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Determination of Heavy Metals in Sheary Fish Lethrinus lentjan Imperors (Family: Lethrinidae “Teleost”) in United Arab Emirates Water

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DETERMINATION OF HEAVY METALS IN SHEARY FISH
LETHRINUS LENTJAN IMPERORS
(FAMILY: LETHRINIDAE "TELEOST")
IN UNITED ARAB EMIRATES WATER

BY


MARYAM HAREB AL-YOUSUF

B.Sc IN CHEMISTRY 1989

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The thesis of Maryam Hareb Al-Yousuf for the degree of Master of Science in Environmental Science is approved.



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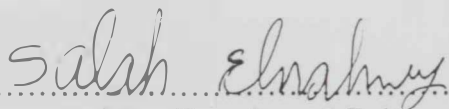
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January, 1995

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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Abstract

Investigation of heavy metals in fish is an important aspect of environmental pollution as human activities contribute to the progressive increase in the concentration of metals in the environment as well as aquatic system. Therefore, an analytical survey for the contents of copper, zinc, manganese, and cadmium in liver, heart, kidney, muscle and skin of *Lethrinus lentjan*, collected from the western coast of the United Arab Emirates (Ras Al-Khaima) was carried out. The range and mean values of the levels of metals were determined and compared with the reported values in the Arabian Gulf.

Significant concentrations of the elements tested were detected by Atomic Absorption Spectrophotometric technique. Their values of metal levels were within the permissible limit for human consumption. The correlation coefficients between the metal concentrations in different tissues and various length groups were also determined.

The accumulation pattern of the essential elements Zn, Cu and Mn, and non-essential element Cd in the liver follows the sequence:



while in skin tissue the sequence of the metals follows the order:



In muscle the sequence of the accumulation behavior follows the order:



The distribution behavior of the elements in fish kidney was found to follow the sequence:



However, in fish heart the sequence is as follows:



The mean concentrations (mean \pm 5.0) of Cu, Zn, Mn, and Cd in fish liver was found to be 48.8 ± 1.71 , 55.3 ± 32.98 , 1.22 ± 0.23 , and 0.66 ± 0.28 ppm, respectively. However, in skin the concentration was much lower and were as follows: 0.33 ± 0.13 , 38.59 ± 8.35 , 0.16 ± 0.11 , and 0.08 ± 0.06 ppm, respectively.

Also in muscle the metals concentrations were found to be much lower than those in liver; the levels obtained were as follows: 0.17 ± 0.06 , 3.31 ± 0.39 , 0.11 ± 0.02 , and 0.11 ± 0.02 ppm, respectively.

The study shows a negative correlation between the concentrations of Mn and Cd in fish muscle and fish length (age). Also in skin tissues the concentration of Mn shows a negative correlation with fish length (age), while a positive correlation was observed with copper. Moreover, a positive correlation was noticed between Cu, Zn and Cd concentrations in liver and fish length (age).

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CHAPTER 1
INTRODUCTION

1. Introduction

The United Arab Emirates (U.A.E.) is situated on the southern coast of the Arabian Gulf. The Arabian Gulf is located in an extremely arid region of the world. It is bordered by the Arabian Peninsula and Iran, and is between 24° and 30° north latitude (Relyea, 1981). The precipitation and runoff is markedly lower than evaporation which results in an increase in the salinities ranging between 35–40‰ in the open water, and higher in protected coastal embayments. The offshore water temperature of the Arabian Gulf ranges between 18–32°C (Abu-Hilal & Khordagui, 1992). According to Hunter (1982), the circular pattern of the water in the Arabian Gulf is counterclockwise, and it takes 2 to 4 years to turnover, while the flushing time takes 3 to 5.5 years (Abu-Hilal & Khordagui, 1993).

The marine environment in the Arabian Gulf region has been a subject of study in recent years due to accidental oil spills, discharge of ballast water, dredging and burial for coastal development, uncontrolled discharge of the sewage and industrial waste waters as well as human activities (Abu-Hilal & Khordagui, 1992). All these stresses and activities are posing a serious threat to the marine environment. Heavy metals released both naturally and through human activities that may accumulate in aquatic environment. Organisms living in such habitat are known to concentrate trace metals pollutants in their body tissues (Schumacher, et al., 1992). Certain marine organisms have been found

useful as indicator of environmental pollution (Fôrstner & Wittman, 1981). As fish are located at the end of the aquatic food chain they may act as an indicator of water pollution in terms of heavy metal contamination (Ramelow, et al., 1989).

