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Copper and Zinc in Three Dominant Brackish Water Fish Species from Paka Estuary, Terengganu, Malaysia

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ABSTRACT The concentrations of Cu and Zn in liver, stomach and gill tissues of three dominant edible fish species (*Arius caelatus, Notopterus notopterus* and *Toxeres jaculatus*) caught in Paka estuary were studied. A marked relationship between metal contents of the species studied was observed. The highest accumulation of the metals studied was found in liver samples, followed by stomach samples and lowest in the gill samples. In all cases, metal levels found were lower than the international standards of reference and the fish examined were not associated with enhanced metal content in their tissues and were safe within the limits for human consumption.

ABSTRAK Kepekatan logam Cu dan Zn didalam tisu hati, perut dan insang pada tiga spesies ikan dominan (*Arius caelatus, Notopterus notopterus* dan *Toxeres jaculatus*) di Muara Paka dikaji. Dalam kajian ini, satu perhubungan yang baik diperolehi di antara kepekatan logam dan spesies ikan. Kandungan logam yang tertinggi adalah diperolehi di dalam tisu hati, dan diikuti oleh tisu perut dan terendah pada tisu insang. Dalam kebanyakkan kes, paras logam dalam specimen yang telah dikaji adalah berada di bawah paras bahan rujukan piawai antarabangsa dan semua spesis ikan yang dikaji didapati tidak menunjukkan peningkatan logam pada tisu dan adalah selamat jika dimakan oleh manusia.

(Brackish water, copper, zinc, Paka estuary)

INTRODUCTION

Increasing industrial and agricultural production has resulted in increasing numbers of brackish systems being impacted by the contaminants present in wastewater releases. Heavy metals from natural and anthropogenic sources are continually released into aquatic systems, and they are serious threat because of their toxicity, long persistence, bioaccumulation and bio-magnification in the food chain [1]. Fish samples are considered as one of the most indicative of trace metals pollution potential [2, 3]. Fisheries managers have focused most of their attention on fisheries exploitation as the major factor affecting fish populations. However, in recent years, other anthropogenic factors, such as habitat destruction and marine pollution, played a major role in the decline of commercial marine fish species [4, 5]. Indeed, in many countries, the substantial development of urban and industrial activities result in increasing inputs of chemical contaminants which leads to the loss or alteration of marine habitats. As their spawning and nursery grounds are mainly located in estuarine and coastal areas, many marine organisms, including many commercially valuable shrimps and fish, are directly affected by human activities [6, 7].

In recent years, the study area especially for the first kilometer along the Paka River has been heavily impacted by discharges from municipal and industrial outflows [8]. This was due to the rapid development of the area via expansion of the industrialization area as well as the increase in population. Steel and petro-chemicals are the main industry in the area and is the catalyst for other supportive industries to develop around the same area. The aim of this study is to determine the levels of heavy metals (Cu and Zn) in the liver, stomach and gill tissues of three selected dominant species that were caught in the study areas. Zn is selected for their toxicity; meanwhile

Cu is selected as it is vital for the growth of the fish.

MATERIALS AND METHODS

Description of the study area

The samplings were done in the river of Paka district, Terengganu (Figure 1). This river is intensively exploited by the surrounding community not only as a route for fisherman but also as a port for shipyard, route of industrial wastes and also an active area for sand mining activities. Nevertheless, this river has a diverse ecosystem and also highly utilizable natural resources such as oyster, crab, prawn and some mangrove species. The outfall of Paka River to estuary was usually influenced by northeast monsoon which prevailed from October to March while southeast monsoon prevailed from April to September. The study area recorded the highest rainfall during the northeast monsoon which highly influenced the flux of some importance parameters in term of geological, chemical as well as physical of the estuary. Three species that were dominantly caught in this study were selected; *Arius caelatus, Notopterus notopterus* and *Toxeres jaculatus*.

