



## Evaluation of trace metal concentrations in Water, Sediment, Edible crab and Prawn from Fishing harbor of Tuticorin

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### Abstract

A study was conducted to determine the level of Cd, Cu, Cr, Pb and Zn in seawater, sea sediment, edible crab (*Portunus sanguinolentus*) and edible prawn (*Penaeus merguensis*) collected from Tuticorin fish landing center (Thirespuram), south India during premonsoon and monsoon 2014. These metal concentrations were measured by Atomic Absorption Spectrometer (AAS) in order to assess the influence of trace metals in prawn/ crab with nexus on seawater and sediment samples. In prawn, the accumulated mean metal concentrations such as Cd, Cr, Cu, Fe, Ne Pb and Zn were 0.25, 0.12, 0.48, 2.91, 0.52, 0.16 and 0.82 mg l<sup>-1</sup> (premonsoon) while in the monsoon season, mean Cd, Cr, Cu, Fe, Ne Pb and Zn concentrations were 0.34, 0.11, 0.60, 3.25, 0.14, 0.11 and 1.15 mg kg<sup>-1</sup> respectively. In this study, the level of all metal concentrations was high in monsoon season than premonsoon season, except Cr, Ni and Pb. In the crab at premonsoon, the mean metal concentrations such as Cd, Cr, Cu, Fe, Ne Pb and Zn were 0.28, 0.20, 0.51, 3.45, 0.12, 0.22, and 1.52 mg l<sup>-1</sup> while in the monsoon season, mean Cd, Cr, Cu, Fe, Ne Pb and Zn concentrations were 0.31, 0.21, 0.56, 4.12, 0.15, 0.14 and 1.35 mg kg<sup>-1</sup> respectively. The metal accumulation in the living things were higher (2-10 folds) than the water samples. The higher trace metal was present in the sediment samples than the other groups and its decreased orders were: Sediment > Crab > Prawn > Water. Based on the results, metal concentrations in the edible crabs and prawns were not in the permissible levels for human consumption. The values of heavy metals in coastal waters were more than TNPCB prescribed level.

**Keywords:** *Portunus sanguinolentus*, *Penaeus merguensis*, Trace metals, Tuticorin, Biochemical constituents.

### Introduction

Environmental water pollution by heavy metals has increased in recent years due to agriculture, and chemical and industrial operations, presenting a severe threat to living beings. The trace metals such as copper, chromium, and iron being major pollutants from industrial wastewaters, agricultural and other waste in an aquatic environment. This leads to cause maximum effects on non-target aquatic organisms resulting in asymmetry of the ecosystem<sup>1</sup>. Heavy metals are inserted into the aqueous environment through industrial and urban effluents, soil leaching, and rain. Fishes occupy high level of xenobiotic/undestroyed compounds in the aquatic environment. Now a day, trace metals in aquatic ecosystems showed higher levels than the accepted levels. Extensive use of various chemical contaminants is known to adversely affect the growth of various organisms<sup>2</sup>. The perniciousness of such chemical compounds in invertebrates is mainly reflected in the cardinal neural scheme and it also affects other physiological processes, including breathing. The bioaccumulation pattern can alter the biochemical changes in the host metabolism. Whatever alteration in the oxygen consumption due to pollution, stress creates a physiological imbalance in the organisms.

Heavy metal is particularly hazardous contaminants in food and

the surroundings. In universal, they are not destroyed and have long biological half-lives. According to the World Health Organization<sup>3</sup> heavy metals must be contained in food sources in order to ensure public safety. Excessive absorption of food heavy metals is caused some of the cardiovascular, renal, neurological, and bone diseases<sup>4</sup>. The monitoring of toxic metals levels in foods is an important one to avoid the bio-magnification. The shrimp and crab may provide useful means of monitoring such elemental concentration levels and their impact on the aquatic environment. Al-Mohanna and Subrahmanyam<sup>5</sup> demonstrated Zn and Cu pollution swimmer crabs and attributed this to the 1991 Gulf War oil spill into Kuwait's marine environment. To the extent of the author's knowledge, few studies reported heavy metals contamination of shrimp and fish in the Persian Gulf water of Iran<sup>6</sup>.

The objectives of this research were: i. To study the concentration of trace metal levels in sea water, sediment and edible prawn and edible crab from Tuticorin coastal region in premonsoon and monsoon seasons; ii. To assess the biochemical constituents of edible prawn and edible crab in the contaminated site; iii. To study weather trace metal affects the biochemical and physiological nature of crab and prawns. Data received from this work should offer insight for using sea foods to remediate metal contaminated sites and also the impacts of trace metals on the ecosystems.