1.1 Lethrinidae

Lethrinids are marine, coastal fishes of Indo-Pacific region and west coast of Africa, and are commonly found around coral reefs (Relyea, 1981). *Lethrinus lentjan* is a commercially important species found in the local U.A.E markets. They are carnivores, feeds on crustaceans, fishes, molluscs, sea urchins and other hard-shelled in-vertebrates, and they feed mainly at night. (Relyea, 1981; Swasubramaniam & Ibrahim, 1982; Randall, 1986).

Lethrinus lentjan (local name Sheari Shekhabi, English name Scavenger) or Red emperor species have compressed bodies, slightly convex interorbital space, have green (olive) grey body above, lighter to silver below; white spots are on scale centres especially above lateral line (Fischer & Bianchi, 1984). The fish can be identified by bright red margin on posterior edge of operculum and often another on pectoral base (Fischer & Bianchi, 1984; Swasubramaniam & Ibrahim 1982; Randal, 1986). Their size ranges from 10 to 43 cm, maximum to 45 cm. Mainly they are found on the sandy bottom in 10–35 F depth (Swasubramaniam & Ibrahim, 1982). These species are fairly abundant, caught throughout the year; the small size dominating at the beginning of the summer while the large size abundant in the winter. The best fishing period is between November and March (Swasubramaniam & Ibrahim, 1982).

1.2 Trace Metals

Trace elements occur in minute concentration in natural biological systems and exert a beneficial or harmful effects on plant, animal, and human life (Förstner & Wittmann, 1981).

Heavy metals are introduced into the aquatic environment through various routes, smelting processes and fuel combustion via atmospheric fallout, dumping wastes, pollution from leaks, effluents from runoff of terrestrial system (industrial and domestic effluents) and geological weathering (Förstner & Wittman, 1981). Trace metals cannot be removed from the aquatic environment like most organic pollutants (Förstner & Wittmann, 1981). Cadmium, arsenic, copper, mercury, and others have the ability to accumulate in bottom sediments. Due to various processes of remobilization these metals may be released and move into the biological or food chain and concentrate in fish and other edible organisms, thereby reaching human beings and causing chronic or acute diseases (Förstner & Wittman, 1981).

Biomagnification, which is the tendency of some chemicals to pass through the food chain resulting in a progressive increase of their levels at each trophic level (Kumar & Mathure, 1991), may occur since the heavy metals enter into the environment. The toxicity and bioavailability of heavy metals depend on their existence, which inturn depends on the water properties such as pH, conductivity and dissolved substances (Kumar & Mathur, 1991). Moderately stable complexation of heavy metals may result due to interaction of heavy metals with dissolved organic carbon and nitrogen (Kumar & Mathur, 1991).

The metal uptake process comprises of two phases: the first phase is metabolism- independent binding to the cell walls and other external materials and the second phase is uptake in the tissues. The interactions of various environmental factors, pH, temperature, organic matter, chlorides, sulphates and others affect on the uptake of heavy metals by an organism (Förstner & Wittmann, 1981). Micro-pollutants such as heavy metals are considered as bio-cumulative. It is found that the age, size, feeding habits of fish or aquatic animals and their retention time in polluted waters affect the heavy metals accumulation in these organisms (Mitra, 1986).

Heavy metals are a matter of concern because of their toxicity and tendency to accumulate in food chains (Mason & Barak, 1990). It was found that heavy metals that are below the detection limit in routine water samples may accumulate significantly in the fish (Mason, 1987; Barak & Mason, 1990). These fish might be a better material than water samples as indicator of metals contamination in an ecosystem (Mason & Barak, 1990).

Metal availability to organisms in the aquatic systems depends on various physico-chemical and biological factors (Förstner & Wittmann, 1981). The species-specific differences such as feeding behavior of the organisms and habitat preferences play an important role, hence, metal passage into aquatic organisms depend on water chemistry, sediments, and biological characteristics of the organisms (Dallinger, et al., 1987). Metals enter the fish body by three ways: the body surface, the gills, and the alimentary track (Dallinger, et al., 1987). Moreover, it was found that the main source of metal concentration in fish is the food than water

where in the aquatic ecosystems the heavy metals may be transferred to the fish tissues through the food chains and accumulated in the tissues (Dallinger, et al., 1987). The degree of contamination of food supply and the reduction of species diversity are the two ecological factors that influence the food chain effects (Dallinger, et al., 1987).

