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Heavy Metals in the Shrimp *Xiphopenaeus kroyeri* (Heller, 1862) (Crustacea, Penaeidae) from Ubatuba Bay, Sâo Paulo, Brazil

F. L. M. Mantelatto,[1] W. E. P. Avelar,[1] D. M. L. Silva,[1] A. C. Tomazelli,[1] J. L. C. Lopez,[2] T. Shuhama[2]

[1] Department of Biology, Faculty of Philosophy, Sciences and Letters of Ribeirão Preto, University of São Paulo (USP), Av. Bandeirantes - 3900, 14040-901, Ribeirão Preto (SP), Brazil
[2] Department of Physics and Chemistry, Faculty of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo (USP), Av. Bandeirantes - 3900, 14040-901, Ribeirão Preto (SP), Brazil

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The significant trace metal concentrations in decapod crustaceans analyses have been made of a range of specimens from temperate coastal waters and from temperate and tropical oceanic waters (see Rainbow 1986 to review this aspects). Ubatuba Bay (23° 26' S and 45° 02' W) is located adjacent to the town of Ubatuba, State of São Paulo northern coastline, Brazil. The total area of the bay is about 8 km^2, with a width of about 4.5 km at the entrance and diminishing landward. Four small rivers flow into this bay (Indaiá River, Grande River, Lagoa River and Acaraú River), which probably supply organic matter, industrial effluents mainly from naval construction and canned fish industries. Among the northern coastline, Ubatuba Bay is important, because its location near the tourist center of Ubatuba, its fishing potential, and because it is considered as a paradigmatic preservation area, althought the biological monitoring of the Ubatuba region is important in view of the significant anthropogenic activity of the last 10 years which has led to consequent progressive deterioration of the marine coastal ecosystem. This slightly altered natural condition will permit to use this bay as a standard for comparison with other areas in Brazil strongly influenced by anthropogenic impact (Mantelatto and Fransozo *in press*).

The shrimp *Xiphopenaeus kroyeri* (Heller, 1862) is popularly known as “camarão sete barbas”, is the most important commercial crustacean of the benthic megafauna from the northern coast of São Paulo State, because principally these shrimp are destined for human consumption. The objective of the present study was to provide information on the seasonal concentration of Cd, Cr, Pb, Cu and Zn in whole of the shrimp *X. kroyeri* from the Ubatuba Bay. Additionally, the relationships between seasonal heavy metal concentration and body weight of male and female individuals were examined. These data are important as a background for the estimation of the future impact of metal pollutants in this area.

MATERIALS AND METHODS

Specimens of *X. kroyeri* were collected at three sites along the Ubatuba Bay, at a depth 4-17 m, quarterly between January and December 1995 (Figure 1). The shrimp were collected with a fishing boat equipped with an double-rig net.

