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Heavy Metals Levels in Sediment and Ray Fish (*Dasyatis bennettii*) from Musa Estuary and Selech Estuary, Persian Gulf

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Abstract: Heavy metals concentration in sediment and Ray fish, *Dasyatis bennettii* from four stations in two estuaries in the north Persian Gulf was determined using a flame atomic absorption spectrometer (AAS). This benthic species was selected in order to determine its ability to be as a bioindicator for the metals. The concentrations of Cd, Co, Cu, Ni and Fe in the sediment were apparently different among stations. Furthermore, the accumulation of all the metals in the liver was significantly higher than the muscle tissue. Liner regression analyze showed that there was significant correlation ($p<0.05$) between Ni concentration in sediment and liver tissue while there was no significant relationship between the concentration of Cd, Co, Cu and Fe in sediment and tissues. According to NOAA and ROPME, heavy metals concentration in sediment was markedly below the permissible level, with exception for Ni metal.

Key words: *Dasyatis bennettii* · Sediment · Bioindicator · Heavy metals · Ray fish

INTRODUCTION

Contamination of marine environment with heavy metals has been receiving increased attention during last decades, due to their resistant to decompose in the environment, toxicity and transference through food chains [1, 2]. Sediment is known to act as a sink for heavy metal in aquatic systems [3]. Thus, benthic fishes occupy an important situation in marine pollution studies particularly in terms of sediment contamination [4].

The Persian Gulf is one of the most oil-contaminated seas, which receive vast amount of contamination from surrounding areas [5]. Supertankers traffic, industrial effluents, domestic waste and agricultural runoffs contribute to metals contamination in the area. On the other hand, because of having various coastal zones and different ecological conditions, this sea is occupied by various species of marine organisms. In addition, the turnover and flushing time, which takes place every 3-5 years, could hold the pollution in the area for a considerable time. Therefore, the aim of this study is to assess the concentration of Cd, Cu, Co, Fe and Ni in sediment and *Dasyatis bennettii* that was taken from two estuaries of the northwest Persian Gulf. This benthic species was selected for its abundance across the northwestern part of the Gulf and its association to sediment.

MATERIALS AND METHODS

Fish and sediment sampling was done at four stations from the northwest Persian Gulf in July 2010 (Fig. 1). The samples were brought to the laboratory of Khoramshahr Marine Science and Technology on the same day and then frozen at -20°C until dissection.

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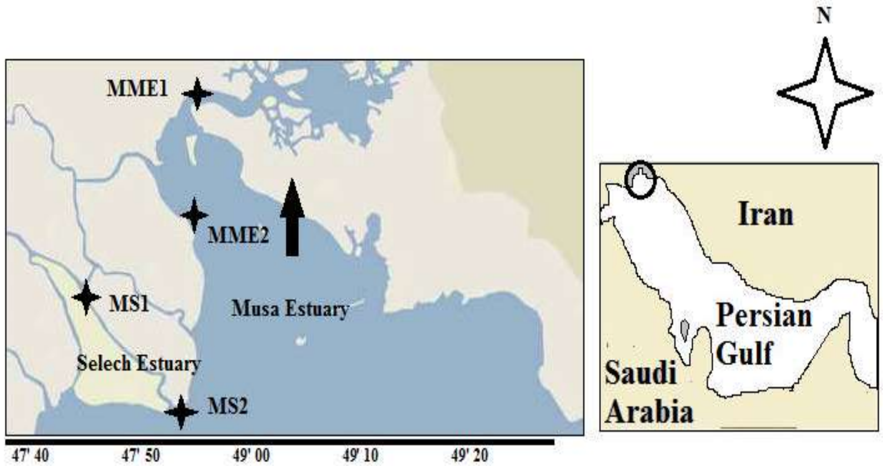

Fig. 1: Map showing Sampling Stations

For analysis, the complete liver and sufficient amount of the muscle of *D. bennettii* were dissected and put into an oven to reach constant weights. The tissues were digested with strong acid nitric (8 ml) and perchloric acid (4 ml) on a hot plate set to 120°C. Sediment samples were oven dried, passed through a 63-μm mesh stainless screen and digested with mixture of acid nitric and perchloric acid in the ratio of 3:1. The digested samples were diluted to 25 ml with distilled water.