Recently, an investigation on the toxicity and bioavailability of heavy metals in the fish have been carried out in low alkalinity lakes by Spry, et al. (1991). The data showed that in water of low pH the body or tissue burdens of mercury, cadmium and lead are higher than other waters of higher pH value (Spry, et al., 1991). The low concentration of calcium in the low alkalinity water causes an increase in biological membranes' permeability to heavy metals and therefore, causing an enhanced uptake of metals from both water and food chain .

Heavy metals are important contaminants present in the marine environment. Iron, manganese, copper, cobalt, zinc are essential elements to the life of most organisms; however, others may be either non-essential or harmful (Devi, 1989). Many species of fish have limited ability to excrete non-essential metal such as cadmium or mercury, so their concentration would increase with size or age (Bryan, 1976). Therefore, the contamination of marine organisms that have a tendency to bioaccumulate rendering them unsafe for consumption would be the problem. The Minamata (Loefron, 1970) and Itai-Itai are diseases caused by mercury and cadmium, respectively (Frieberg, et al., 1974; Kobayashi, 1971).

Recently, Devi, 1989 monitored the heavy metal levels in Malaysian Fish and shellfish. The concentrations were found as follow:

Ca 0.07–3.00, Zn 1.67–19.42, Cd 0.002–0.308, Pb 0.06–0.647 and Hg 0.007–0.758 ppm. These wide ranges were attributed to the differences in species that are different in their habits and diets and also to the different sampling locations — i.e, habitats (Devi, 1989).

A survey of cadmium and lead levels in the liver and muscle of eels from eleven rivers in East Anglia, England was reported by Barak & Mason, 1990. They found that eels from some sites showed high metal levels indicating sources of metal contamination. The concentration range was as follows: Cd 0.06–0.47 ppm in liver and 0.02–0.08 ppm in muscle while Pb concentration in liver was 0.26–0.8 ppm and in muscle was 0.03–0.08 ppm. They concluded that eel liver is a suitable indicator of inorganic pollution and the muscle is a suitable indicator of organic pollution.

Heavy metals concentration such as Cu, Zn, Pb, and Cr were determined in flounder flesh caught off the Belgian coast by Guns, et al., 1988. They observed no significant correlation between metals concentration and length categories. Their levels in muscle were as follows: Cu 0.29–0.56, Zn 4.6–14.0, Pb 0.02–0.149, and Cr 0.07–0.45 ppm.

Many bottom and pelagic fish in Baltic sea were examined for heavy metals concentration. The mean concentrations of Cu, Zn, and Cd in the muscle of cod (bottom species) were significantly lower than those in herring and spart (pelagic species). Also it was found that spart species have greater amount of Mn, Zn, and Cd as compared with herring. Moreover, some regional variations in metal concentrations

were found in the bottom fish and pelagic fish (Szefer & Falandysz, 1985).

Recently Schuhmacher, et al. 1992 have analyzed the edible parts of several species of fish, molluscs and crustaceans from the Tarragona Coast (Spain) for heavy metals. The levels of heavy metals contents were found in the range of 0.113–1.727 ppm for manganese; 0.006 to 0.469 ppm for chromium; 3.35 to 20.79 ppm for zinc, and 0.004 to 0.304 ppm for cobalt. These metal levels in the marine species do not pose a health hazard to consumers.

The eel species (*Anguilla Anguilla*) were analyzed for Hg, Cd, and Pb concentrations in eastern England rivers. The range of concentrations were found as follows: Hg in muscle was 0.09–1.3 ppm, Hg in liver 0.01–0.82 ppm; Cd in liver 0.04–1.95 ppm; Pb in liver 0.07–3.37 ppm (Mason & Barak, 1990). The eel *Anguilla* is a useful bioindicator because of its several properties, e.g. size, abundance, worldwide distribution, long life span and euryhalinity (Amiard–Triquet, et al., 1987).