Correspondence to: F. L. M. Mantelatto

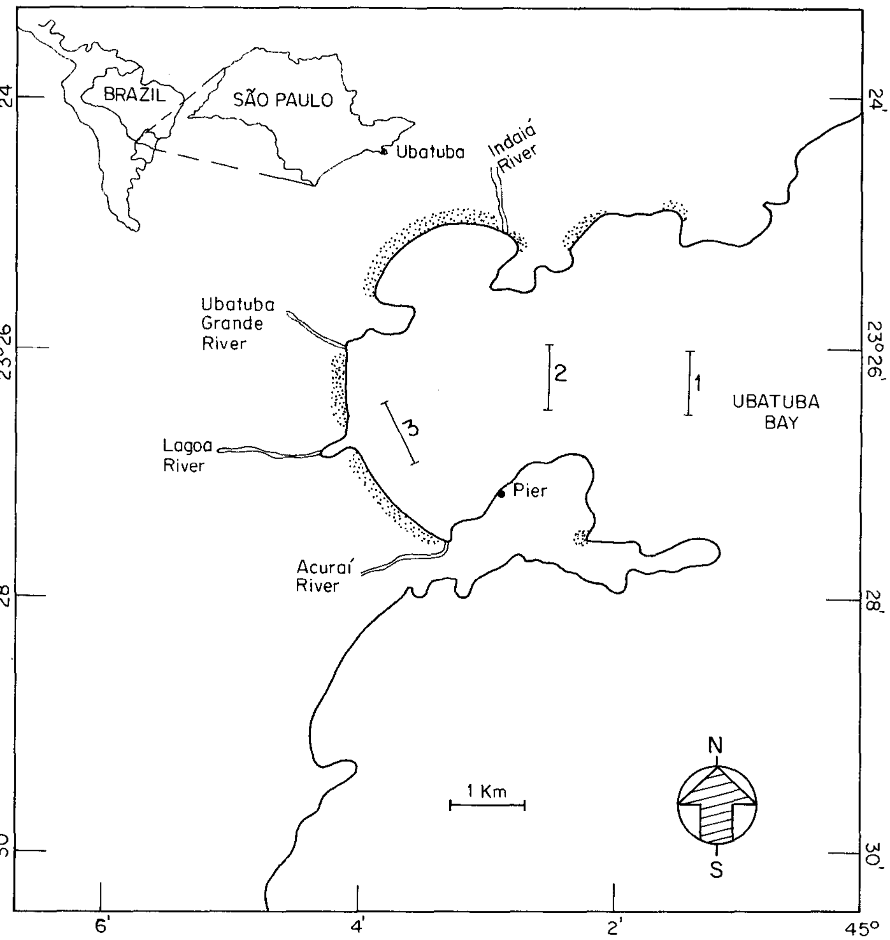

Figure. 1. Collection sites along Ubatuba Bay, Ubatuba (SP), Brazil. The numbers indicate the sampling areas.

Immediately after collection, the shrimp were stored on ice in an insulated box, carried to the laboratory within 3 h of collection and bagged and stored frozen at -15 °C until required for analysis.

While choosing shrimp for the preparation of composite samples, emphasis was placed on organisms of nearly equal length (between 10 - 30 mm). The cephalothoracic length (CL) was measured with a caliper (0,1 mm) in order to use mature organisms (based on morphologic maturity in according to Nakagaki 1994) and intermolt stage (based on carapace rigidity). Twenty-four specimens (twelve males and twelve females) per season were selected separately for analysis. The individuals were sexed by direct examination of morphological traits.

Each sample of entire specimens (including the exoskeleton) were prepared by digesting wet material with concentrated sulfuric acid (2 ml) and hydrogen peroxide (5 ml) at high temperature (> 100 °C). Procedural blanks were prepared with shrimps from another site (Grande Beach) without pollution. The metal concentrations were determined by flame atomic absorption spectrophotometry using a Shimadzu AA 680G apparatus. All glassware used for analysis was washed with sulphochromic solution and distilled water. All metal concentrations were obtained in absolute values and transformed to 1 g of dry weight and are expressed as µg/g. Replicates (twelve) were utilized to analysis of metals concentration.

Differences in heavy metal levels between seasons and sexes were compared by one-way ANOVA (Kruskal-Wallis one way analysis of variance). Linear regressions were used to determine weight-related variations in metal levels. The levels of significance were $P < 0,05$.

RESULTS AND DISCUSSION

The results show that metals behave in a similar way although their respective quantities were very different. The mean metal concentrations obtained for the entire males and females of *X. kroyeri* are shown in Table 1. Zinc, Cu and Pb were the most abundant elements in the different samples analyzed throughout the year, whereas Cd and Cr were the least abundant.

According to Rainbow (1988), Zn is taken up by shrimp at an increasing rate during exposure but the excess is eliminated by excretion. The concentration of Zn is about 50-120 µg/g dry weight. According to the same author, when the concentration of Zn exceeds 200 µg/g, shrimp like *Palaemon elegans* and crabs of the species *Carcinus maenas* (Linnaeus, 1758) die. In the present study, Zn concentrations ranged from 25 to 171 µg/g, and were therefore within the reported pattern. Such statements need to be supported with experimental evidence, because this species of shrimp may be more or less sensitive to zinc than the two species studied by Rainbow (1988). The high concentration of Zn is associated with the activity of nearly 100 enzymes involved in lipid, protein, carbohydrate and nucleic acid metabolism (Elinder 1986), in all organisms.