Analytical procedure

The fish were caught with a beam trawl at 3 locations in the Paka estuary (Figure 1). The fish were sampled at each station over 24 hours until a sufficient number of individuals, at least 5 – 10 fishes, were caught. The samples were transported to the laboratory and stored at -20 ^{0}C prior to analysis. Fish samples were thawed at room temperature, and their length and weight were recorded using the callipers and 3 decimal points of measuring weight, respectively. They were dissected using stainless steel scalpels and Teflon forceps using a laminar flow bench. A part of the muscle (liver, stomach and gill) were removed and transferred in polypropylene vials. Before acid digestion, a porcelain mortar was employed to grind and homogenize the dry tissue samples. Briefly, the digestion method involved the heating of 1.0 g of tissues sample in a teflon beaker with mixed concentrated acids of HNO_3 and H_2SO_4 in the ratio of 1:1. The teflon beakers were kept at 100 ^{0}C for 2 - 3 hours. After cooling, a H_2O_2 solution was added in order to break down any recalcitrant lipid material in the tissue and a clear solution with no residue should be obtained at this stage. Deionized water was added and allowed to evaporate a few times to dryness and finally the digested tissues were transferred into a 50 ml volumetric flask. An inductively coupled plasma mass spectrometer (ICP-MS) was used for the quick and precise determination of Cu and Zn in the tissue samples. The precision assessed by replicate analyses was within 3%. The accuracy was also examined by analyzing a blank and a material standard from the National Research Council of Canada standard (NBS DORM 2) and the results coincided with the certified values within a difference of ± 3%.

Statistical analysis

Statistics were performed using a two factor analysis of variance. This method was based on the procedure of general linear models, where samples were examined for potential influence on Cu and Zn. Differences between level means per factor were treated using Tukey's multiple comparisons of means. When ANOVA assumptions such as sample normality and homoscedasticity were not respected, multiple ($n > 2$), sample comparisons were performed by nonparametric Kruskal-Wallis tests. An ANOVA paired tests were then used for two-sample comparisons. A p-value of 0.05 or less was considered statistically significant.

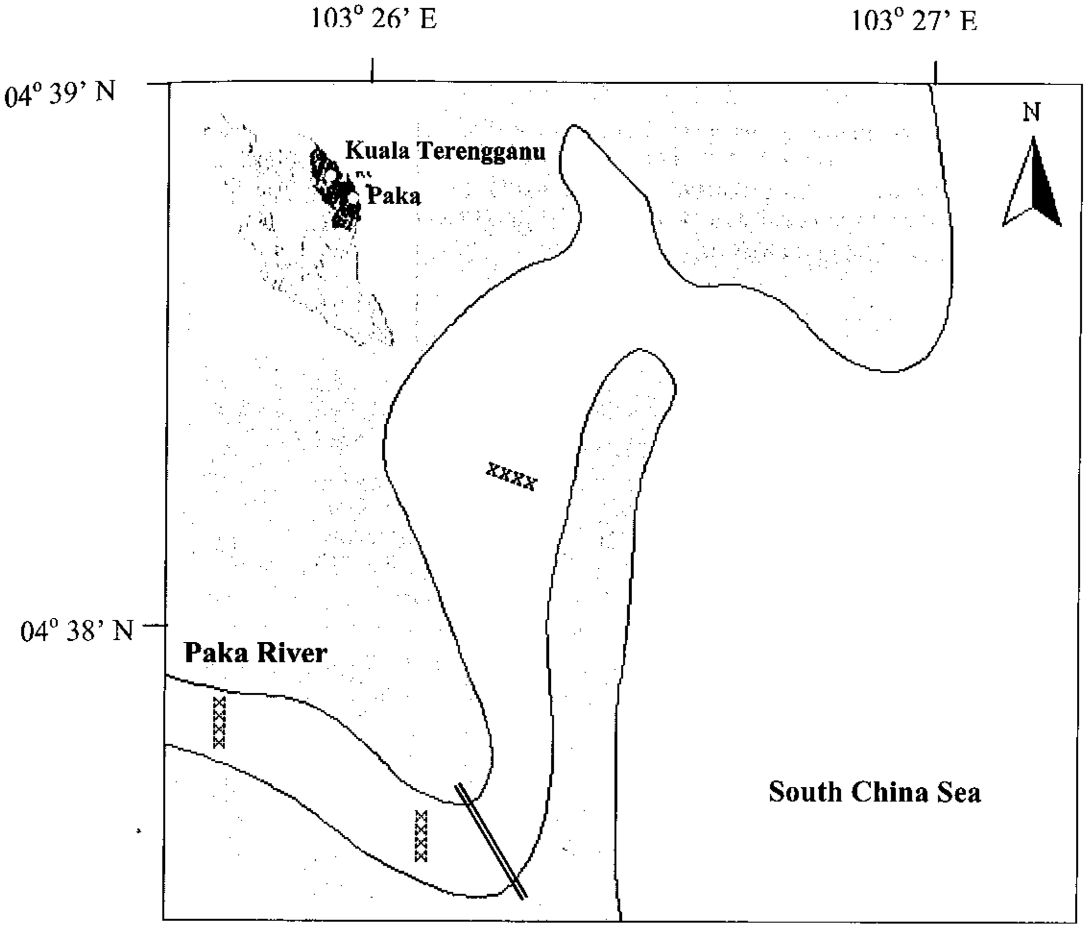

Figure 1. The location of fish caught (xxxx) in the Paka Estuary, Terengganu, Malaysia