## Material and Methods

**Sampling and processing:** The seawater, sediment, edible crab (*Portunus sanguinolentus*) and edible prawn (*Penaeus merguensis*) samples were collected from Tuticorin coast of southern India in premonsoon and monsoon 2013. The two sampling stations were choosed for its severe anthropogenic impacts on coastal regions. The 2000 ml of sea water samples were collected with a 2500 ml sterile container and 250 g of surface sediment samples were collected with a sterile spatula. All samples were kept in ice boxes and transported to the lab at once. For heavy metal analysis, the one liter of ocean water was acidified immediately with concentrated nitric acid (HNO<sub>3</sub>). For trace metal stud, acidified seawater samples were filtered by Whatman No.1 filter paper and processed (APDC + MIBK) for metal analysis. Sea sediment samples were air-dried and smaller than (>) 63 µm in size were kept back in pre-cleaned properly. Thenceforth, the dried sediment and crab/ prawn samples were crushed by agate mortar and pestle. Both the samples were processed with an aqua - regia mixture (i.e. HCl: HNO<sub>3</sub>= 3:1) in Teflon bomb and were incubated at 140 °C for 2-3 days after dried and sieved samples. After incubation, the reaction mixture was filtered with Whatman No.1 filter paper. The trace metals in the sea water, sea sediment and crab samples were determined by the atomic absorption spectrophotometry (GBC SensAA - AAS, Australia) in flame mode.

Total lipids of triplicate samples of each finely ground meat samples were extracted using chloroform: methanol (2:1, v/v)<sup>7</sup>. The carbohydrate of the samples was analyzed by standard method<sup>8</sup>. Protein in the samples was determined by the standard method<sup>9</sup> and comparison to bovine serum albumin as a standard [dye-binding, using concentrated Coomassie Brilliant Blue (G-250)], which can be quantified 595 nm in UV-vis spectrophotometer. The CAT activity was determined by use of the standard method<sup>10</sup> (10 µl of sample; 3.0 ml of H<sub>2</sub>O<sub>2</sub> phosphate buffer; H<sub>2</sub>O<sub>2</sub>) and was measured at 250 nm with an UV-vis spectrophotometer. The GSH levels were measured by the standard method<sup>11</sup> (0.5 ml tissue supernatant; 4.5 ml of the phosphate-EDTA buffer; pH 8.0; OPT (*O*-phthalaldehyde) solution) and was measured at 350 nm with an UV-vis spectrophotometer. GSH concentration was calculated from a standard curve and reported as µmol GSH/mg protein.

## Results and Discussion

During the premonsoon 2014, the concentration of Cd in seawater and sea sediment level was 0.18 mg l<sup>-1</sup> and 0.62 mg kg<sup>-1</sup> respectively. But in monsoon, the levels were 0.23 mg l<sup>-1</sup> and 0.87 mg kg<sup>-1</sup> respectively. The sea sediment of premonsoon season, concentration of Cr was 0.27 mg kg<sup>-1</sup> while in saltwater, the mean Cr concentration was 0.11 mg l<sup>-1</sup>. The mean Cu concentrations in the premonsoon of water and sediment were 0.38 mg l<sup>-1</sup> and 0.74 mg kg<sup>-1</sup> respectively. In monsoon, Cu levels in water and sediment samples were 0.41 mg l<sup>-1</sup> and 1.48 mg kg<sup>-1</sup> respectively. The average Ni concentration in a premonsoon

season of water and sediment was 0.06 mg l<sup>-1</sup> and 0.16 mg kg<sup>-1</sup>, respectively. In monsoon, the seawater and sediment levels were 0.10 mg l<sup>-1</sup> and 0.42 mg kg<sup>-1</sup>, respectively (table-1). The sea sediment of premonsoon season, concentration of Fe was 6.48 mg kg<sup>-1</sup> while in saltwater, the mean Fe concentration was 1.54 mg l<sup>-1</sup>. But in monsoon season, the level of Fe content was higher than premonsoon season due to the heavy rainfall<sup>12</sup>. In sea water at premonsoon, Pb concentrations were 0.15 mg l<sup>-1</sup> while in sea sediment average level was 0.20 mg kg<sup>-1</sup>. But in monsoon season, the level of Pb was 0.15 mg l<sup>-1</sup> at seawater whereas the level of Pb in sea sediment was 0.49 mg kg<sup>-1</sup>. In premonsoon, Zn levels in water and sediment samples were 0.58 mg l<sup>-1</sup> and 3.15 mg kg<sup>-1</sup>, respectively while in monsoon the Fe levels at water and sediment samples were 0.84 mg l<sup>-1</sup> and 5.24 mg kg<sup>-1</sup>, respectively. The values of heavy metals in coastal waters were crossing the TNPCB prescribed level<sup>13</sup>. Interestingly, all the metal content was higher in sea sediment samples than the sea water samples in order to the flocculation process<sup>14</sup> of living and non-living things nexus on wet surfaces and other environmental agents such as microbial flora and fauna<sup>15,16</sup>.