A fully computer-controlled flame atomic absorption spectrometer (SavantAA Sigma; GBC Scientific Equipment Ltd., Dandenong, Australia) with a deuterium background corrector was used for metal ion determination. Cd, Cu, Co, Fe and Ni hollow cathode lamps (Photron) were used as radiation sources at their respective wavelengths (resonance lines) throughout the measurements. An air-acetylene flame was used for the determination of the metals ions by FAAS. The instrument settings used were as recommended by the manufacturer.

Accuracy of the used method and the AAS were tested by standard reference material DORM 2 (National Research Council of Canada: dogfish muscle) for Ray fish and SRM 1645 (National Bureau of Standards) for sediment. Used CRM showed a good agreement with recovery rates of metals between 82% and 110% for sediment and between 85% and 108% for fish. All chemical reagents were analytical reagent grade (Merk, Germany).

The glassware and plastic containers were soaked in nitric acid solution and washed with double distilled water before use. In order to avoid any samples contamination blank samples were digested and analysed in a similar manner without samples.

One-way ANOVA and Duncan multiple comparison test were applied in order to determine the difference between stations. To compare the metals concentration between tissues, t-test analyze was performed. Pearson correlation coefficients were used to examine the relationship between sediment and *D. bennettii* tissues. The level of significance was set at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Heavy Metals in Sediment: Heavy metals concentration in the sediment collected from the northwest Persian Gulf are represented in Table 1. The comparison between stations showed that, there is no significant difference in Co concentration in sediment among stations. The highest concentration of Cd, Cu and Ni was found in the sediment of MME1 (Mouth of Musa Estuary) while the maximum concentration of Pb was found in the sediment of MME2. Table 1 also shows the comparison of our results with NOAA sediment quality guidelines and Regional Organization for the Protection of The Marine Environment (ROPME).

Comparison the metals concentration in the sediment with ISQG, ERL, ERM, REL and PEL values showed that the level of Cd in MME1 and MME2 was higher than ISQG guideline. Besides, the concentration of Cu in MME1 was higher than the ISQG and ERL values. In addition, the concentration of all the metals was lower than those in ROPME, with exception for Ni element.

The observed variation in the metals concentration could be due to difference in physicochemical factors among stations (pH, DO, temperature, salinity and redox condition) [6], variation in the sources of the metals and geochemical properties of the sediment [7]. In general,

Table 1: Heavy metal concentration (µg/g d.w) in sediment taken from the northwest Persian Gulf and compared to guidelines.

Stations	Cd	Co	Cu	Ni	Fe	Reference
MME 1	0.98 ± 0.01[d]	7.97 ± 1.2	23.16 ± 1.2[b]	24.65 ± 2.08[b]	2.4 ± 0.29[ab]	This study
MME 2	0.86 ± 0.02[c]	7.05 ± 1.17	17.43 ± 2.5[ab]	23.87 ± 1.51[b]	2.8 ± 0.41[b]	This study
MS 1	0.33 ± 0.02[a]	6.55 ± 0.5	13.25 ± 1.29[a]	18.51 ± 0.37[a]	1.48 ± 0.46[a]	This study
MS 2	0.45 ± 0.04[b]	4.87 ± 2	14.57 ± 2.07[a]	17.81 ± 1.65[a]	2.13 ± 0.38[ab]	This study
ROPME (1999)	1.2-2		70-80	15-30		[14]
ISQG	0.7	18.7	15.9	30.2	124	[8, 15]
ERL (NOAA)	1.2	34	21	47	150	[8, 15]
PEL (NOAA)	4.21	108.2	42.8	112.2	271	[8, 15]
ERM (NOAA)	9.6	270	52	218	410	[8, 15]
PEC (NOAA)	5	149		128	459	[15]

[a,b,c,d] show significant differences of metals concentration between stations. ISQG= interim marine sediment quality guideline. PEL= probable effects levels. ERL= effects range low. ERM= effects range medium. PEC= probable effect concentration. MME = Mouth of Musa Estuary, MS = Mouth of Selech Estuary.

Table 2: Heavy metals concentration (µg/g d.w) in *D. bennettii* taken from the northwest Persian Gulf.

