Assessment of Current Trace Metal Pollution Status of the South-east Arabian Sea Coast of Pakistan Through Fish Analysis

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Summary: Eleven trace metals (Ag, As, Cd, Cu, Fe, Mn, Ni, Pb, Zn and Hg) and four macronutrients (Na, K, Ca and Mg) were estimated in 143 fish samples pertaining to 6 commercial marine fish species (*Pampus argenteus, Dussumieria acuta, Gazza minuta, Lepturocanthus savala, Parastromateus niger, Pseudorhombus arsius*) harvested during September-March 1993, from locations along the south-west coast of the Arabian Sea, Pakistan using the atomic absorption method. To assess the enhancement of pollution over the past six years the present trace metal data is compared with the counterpart for a common fish (*Pampus argenteus*) harvested from the same location during September-March, 1987. Arsenic, iron, nickel, zinc and mercury showed dominant concentrations, with the values of 7.317, 5.908, 1.891, 10.201 and 0.746 μg/g. The data reflected species specificity towards metal uptake and showed no direct relationship for macronutrient levels. The average metal concentrations found in various fish species were higher for industrial metals, such as As, Cd, Cr, Cu, Fe, Ni, Zn and Hg. The overall pattern of increasing metal concentrations are: Hg < Pb < Cd < Zn < Ni < Cu < Fe < As < Mn < Cr. The study based on *Pampus argenteus*, selected as a common species, revealed that Cr and Mn concentrations have increased to about 4-fold, and As by about 2.5 fold during the past 6 years, indicated a gross metal pollution of the coastal waters of the sea.

Introduction

Heavy metal pollution of aquatic bodies arising mainly from rapid industrialization and urbanization has created a grave health concern throughout the world [1]. The situation is more serious with marine ecosystem which has been, therefore, keenly investigated during recent years [2,3]. The trace metal levels in marine organisms are found to reflect localized industrial and agricultural burdens carried to the sea [4]. In Pakistan, trace metal pollution of the marine environment is attributed to a number of ever-increasing anthropogenic activities which have resulted in enhanced level of trace metals in certain local commercial fish [5-7]. The purpose of the present study is to present the levels of selected trace metals and macronutrients in some commercial marine fish species harvested form the south-west coast of the Arabian Sea, Pakistan. To assess the rate of increase of pollution over the past six years, the present trace metal data is compared with the counterpart for a common fish harvested from the same location during September-March, 1987. It is, therefore, expected that the study would be helpful in predicting the future metal pollution trends in local fish which have a vast domestic and foreign market.

Results and Discussion

The measured levels of various metals in six species of fish along with those of macronutrients are presented in Table-1. The location of the sampling sites is given in Fig. 1. The data appearing in Table-1 pertain to the total number of samples (n) of a given species harvested from relevant sites. The measurement based on triplicate runs agreed within 1.5-2.0 % and the standard fish samples analysis within ± 2-3 % during inter-laboratory comparison.

The data in Table-1 reflected a species-specificity towards metal uptake and evidenced divergent levels of the metals in various fish. Of all the six species investigated *Dussumieria acuta* showed maximum levels of Ag and Fe, respectively at 0.559 and 5.908 μg/g. Similarly *Pseudorhombus arsius* exhibit maximum levels of As, Cr, Mn and Ni, with respective concentrations of 7.317, 0.590, 0.264 and 1.891 μg/g. *Parastromateus niger* showed highest level of Zn(10.201 μg/g) and Hg(0.746 μg/g). The occurrence of maximum metal concentration had, therefore, the maximum incidence in *Pseudorohombous arsius* followed by *Dussumieria aeuta* and *Parastromateus niger*. These fish were thus found to have maximum

Table-1: Trace metal concentrations(μg/g, wet.wt.) in the muscle of various species from the Arabian Sea.