RESULTS AND DISCUSSION

A total of 143 fishes were analyzed with a mean size and weight varying from 146 to 285 mm and 155 to 320 g, respectively. As reported by Cossa *et al.* [9] and Kress *et al.* [10], the size of fish could have an influence on contaminant concentrations in different tissues and are independent to the exposure. However, in this study, there were no significant correlations observed between metal concentrations in liver, stomach and gill with the size of the fish. Concentrations of heavy metals detected in the liver, stomach, gill and stomach samples (expressed as $\mu g\ g^{-1}$ dry weight) are shown in Figure 2. Both Cu and Zn concentrations between fish species were statistically significant ($p < 0.001$) and also, the statistic comparison among fish tissues showed great significant ($p < 0.001$). The mean concentration of Cu was relatively high in *Notopterus notopterus*, ($19.6 \pm 1.2\ \mu g\ g^{-1}$ dry weights) followed by *Arius caelatus* ($9.45 \pm 0.6\ \mu g\ g^{-1}$ dry weights) and lowest in *Toxeres jaculatus* ($9.19 \pm 0.5\ \mu g\ g^{-1}$ dry weights). Meanwhile, Zn has higher mean concentration in *Arius caelatus* ($148.6 \pm 5.4\ \mu g\ g^{-1}$ dry weights), followed by *Toxeres jaculatus* ($87.6 \pm 3.6\ \mu g\ g^{-1}$ dry weights) and lowest in *Notopterus notopterus*, ($79.5 \pm 3.2\ \mu g\ g^{-1}$ dry weights), respectively.

One possible explanation for the higher metal concentrations in fish is due to their dietary habits. Cu and Zn are essential elements and are carefully regulated by physiological mechanisms in most organisms [1]. However, they are regarded as potential hazards that can endanger both animal and human health. Knowledge of their concentrations in fish is therefore important both with respect to nature management and human consumption of fish [11]. Even though there is no clear evidence about Cu dietary transfer; many studies have demonstrated that diet is the most important route of Cu accumulation in aquatic animals [12, 13]. According to Eisler [1], little or no biomagnifications of Cu is evident in freshwater food chains; therefore, species like *Toxeres jaculatus* which are mostly predators appear the lowest in Cu content. Chen *et al.* [14] suggested that Zn may be biomagnified in a variety of aquatic food webs and lake types. Strong relationships were also found between Zn concentrations in zooplankton and fish [15]. In this study, fish like *Arius* species that feed most on invertebrates display higher concentrations of Zn, compared to *Toxeres* sp. and *Notopterus* sp.

In this study, it is interesting to note that the mean concentrations of both metals behave in a similar way in the examined tissues. It appears that the mean concentrations were high in liver followed by stomach and gill tissue. A liver tissue metal concentration has 0.5 times higher than those presented in stomach tissue and 10-12 times higher than in gill tissue. In this study, Cu in liver ranged from 8.2 to 43.7 µg g^{-1} dry weights, 11.8 to 17.7 µg g^{-1} dry weights in stomach and 1.59 to 1.95 µg g^{-1} dry weights in gill tissue. Meanwhile, Zn in liver, stomach and gill ranged from 130.8 to 150.7 µg g^{-1} dry weights, 69.3 to 159.3 µg g^{-1} dry weights and 38.0 to 150.2 µg g^{-1} dry weights, respectively. As in other studies, we also observed higher levels of metals in liver than in the muscle or gill tissues. This finding is in agreement with those of other studies [16, 17]. Bioaccumulation in liver was observed for most metals [12], since the liver is a major organ involved in xenobiotic metabolism in fish [18]. Organisms retain both metals, Cu and Zn, through specific binding proteins, metallothioneins, which play an important role in metal homeostasis and in protection against heavy metal toxicity [19]. On the other hand, the low concentrations of Cu and Zn in the muscles of the examined fish species may reflect the low levels of these binding proteins in muscles. The differences in concentration are at least one order of magnitude and originate from differences in physiological functions of muscle and liver. Thus, the liver is often recommended as a target tissue when monitoring metal concentrations in aquatic environments. However, muscle is commonly analyzed because it is the main fish part consumed by humans and implicated in health risks.

