4.	Cod, plaice, mackerel	0.05-0.18	0.5-1.80	0.05-0.99	4.35-6.60		Wales, U K (Portmann, 1972)
5.	Belones	0.05-0.9	3.0-5.1	0.2	42-54	-	N E.Atlantic (Stevens et al 1974)
6.	Solea	2.1	4.4	2.0	57	0.17	Portugal (Stenner et al 1975)
7.	Harpodon, argentus	0.01-0.16	3.33-4.69	1.67-2.58	18.8-26.5		Bay of Bengal, Bangladesh (Khan <i>et al</i> 1987)
8.	Present work	0.03-0.11	0.19-0.38	0.03-0.36	1.72-3.21	0.04-0.15	Arabian Sea, Pakistan

A comparison of some trace metal concentrations (µg g⁻¹ wet wt.) in the muscle of various marine fishes from different areas of the world.

Table 3

the study indicated that As was present at the minimum concentration of $0.017 \,\mu g \, g^{-1}$ in *Nemipterius japonicus* while the maximum concentration was found at 3.712 $\,\mu g \, g^{-1}$ in *Lutjanus fulviflamma*. Of the macro-nutrients, the maximum concentration was that of K in *Lutjanus fulviflamma* and the maximum of Mg in *Platycephalus indicus*.

Compared with the previous work on the levels of heavy metals in Aruis thalassinus, selected from the same area, it was noted out that the metals investigated in the present work showed an overall enhancement with respect to the previous levels (Table 2). For example, the enhancement ratio (defined hereafter as the ratio of the current concentration of a metal to that determined previously), was found to vary between 1.33 to 1.93, respectively for Zn and Cr. The results indicated that the percent enhancement in concentration of a metal per year (% E year⁻¹) rose to a maximum of 15.59% in case of Cr, followed by Pb at 13.24%, taking the previous concentration as reference value. The data in Table 2 may be classified for elements having %ER<50 (As, Cu, Fe, Mn, Ni and Zn), %ER between 50-75 (Cd and Hg) and %ER>75 (Cr and Pb). Thus, as the data go, at least Aruis thalassinus has a greater tendency for bio-accumulation of Cr and Pb. The data, therefore, reflected a substantial increase in metal concentration per year thereby indicating that no check or control has been imposed on regulating the industrial and municipal effluents being dumped finally into the Sea via tributary Rivers Fig.1. Another contributory factor could be the mining and related waste disposal carried by the Malir and Hub Rivers into the Sea.

1

1

The overall analysis of the data also revealed that *Lutjanus fulviflamma* which showed higher concentration of As, Cr,

Cu, Fe and Zn, and *Platycephalus indicus* which had maximum concentration of Cd, Mn, Ni, Pb and Mg in their muscle part may be very useful to understand trace metal bio-accumulation. Either of these fish, therefore, could be used as indicator species for monitoring marine trace metal pollution.

The present study brought out some interesting features upon comparison with species from different areas of the world; the relevant data are provided in Table 3. It is evident that, in general, the concentration levels of various trace metals analyzed in the edible fish muscle for the present study are closely comparable with muscle of several common fish from various areas of the world (Eislor 1981). The trace metal build up in the edible muscle of the fish appears to be significant requiring prompt attention and preventive measures. Though the present study is a preliminary one involving only limited data set, it emphasizes a need for detailed location and species based further investigation.

References

- Ashraf M, Jaffar M 1989 Trace metal content of six Arabian Sea fish species using a direct nitric acid-based wet oxidation method. *Toxicol Environ Chem* **19** 63-68.
- Ashraf M, Jaffar M 1990 Trace metal concentration in edible muscle of six species of fish from the Arabian Sea. *Fisheries Res* 8 287-291.
- Ashraf M, Tariq J, Jaffar M 1992 Trace metals in fish, sediment and water from the south west coast of the Arabian Sea, Pakistan. *Toxicol Environ Chem* 34 99-104.
- Bagatto G, Alikhan M A 1987 Copper, cadmium and nickel accumulation in crayfish population near copper-nickel

smelters at Sudbury, Ontario, Canada. Bull Environ Contam Toxicol 38 540-545.

- Eislor R 1981 Trace metal concentration in marine organisms. Pergamon Press, pp 493-623.
- FAO Report 1986 Food contamination study and control in Asia and Far East, Project RAS/078/NOR, Islamabad, Pakistan.
- Galindo L, Hardisson A, Montelongo F G 1986 Correlation between lead, cadmium, copper, zinc and iron concentrations in frozen tuna fish. *Bull Environ Contam Toxicol* 36 595-599.
- Hatch W R, Ott W L 1968 Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Anal Chem 40 2085-2087.
- Jaffar M Ashraf M 1988 Selected trace metal concentrations in different tissues of fish from coastal waters of Pakistan (Arabian Sea). Indian J Mar Sci 17 231-234.
- Lester J N, Sterritt R M, Kirk P W W 1983 Significance and behavior of heavy metals in wastewater treatment processes. II. Sludge treatment and disposal. *Sci Total Environ* 30 45-83.
- Maria I S, Gonzalez M, Lara W, Ober A 1986 Arsenic levels in Chilean marine species. *Bull Environ Contam Toxicol*

37 593-598.

- Ober A G, Gonzalez M, Maria I S 1987 Heavy metals in molluscan, crustacean and other commercially important Chilean marine coastal water species. *Bull Environ Contam Toxicol* **38** 534-539.
- Pastor A, Madina J, Del Ramo J, Torreblanca A, Diaz-Mayans J, Hernandez F 1988 Determination of lead in crayfish *Procambarus clarkii*; accumulation in different tissues. *Bull Environ Contam Toxicol* **41** 412-418.
- Pena J, Alberto L 1984 Distribution del mercurio enreces langunarees del Datta de Ebro. *Rev of Toxicol* 1 103-113.
- Puel D, Zsuerger N, Breittmayer J P 1987 Statistical assessment of a sampling pattern for evaluation of changes in mercury and zinc concentrations in *Patella coerulea Bull Environ Contam Toxicol* 38 700-706.
- Tariq J, Jaffar M 1991 Mercury concentrations in ten fish species from the Arabian Sea, Pakistan. *Toxicol Environ Chem* 34 57-63.
- Tariq J, Jaffar M, Ashraf M, Moazzam M 1993 Heavy metal concentrations in fish, shrimp, sea weed, sediment and water from the Arabian Sea, Pakistan. *Mar Pollut Bull* 26 644-647.

140