Tissues	Station	Cd	Co	Cu	Ni	Fe
Muscle	MME 1	0.45 ± 0.08	3.2 ± 0.58	8.5 ± 1.97	2.09 ± 0.85	1.32 ± 0.74
	MME 2	0.42 ± 0.07	3.8 ± 0.65	9.42 ± 2.38	1.86 ± 0.67	1.04 ± 0.31
	MS 1	0.24 ± 0.04	1.43 ± 0.21	6.08 ± 2.63	2.79 ± 0.72	1.48 ± 0.4
	MS 2	0.18 ± 0.06	1.16 ± 0.62	6.33 ± 1.83	1.96 ± 0.46	1.07 ± 0.3
Liver	MME 1	1.04 ± 0.15	14.28 ± 2.37	49.47 ± 5.82	35.61 ± 4.53	28.93 ± 3.52
	MME 2	1 ± 0.13	10.04 ± 2.44	38.42 ± 4.73	31.06 ± 3.82	24.26 ± 3.88
	MS 1	0.94 ± 0.08	7.04 ± 1.42	37.04 ± 7.14	57.62 ± 6.18	25.34 ± 3.04
	MS 2	0.64 ± 0.15	6.38 ± 1.16	32 ± 4.57	58.35 ± 7.65	23.76 ± 4.53

MME = Mouth of Musa Estuary, MS = Mouth of Khor-Selech.

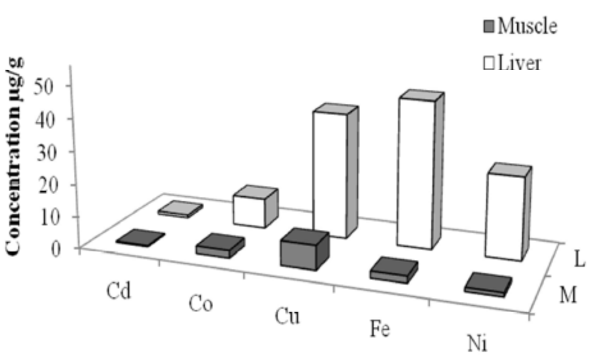

Fig. 2: Comparison of metals concentration between muscle and liver of D. bennettii.

the sediment collected from MME1 has the highest level of all the metals. Moving toward Khor-Selech, the metals level progressively decreases, reaching the lower values in MS2 site. The observed metal enrichment in MME1 could be attributed to metal contamination in Musa Estuary. Due to this estuary are served as a water way for supertankers and ships traffic as well as receives enormous amount of petrochemical wastewaters, agricultural runoff and urban effluent [8, 9]. High Nickel content in the stations may be related to oil pollution in the area. Because the Persian Gulf has been suffering from oil pollution that resulted from oil terminals, offshore oil exploration and oil refineries more than any other semi-enclosed sea in the world [5].

Heavy Metals in Fish: Results obtained by analysis of fish from different stations are presented in Table 2. The comparison showed that among the stations the fish at MME1 represented the higher level of all the heavy metals except for Ni element, which showed higher concentration at MS2. Amongst various tissues, the liver accumulated significantly higher concentration of all the elements (Fig. 2). The higher level of the metals in fish taken from MME1 relative to fish from other stations could be related to Musa Estuary-originated metals.

According to other studies, liver have a striking efficiency to accumulate and storage heavy metals from surrounding area [10, 11, 12]. This enormous capacity in accumulation could be brought about from its role in the detoxification activity [10, 13]. Furthermore, metallothionein, a metal-binding protein, are found in high level in liver tissue compared to other tissues like muscle [1].

Relationship Between Metal Contents in Sediment and Tissues: The correlation between the metals in sediment and fish tissues was tested. A highly significant relationship was found for Ni ($r=0.96$, $p<0.05$) element between sediment and liver tissue, while no significant relationship was found between sediment and muscle as well as the other elements in liver. *D. bennettii* is a benthic species and feeding on benthic organisms, hence, we can argue that Ni metal in the liver of this fish can be applied for monitoring the heavy metals contamination in the area.

CONCLUSION

The result of current study supply valuable information on the heavy metals concentration in sediment and Ray fish from the northwest Persian Gulf. This study indicated that despite being benthic and completely sediment-associated species, *D. bennettii* could not be a good bioindicator for the metals in its habitat sediment, with exception for Ni metal. Comparison the obtained data with guidelines showed that the metals concentration in the sediment is below the permissible level defined by NOAA and ROPME, except for Ni element.

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