Species n (Sites)	Level	Wt. (g)	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg	Na	K	Ca	Mg
Pampus argenteus	X	105	0.050	1.653	0.047	0.347	0.322	3.414	0.187	0.103	0.036	0.512	0.083	207	187	124	152
25 (S1,S3,S4,S5,S6)	±SD	20	0.031	0.435	0.029	0.098	0.180	0.713	0.073	0.035	0.019	0.138	0.037	51	41	27	33
Dussumieria acuta	X	120	0.559	1.433	0.145	0.218	0.291	5.908	0.189	0.321	0.021	6.803	0.029	333	132	369	490
21 (S1,S2,S3,S4,S5,S6)	±SD	25	0.201	0.371	0.069	0.112	0.108	0.689	0.069	0.084	0.013	1.612	0.012	49	24	53	110
Gazza minuta	X	135	0.163	1.124	0.144	0.116	0.299	4.813	0.084	0.368	0.204	3.633	0.391	140	343	702	635
23(S1,S3,S4,S5,S6)	±SD	29	0.062	0.327	0.133	0.052	0.086	0.887	0.043	0.063	0.104	0.819	0.093	33	43	193	130
Lepturocanthus savala	X	140	0.021	3.173	0.024	0.318	0.147	5.208	0.081	0.565	0.658	2.412	0.136	212	623	396	515
28 (S1, S3, S4,S5)	±SD	30	0.016	0.932	0.010	0.084	0.063	1.081	0.033	0.123	0.283	0.631	0.079	42	129	37	129
Parastromateus niger	X	110	0.223	0.483	0.121	0.095	0.059	4.611	0.095	1.215	0.141	10.201	0.746	457	274	450	268
26 (S1, S2, S4,S5)	±SD	29	0.098	0.135	0.053	0.033	0.030	1.013	0.047	0.418	0.052	2.010	0.234	37	102	99	78
Pseudorhombus arsius	X	107	0.034	7.317	0.050	0.590	0.181	1.134	0.264	1.891	0.640	1.432	0.372	124	185	486	167
20 (S1, S2, S4, S5, S6)	±SD	27	0.021	1.013	0.027	0.139	0.048	0.310	0.099	0.719	0.260	0.313	0.131	39	85	91	66

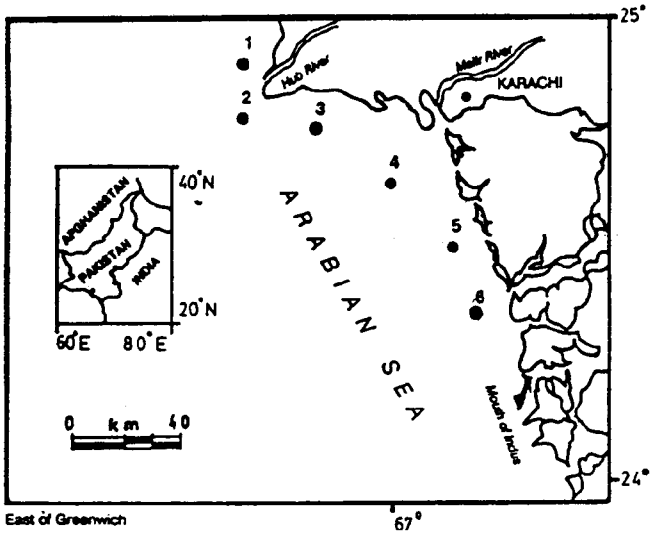

Fig. 1: Location of the sampling sites

bioaccumulation and uptake of the relevant metals and were significantly different from other species belonging to the same habitat but exhibiting distinctly different metal levels.

The individual variability of fish in relation to the maximum levels of various metals was quite revealing also. *Parastromateus niger* was found to contain minimum As (0.483 μg/g), Cr(0.095 μg/g) and Cu (0.059 μg/g) levels in its muscle. On the same lines *Lepturocanthus savala* was found to be identical to *Parastromateus niger* in relation of Ag, Cd and Mn contents which were present at the lowest levels in this fish. The maximum and minimum concentration levels in the muscle of these fish were not found to be dependent upon age (weight) and other variables, such as water quality, seasonal variations, diet, temperature, salinity, etc., since the sampling was conducted keeping all these parameters as constant.

The macronutrient data in Table-1 again revealed divergent levels of Na, K, Ca and Mg in the muscle of various fish. *Parastromateus niger* was found to contain maximum Na and *Lepturocanthus savala* maximum K, respectively at 457 and 623 μg/g. *Gazza minuta* was found to contain maximum levels of Ca and Mg at 702 and 635 μg/g, respectively. The study thus revealed that *Parastromateus niger, Lepturocanthus savala* and *Gazza minuta* were quite rich in nutritional levels of these macronutrients and may meet the required dietary allowance of the consumers. In addition, the data on macronutrients did not show relationship for trace metals. According, the macronutrients exhibited their own variability and specificity in the fish investigated.