In this study, the famed edible prawn and crab such as *Penaeus merguensis* and *Portunus sanguinolentus* were processed for study their protein, lipid, carbohydrate and antioxidant (Catalase and Glutathione) contents, respectively (table-2). The metal contents were high in sea crab (*Portunus sanguinolentus*) than sea prawn (*Penaeus merguensis*). Among seafood, shrimps contribute about 20% by volume of the world seafood market. They have great importance in food consumed by human and other organisms. They are valuable in the diet, because aside from supply of good quality proteins and vitamins, they also contain several dietary minerals such as calcium, iron etc. These are beneficial to human and other organisms; these minerals play an important part in preserving the survival of organisms in a sound and normal metabolism. In the prawn at premonsoon, the average concentrations of carbohydrate, protein, lipid, catalase and Glutathione were 7.8 µg/g, 131.22 µg/g, 32.45 µg/g, 22.36 µ Mol/mg and 0.41 µg Mol/mg while in the monsoon season, mean carbohydrate, protein, lipid, catalase and Glutathione were 24.56 µg/g, 134.98 µg/g, 35.64 µg/g, 24.16 µ Mol/mg and 0.64 µg Mol/mg respectively. But the biochemical constituents in crab sample were lower than prawn samples in both seasons.

The accumulation trace metal levels in prawn are follows. In the premonsoon, the mean metal concentrations such as Cd, Cr, Cu, Fe, Ne Pb and Zn were 0.25, 0.12, 0.48, 2.91, 0.52, 0.16 and 0.82 mg l<sup>-1</sup> while in the monsoon season, mean Cd, Cr, Cu, Fe, Ne Pb and Zn concentrations were 0.34, 0.11, 0.60, 3.25, 0.14, 0.11 and 1.15 mg kg<sup>-1</sup>, respectively. In this study, the level of all metal concentration is high in monsoon season than premonsoon season, except Cr, Ni and Pb. Edible crustaceans, such as crab, prawn, crayfish and lobster constitute one of the major sources of nutritious food for human beings. The nutrient values of crustaceans/ prawns depend upon their biochemical

composition, such as protein, amino acids, lipid, fatty acids, carbohydrate, vitamins and minerals. In the sea crabs at premonsoon, the mean metal concentrations such as Cd, Cr, Cu, Fe, Ne Pb and Zn were 0.28, 0.20, 0.51, 3.45, 0.12, 0.22, and 1.52 mg l<sup>-1</sup> while in the monsoon season, mean Cd, Cr, Cu, Fe, Ne Pb and Zn concentrations were 0.31, 0.21, 0.56, 4.12, 0.15, 0.14 and 1.35 mg kg<sup>-1</sup>, respectively. The routine monitoring of toxic metals in foods is an important phenomenon to find the contamination of the general environment.

reduced while increasing the level of trace metals. It indicated that the trace metals affect the biochemical and physiological nature of prawn and crab. The crab samples contain high level of trace metals than the prawn samples. Based on this investigation, we concluded that this location is highly vulnerable and received massive amount of sewage, agricultural, industrial, ship activities and other waste materials. It requires further investigation to monitor the contamination levels.

## Conclusion

In this study, the level of all metal concentration was high in monsoon season than premonsoon season. The protein, carbohydrate, lipid and other antioxidant levels were gradually

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Table-1

Trace metal concentrations in sea water, sediment, prawn and crab samples of Tuticorin coast premonsoon and monsoon seasons

Sample Type	Sample Name	Trace metal concentrations (Water - mg/L) (Sediment/Prawn tissue - g/kg or µg/g)													
		Tuticorin													
		Premonsoon							Monsoon						
		Cd	Cr	Cu	Fe	Ni	Pb	Zn	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Water	Seawater	0.18	0.11	0.38	1.54	0.06	0.15	0.58	0.23	0.15	0.41	1.92	0.10	0.15	0.84
Sediment	Sea sediment	0.62	0.27	0.74	6.48	0.16	0.20	3.15	0.87	0.35	1.48	10.25	0.42	0.49	5.24
Crab	<i>Portunus sanguinolentus</i>	0.28	0.20	0.51	3.45	0.12	0.22	1.52	0.31	0.21	0.56	4.12	0.15	0.14	1.35
Prawn	<i>Penaeus merguensis</i>	0.25	0.12	0.48	2.91	0.52	0.16	0.82	0.34	0.11	0.60	3.25	0.14	0.11	1.15

Table-2

Biochemical constituents in prawn and crab samples of Tuticorin coast premonsoon and monsoon seasons

Sample Type	Sample Name	Biochemical constituents (Carbohydrates, Protein, Lipid = g/kg or µg/g) (Catalase, Glutathione = µ mol / mg protein)									
		Tuticorin									
		Premonsoon					Monsoon				
		CHO	PRO	LIP	CAT	GSH	CHO	PRO	LIP	CAT	GSH
Crab	<i>Portunus sanguinolentus</i>	21.54	131.22	32.45	22.36	0.41	24.56	134.98	35.64	24.16	0.64
Prawn	<i>Penaeus merguensis</i>	7.8	72.4	7.45	8.32	0.18	6.12	71.24	10.62	10.22	0.26

CHO – Carbohydrates; PRO – Proteins; LIP – Lipids, CAT – Catalase; GSH – Glutathione.

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