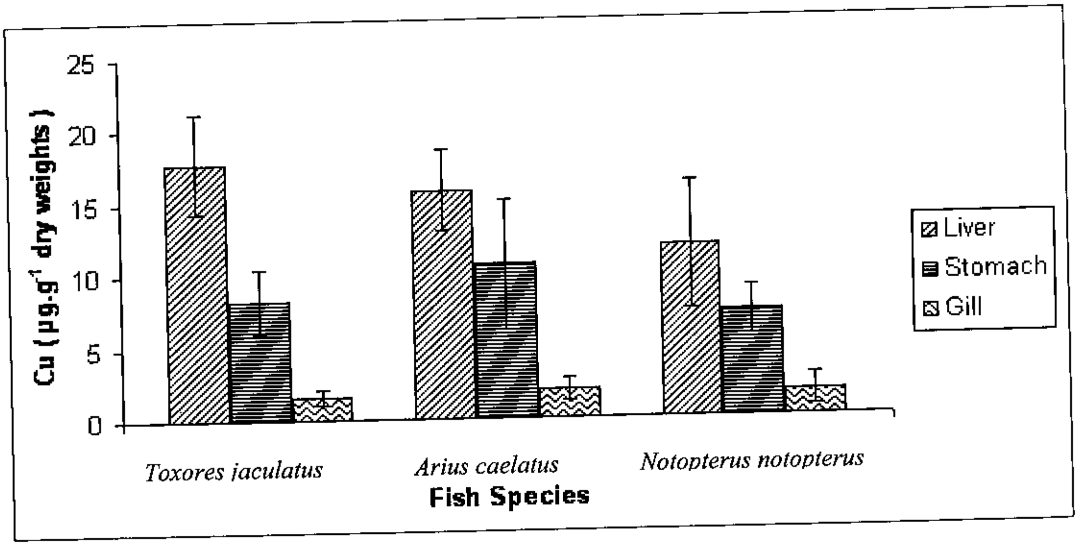

Figure 2. Mean Cu and Zn concentrations (µg g^{-1} dry weights) in different tissues of three blackish water fish species from Paka Estuary, Terengganu, Malaysia

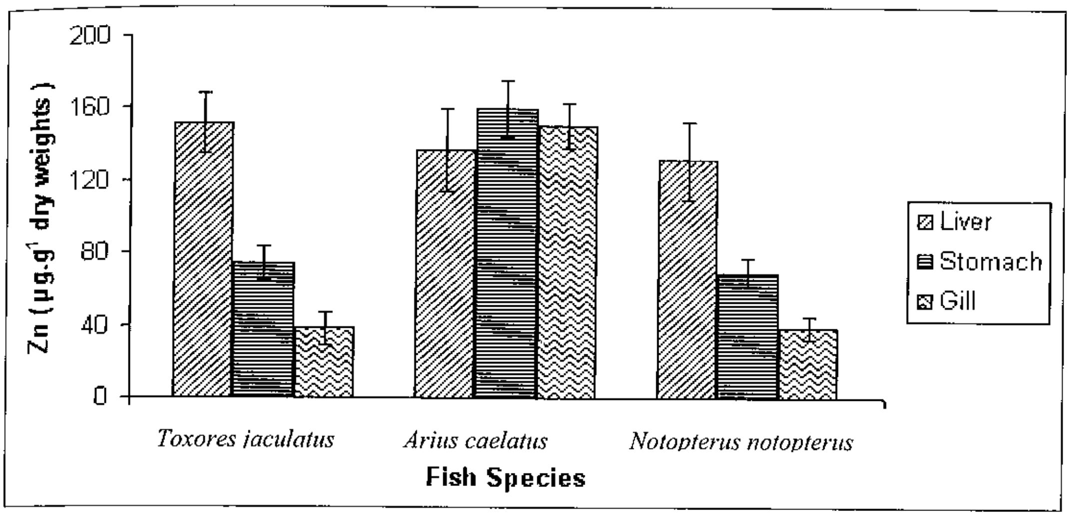

Figure 2. Mean Cu and Zn concentrations (µg g^{-1} dry weights) in different tissues of three blackish water fish species from Paka Estuary, Terengganu, Malaysia (contd.)

CONCLUSION

It remains very difficult to compare the metal concentrations even between the same tissues of different species because of the different feeding habits and the differences in the aquatic environments concerning the type and level of water pollution. Furthermore, there are no guidelines on acceptable levels of Cu and Zn in the edible parts of fish suggested by EEC or FAO/WHO. On the basis of the recommended daily dietary allowances (RDA) for safe consumption of fish muscle, the allowed intake is regulated at 50 - 350 mg of metal per 100 g serving of the muscle [19]. According to our results, the examined fish were not associated with enhanced metal content in their muscle and were safe within the limits for human consumption.