Copper was present at relatively high concentrations in the tissues, with only significant differences between males and females in the autumn and spring (Table 1). The high levels of this element can be due, in part to its high capacity of hemocyanin for binding Cu to a respiratory pigment present in large amounts in the gills of crustaceans (Páez-Osuna *et al.* 1995). The available evidence leads us to postulate that *X. kroyeri* males and females differ in their physiological requirements for this metal. The high concentrations detected in females were probably due to the greater development of their gonads in relation to males, during a phase characterized by an accelerated metabolic rate, with somatization of metal absorption. Gonads maturation in males and females of *X. kroyeri* at

Ubatuba Bay occurs during all seasons with a high incidence in summer, and involves the simultaneous increase of organic constituents and ovary mass (Nakagaki 1994). A similar pattern was described for *Pleoticus muelleri* (Bate 1888) studied in San Jorge Gulf, Argentina, by Jeckel *et al.* (1996), with copper concentrations tending to increase in the male gonad in parallel to increases of these trace metals in the digestive gland, indicating that their levels in the male reproductive system reflect, at least partly, their levels of intake. In accord to this same author, for the female gonad is the clearly defined changes in the concentrations of trace metals throughout oogenesis. There is evidence that the ability to regulate body concentrations of zinc and copper is a feature of decapod crustaceans, not extended to other crustacean taxa and no crustacean appears to regulate the body concentration of non-essential metals such as cadmium (Rainbow 1985). According to this author, the accumulation of increasing body concentrations of the metal as bioavailability increases, in association with the detoxification of accumulated zinc and copper.

Sex-based differences in trace metal concentrations may similarly be due also to differences in the preferred diets of males and females, through in *X. kroyeri* detailed information on diet is unknown. Differences in heavy metals concentration shrimp could occur because of the variation in growth rates between the sexes (Páez-Osuna and Ruiz-Fernández 1995). With the pattern of faster growth in females (Castro 1997), one would suspect this to infer smaller trace metal levels in females compared with males, if the metabolism and the metal quantities ingested were similar, how related to *Penaeus californiensis* Holmes by Páez-Osuna and Tron-Mayen (1995).

Páez-Osuna and Ruiz-Fernández (1995) reported this relationship, showing that Zn and Cu occurs at high concentrations in sexually mature individuals. In the present study the high levels of these metals detected in adult shrimp suggest a greater incorporation by the shrimp. The digestive gland plays an important role in the metabolism, storage and detoxification of many metals (Dal1 and Moriarty 1983). The levels of Cu and Zn in this gland may be also related to the molting cycle (Engel 1987), and to the gonadal cycle.

According to Jeckel *et al.* (1996), the physiological meaning of the increase or decrease in Zn, Cd and Cu concentrations for isolated tissues of shrimp is not clear, but the variations in these levels have been suggested to reflect effects of interaction between age, physiological conditions and availability of these metals in food and in the environment. A complicated relation exists between the total amounts of metals in tissues and the physiological state of the invertebrate, with variation between individual “physiotypes” discussed in the case of crustaceans (Rainbow 1996).

The concentrations of Cd found in whole individuals of *X. kroyeri* were higher than values reported in other crustaceans, e.g., in the Mexican shrimp *Penaeus vannamei* Boone (Páez-Osuna and Ruiz-Fernández, 1995). According to Páez-

Osuna and Tron-Mayen (1995), several authors have found that squids are characterized by elevated concentrations of Cd (e.g., Martin and Flegal 1975). Fish an squid form a major part of the diet of several species of penaeids (Dall *et al.* 1990). To *X. kroyeri* from Caribbean site collection the food items were determined in order of as: detritus and fragments of bivalve shells, polychaeta worms, foramineferans, crustaceans and fish (Cortés and Criales 1990). Despite the specific studies of the diet in this species from the Ubatuba region do not exist, we can not exclude the possibility of *X. kroyeri* make a natural enrichment of the Cd by food squid which is very abundant at the summer in Ubatuba region (Mantelatto pers. obs.).