Of all the metals investigated the maximum average concentration found in various fish species was higher for industrial metals such as As, Cd,

Table-2: Comparative enhancement of metal levels in Pampus argenteus over the past six years

Trace metal Concentrations**	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
Present work (X)	0.050	1.653	0.047	0.347	0.322	3.414	0.187	0.103	0.036	0.512	0.083
Earlier work* (X)	ND	0.680	0.036	0.086	0.211	2.061	0.047	0.073	0.031	0.383	0.072
Enhancement ratio	–	2.430	1.305	4.034	1.526	1.693	3.978	1.410	1.161	1.337	1.153

* reference [7], **µg/g, wet weight

Cr, Cu, Fe, Ni, Zn and Hg. The obvious reason for the contamination of the local fish with these toxic trace metals is the unregulated municipal waste and the industrial effluents that are being dumped into the sea continuously through its tributary rivers and streams. The situation has worsen over the past few years. This is indicated by the trace metal data of *Pampus argenteus* (Table-2) that provide a ready reference for comparison of the relevant metals in the same fish over a period of six years. Accordingly, an increase has been observed in the average levels of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn and Hg, the only exception being that of Ag which was not previously reported in our work [7]. This comparison reveals an overall increase in the concentrations of the metals in this fish with enhancement ratios given in Table-2. Accordingly, the maximum enhancement ratios (defined as the ratio of average concentration of metal based on the present and previous work) are found to be maximum for Cr and Mn followed by As. Nickel concentration has increased by about a factor of 1.4 and Zn and Cd concentration by a factor of 1.3, while Cu by a factor of 1.5. The overall pattern of increasing concentrations is Hg < Pb < Cd < Zn < Ni < Cu < Fe < As < Mn < Cr. As a result, the study revealed a gross pollution of the coastal waters of Pakistan with respect to As, Cr, Cu, Fe and Mn, all of which have industrial origin.

Unfortunately, data on the distribution of these metals in commercial fish included in the present study are only scarcely available and that too under different environmental conditions. Hence, a direct comparison was not possible. Some earlier work pertaining to *Pampus argenteus* from the Indian Ocean reported the levels of As, Cd, Fe, Ni and Zn as greater than 2 µg/g, 0.043 µg/g, 0.069 µg/g, 0.075 µg/g and 0.011 µg/g respectively [8]. It may be seen with reference to Table-2 that the present levels of As, Cd, Fe, Ni and Zn are higher than these reported levels, indicating that the Arabian Sea coastal waters are currently under a great pollution stress for which appropriate planning for control is the requirement of the day. The municipal and industrial source of metal pollution require immediate control so that the human health exposure via fish used as a food is minimized in future.

Experimental

The 143 fish samples pertaining to six species were harvested from 6 sites (S1 to S6, Fig. 1) along the south-west coast of the Arabian Sea, Pakistan, through the help of local fishermen during September-March, 1993. The sites selection was based on our previous work conducted during the same period in 1987. The number of samples from each site ranged between 20-28 as per availability, within a narrow weight range of 100-140 g. The muscle of each fish sample was dissected, briefly washed with deionized water, dried in folds of filter paper, packed in strong polythene bage and kept at -10°C until analyzed. The muscle sample was digested using the nitric acid based wet oxidation procedure [7]. The concentrations of trace metals (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and macronutrients (Na, K, Ca and Mg) were estimated using Shimadzu atomic absorption spectrophotometer (Model AA-670) operating in the background compensation mode. Arsenic was estimated by the hydride generation method of Santa Maria [9], whereas Hg was estimated by the cold vapour techniques of Hatch and Ott [10]. All reagents used were of spectroscopic grade and guaranteed purity. Subsamples of each fish from each site were subjected to triplicate runs and the results of each species were averaged. Standard FAO fish samples [11] were run in parallel to check the accuracy of the results by inter-laboratory comparisons carried out at the National Institute of Health.

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References

1. H. Nishida and M. Miyai, *Bull. Environ. Contam. Toxicol.*, **32**, 212 (1984).
2. M. Sadiq, T.H. Zaidi, A. Huda and A.A. Mian, *Bull. Environ. Cotam. Toxicol.*, **29**, 312 (1982).
3. W.H. Benson, P.C. Francis, W.J. Brige and J.A. Black, *Atomic Spectroscopy*, **4**, 212 (1983).
4. C.J. Cappon, *Bull. Environ. Contam. Toxicol.*, **38**, 695 (1987).
5. M. Jaffar and M. Ashraf, *Fisheries Res.*, **7**, 11 (1989).
6. M. Ashraf and M. Jaffar, *Fisheries Res.*, **8**, 287 (1990).
7. M. Ashraf and M. Jaffar, *Toxicol. & Environ. Chem.*, **19**, 63 (1989).
8. J.B. Khot, A.T. Sherikar and H.V. Karale, Pesticides (India), January, 21 (1984).
9. I. Santa Maria, M. Gonzelez, W. Lara and A. Ober., *Bull. Environ. Contam. Toxicol.*, **37**, 852 (1984).
10. W.R. Hatch and W. L. Ott, *Anal. Chem.*, **40**, 2085 (1968).
11. F.A.O. Food contamination study and control in Asia and Far-east, Project RAS/078/NOR, FAO, Islamabad (1986).