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REFERENCES

1. Eisler, R. (1988). Zink Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review. *U. S. Fish Wildlife Serv. Biol. Rep.* Volume 85.
2. Evans D. W., Dodoo, D. K. and Hanson, D. J. (1993). Trace elements concentration in fish livers implication of variations with fish size in pollution monitoring. *Mar. Pollut. Bull.* **26** (6): 329 – 334.
3. Rashed, M. N. (2001). Monitoring of environmental heavy metals in fish from Nasser Lake. *Environ. Int.* **27**: 27 – 33.
4. Grosse, D. J., Scholz, P. M., Hirshfield, M. F., Meaburn, M. F. and Fletcher, M. (1997). Fisheries and pollution: An overview. *Trans. Am. Fish. Soc.* **126**: 504 – 505.
5. Johnson, L. L., Landahl, J. T., Kubin, L. A., Horness, B. H., Myers, M. S. and Collier, T. K., (1998). Assessing the effects of anthropogenetic stressors on Puget Sound flatfish populations. *J. Sea. Res.* **39**: 125 - 137.
6. Amara, R., Lagardere, F., Desaunay, Y. and Marchand, J. (2000). Metamorphosis and estuarine colonisation in the common sole, *Solea solea* (L): Implication for recruitment regulation. *Oceanol. Acta.* **23**: 469 – 484.
7. Gibson, R. N. (1994). Impact of habitat quality and quantity in the recruitment of juvenile flatfishes. *Neth. J. Sea. Res.* **32**: 191 – 206.

8. Kamaruzzaman, B. Y., (1994). *A Study of some Physico-Chemical Parameters in the Estuarine System of Chukai-Kemaman River, Terengganu, Malaysia.* Master of Science (MSc) thesis, University Pertanian Malaysia.
9. Cossa, D., Auger, D., Averty, B., Lucon, M., Masselin, P. and Noel, J. (1992). Flounder *(Plattichthys flesus)* muscle as an indicator of metal and organochlorine contamination of French Atlantic Coastal waters, *Ambio.* **21**: 176 – 182.
10. Kress, N., Herut, B., Shefer, E. and Hornung, H. (1999). Trace element levels in fish from clean and polluted coastal marine sites in the Mediterranean Sea, Red Sea and North Sea, Helgoland. *Mar. Res.* **53**: 163 – 170.
11. Amundsen, P. A., Staldvik, F. J., Lukin, A., Kashulin, N., Popova, O. and Reshetnikov, Y. (1994). Heavy metals contamination in freshwater fish from the border region between Norway and Russia. *Sci. Total. Environ.* **201**: 211 – 224.
12. Sindayigaya, E., Cauwenbergh, R. V., Robberecht, H. and Deelstra, H. (1994). Copper, zinc, manganese, iron, lead, cadmium, mercury and arsenic in fish from Lake Tanganyika, Burundi. *Sci. Total. Environ.* **144**: 103 – 115.
13. Fisher, N. S. and Reinfelder, J.R. (1995). The trophic transfer of metals in marine systems. In: *Metal Speciation and Bioavailability in Aquatic Systems* (eds. Tessier A. and Turner D. R.). London: Wiley. pp. 363 – 406.
14. Chen, C. Y., Stemberger, R. S. and Klaue, B. (2000). Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol. Oceanogr.* **45**: 1525 – 1536.
15. Spry, D., Hodson, P. and Wood, C. (1988). Relative contributions of dietary and water borne zinc in the rainbow trout, *Salmo gairdneri. Can. J. Fish. Aquat. Sci.* 45: 32 – 41.
16. Carpene, M. and Vasak, M. (1989). Hepatic metallothionin from goldfish *(Carassius auratus). Comp. Biochem. Physiol.* **92B**: 463 – 8.
17. Allen-Gil, S. M. and Martynov, V. G. (1995). Heavy metals burdens in nine species of freshwater and anadromous fish from the Pechora River, northern Russia. *Sci. Total. Environ.* **160 – 161**: 653 – 659.
18. Romeo, M., Mathieu, A., Gnassia-Barelli, M., Romana, A. and Lafaurie, M. (1994). Heavy metal content and biotransformation enzymes in two fish species from NW Mediterranean. *Mar. Ecol. Prog. Ser.* **107**: 15 – 22.
19. Olsson, P. E., Larsson, A. and Haux, C. (1989). Metalloyhionein and heavy metal levels in rainbow throut and *Salmo gairdneri*, during exposure to cadmium in water. *Mar. Environ. Res.* **24**: 151 – 153.
20. National Research Council, Committee on Dietary Allowances. Food and Nutrition Board, USA; 1980.