With respect to the seasonal pattern, the highest concentrations were detected for Cu, Pb and Zn in summer (Table 1), i.e., vacation time. Since this is a tourist place, in summer there is a high increase in the population. This factor may cause a slow but progressive increase in the sources of pollution (commercial and leisure boats and dumping of sewage without treatment), generating very probably a higher accumulation of metals in the Bay. The presence of Cu can probably be accounted for by the leaching of antifouling paint (Alzieu 1981), very common in adjacent areas of Ubatuba Bay (Mantelatto pers. obs.).

Mean dry weights of males and females in summer notably differed from these of the other seasons. This situation occurs because despite the size ranges were similar throughout the year, the specimens from summer samples are mature, but with gonads in developing with low quantity of accumulation organic components in gonads tissues.

The scarcity of studies of this type in Brazil and in this particular region prevents a comparative analysis and does not permit a description of the dynamics of these metals. However, in the present study was detected a worrying outline with respect to the concentrations of these metals in shrimp from Ubatuba Bay, indicate that metals have been available in this area.

It should be taken into account that these animals occupy the final level in the food chain (omnivorous), with a consequent high accumulation power that makes them important metal accumulators. In this case, values above permitted levels, as is the case for Cr and Pb, may cause human damage since the organism under study is extensively commercialized and consumed as food in the region. Thus, it is of vital importance to conduct further studies on the entire Ubatuba region using different indicators at all levels in the food chain for a better understanding of the dynamics and the role of metals along the North coast.

The seasonal variation should be discussed in relation to size per sex because other changes in biological activity associated with season (e.g. reproductive cycle, molting stage) should be considered relative to other studies. Changes in land drainage connected with changes of metal inputs into the study area (e.g. from rivers in different seasons) also should be considered.

Table 1. *Xiphopenaeus kroyeri*. ANOVA ($P < 0.05$) of metal concentrations between seasons and sexes during the study period [CL = cephalothoracic length (mm); M = males; F = females; x = mean size (mm) and mean concentration (µg/g); sd = standard deviation].

	Sex	Summer		Autumn		Winter		Spring	
				x ± sd					
CL	M	16.3 ± 1.90		17.6 ± 1.70		17.4 ± 1.40		17.9 ± 0.80	
	F	16.0 ± 1.60		17.0 ± 2.10		17.6 ± 2.80		18.0 ± 1.10	
Dry Weight	M	0.34 ± 0.12		0.84 ± 0.31		0.83 ± 0.21		0.86 ± 0.13	
	F	0.34 ± 0.13		0.67 ± 0.29		0.85 ± 0.19		0.85 ± 0.11	
Cd	M	3.87 ± 1.09a*	A	1.54 ± 0.37b	A	1.50 ± 0.35b	A	1.08 ± 0.41c	A
	F	4.41 ± 2.14a	A	1.99 ± 0.78b	B	1.11 ± 0.19c	B	1.24 ± 0.34c	A
Cr	M	5.25 ± 1.78a	A	1.49 ± 1.04a	A	1.87 ± 1.15a	A	1.39 ± 1.98a	A
	F	2.47 ± 1.94a	A	1.57 ± 1.11a	A	1.50 ± 0.67a	A	1.61 ± 2.48a	A
Cu	M	73.03 ± 34.45a	A	48.66 ± 16.61b	A	42.42 ± 8.94c	A	37.63 ± 13.68c	A
	F	71.64 ± 33.80a	A	47.68 ± 23.55b	B	39.54 ± 11.59b	A	31.22 ± 8.88c	B
Pb	M	63.48 ± 23.40a	A	22.22 ± 7.09b	A	26.87 ± 5.92b	A	17.45 ± 4.97c	A
	F	73.11 ± 37.81a	A	30.12 ± 13.67b	A	21.59 ± 4.71b	B	21.15 ± 4.55b	A
Zn	M	104.60 ± 35.23a	A	55.41 ± 6.02b	A	50.50 ± 8.02b	A	52.20 ± 12.47b	A
	F	111.50 ± 40.59a	A	67.60 ± 31.36b	A	48.30± 8.97b	A	52.60± 11.94b	A

* Mean values followed by the same letter on the line did not differ significantly
Note: lower case letters correspond to the comparison of each group of interest along the seasons and capital letters correspond to group comparisons between metals.

Unfortunately no work have been conducted about metal contamination in this area and this work can provide valuable data for local public health authorities, This manner to solve the doubts raised about metal concentrations in shrimp of this species, we suggest that future studies be conducted to investigate the gonadal development and biochemical variations associated with reproduction rather and trace-metal distribution in tissues of the shrimp *X. kroyeri.*

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REFERENCES

Alzieu C (1981) Evaluation des risques dus a l'emploi des peintures antisalissures dans les zones conchylicoles. Repport I.S.T.P.M., 15 juin.

Castro RH (1997) Padrões distribucionais do camarão *Xiphopenaeus koyeri* (Heller, 1862) (Crustacea, Decapoda, Penaeidae) na Enseada de Ubatuba, Ubatuba, SP. Master's Thesis, IB - UNESP, Botucatu (SP), Brazil, 143pp.

Cortés ML, Criales MM (1990) Analisis del contenido estomacal del camaron titi *Xiphopenaeus kroyeri* (Heller) (Crustacea: Natantia: Penaeidae). An Inst Invest Mar 19-20: 23-33.

Dall W, Moriarty DJW (1983) Functional aspects of nutrition and digestion. In: Bliss DE, Mantel LH (Ed.). The biology of crustacea. New York, Academic Press, 5: 215-261.

Dall W, Hill BJ, Rothlisberg PC, Sharples DJ (1990) The biology of the Penaeidae. In: Blaxter JHS, Southward AJ (Ed.). Advances in marine biology. Academic Press, San Diego, 27: p. 489.

Elinder CG (1986) Zinc. In: Friberg L, Nordberg GF, Vouk VB (Ed.). Handbook on the toxicology of metals. Specific metals. Elsevier, Amsterdam, 2:664-679.

Engel DW (1987) Metal regulation and moulting in the blue crab *Callinectes sapidus:* copper, zinc and metallothionein. Biol Bull Mar Biol Lab 172:69-82.

Jeckel WH, Roth RR, Ricci L (1996) Patterns of trace metals distribution in tissues of *Pleoticus muelleri* (Crustacea: Decapoda: Solenoceridae). Mar Biol 125:297-306.

Mantelatto FLM, Fransozo A (in press) Characterization of the physical and chemical parameters of Ubatuba Bay, northern coast of São Paulo State, Brazil. Rev Brasil Biol 59

Martin JH, Flegal AR (1975) High copper concentrations in squid livers in association with elevated levels of silver, cadmium, and zinc. Mar Biol 30:51-55.

Nakagaki JM (1994) Biologia de Penaoidea (Crustacea, Decapoda) em Ubatuba (SP). Master's Thesis, IB-UNESP, Botucatu (SP), Brazil, 76pp.

Páez-Osuna F, Ruiz-Fernández C (1995) Trace metals in the mexican shrimp *Pennaeus vannamei* from estuarine and marine envinroments. Environ Pollut 87:243-247.

Páez-Osuna F, Tron-Mayen L (1995) Distribution of heavy metals in tissues of the shrimp *Penaeus californiensis* from northwest coast of Mexico. Bull Environ Contam Toxicol 55:209-215

Páez-Osuna F, Pérez-Gonzalez R, Izaguirre-Fierro G, Zazueta-Padilla HM, Flores-Campaña LM (1995) Trace metals concentration and their distribution in the lobster *Panulirus inflatus* (Bouvier, 1895) from the mexican pacific coast. Environ Pollut 90: 163-170

Rainbow PS (1985) The biology of heavy metals in the sea. Int J Envir Studies 25:195-211.

Rainbow PS (1986) Trace metals concentrations in a Hong Kong penaeid prawn, *Metapenaeopsis palmensis* (Haswell). Proceedings of the second international marine biological workshop: The marine flora and fauna of Hong Kong and southern China, 1:1221-1228.

Rainbow PS (1988) The significance of trace metals concentration in decapods. Symp Zool Soc London, 19:291-313.

Rainbow PS (1996) Heavy metals in aquatic invertebrates. p. 405 - 425. In: Beyer WN, Heinz GH, Redmon-Norwood AM (Eds.). Environmental contaminants in wildlife: Interpreting tissue concentrations. Lewis Publishers.