There are natural factors influencing the metal levels in the eel such as season of sampling, developmental stages, and salinity (Amiard–Triquet, et al., 1987). A little influence of the sampling period or season on both metal body burdens and concentrations were found. In case of Cd, Pb, Cu, and Zn there was minor influence of the pigimentary stage on the metal bioaccumulation (Amiard–Triquet, et al., 1987). The increase of lead in the elvers of one of the estuary was the only noticeable observation when they started to ingest food (Lecomte–Finger, 1983). They also found a little or no short-term effect of the salinity upon the accumulation of Cd, Cu, and Zn in livers. It was

suggested that livers are not useful bioindicators for the essential metals Cu and Zn because of their ability to regulate whole body level of the Cu and Zn. However, the internal level of Cd reflected its environmental contamination. Moreover, Pb bioaccumulation in elvers prior to the pigimentary stage is very limited (Amiard-Triquet, et al., 1987).

El-Nabawi, et al., 1987 investigated different species, e.g. *Pagellus erythrinus*, *Siganus rivulatus*, *Sphyræna sphyræna*, *Trigla hirundo*, *Tilapia nilotica*, and *Tilapia zillii* for heavy metals in different parts of Alexandria region (Egypt). The Arsenic concentrations in muscles tissue of fish ranged from 0.97 to 10.5 ppm and 0.11 to 0.18 ppm in different areas; Cd concentration in muscles ranged from 0.012–0.023 and 0.018–0.023 ppm; Cu 6.9–10.2 ppm and 3–15.4 ppm; Pb 0.18–0.6 ppm and 0.28–0.42 ppm; Hg 0.08–0.65 ppm and 0.04–0.06 ppm; Zn 16.5–27.0 ppm and 31.5–40.5 ppm. The data also showed that, in the liver samples the levels ranged from 4.5–7.1 ppm; Cd 0.018–0.108 ppm; Cu 11.7–31.8 ppm; Pb 0.35–0.98 ppm; Hg 0.14–0.95 ppm; Zn 60.0–78.0 ppm.

The lead levels in the edible tissues of fish collected from the Bay of Bengal (tropical marine species) were in the range of 0.58–4.03 ppm per dry weight with an average of 1.78 ppm lead. The cadmium levels varied from 0.04–0.13 ppm with an average value of 0.08 ppm, these values are below the permissible levels (Sharif et al., 1993). Moreover, the muscles of tropical marine fish species from the Bay of Bengal were examined for Mn, Ni, Cu, Zn, Pb, and Cd levels by Sharif et al., 1991. The manganese was found in the range of 5–11 ppm; the maximum nickel concentration was 7.58 ppm for beta (*Cirrhina reba*); the

maximum concentration of copper was 4.688 ppm in churi (*Lepturacanthus savala*) while zinc was 33.89 ppm in latia (*Harpodon nehereus*). The cadmium level in fish muscle was below 0.1 ppm wet weight (Eisler, 1981), and the Cd concentration ranged between 0.009–0.17 ppm in bata (*Cirrhina reba*), latia (*Harpodon nehereus*) and thassa (*Setipinna phasa*) (Eisler, 1981). The lead levels in the muscle ranged between 0.33 to 0.52 ppm wet weight (Sharif, et al., 1991). The accepted limits for consumption for Zn, Cu, Cd, Ni, and Pb in human are 150, 10, 0.2, 1 and 1.5 ppm wet weight respectively. Thus, the reported results were below the permissible values of these metals.

The relationship between heavy metal levels (e.g. Ag, As, Cd, Cu, Fe, Hg, Mn, Pb, Se, and Zn) in Atlantic croaker's (*Micropogonias undulatus*) liver and the fish length (age) have been reported by Evans, et al. (1993). They observed that metal levels increased with length. This pattern is expected for non-essential elements Ag, Cd, Hg, and Pb, but not for Cu, Fe, Mn, Se, and Zn which are biologically essential elements and are falling under homeostatic control.

Recently, Abdelmoniem & El-Deek, 1992, have investigated the concentration of heavy metal content in the Red Sea and Arabian Gulf fish. They reported that the average concentrations of Cu, Zn, Mn, Pb, Cr, Ce, and Fe in *Lethrinus mahsenoides* muscle were 0.34, 4.81, 0.32, 1.14, 0.39, 0.51, and 20.14 ppm and in *Lethrinus nebulosus* species muscle were 0.45, 6.87, 1.13, 0.64, 0.43, 0.39, and 19.25 ppm, respectively. These values are below the permissible values given by the World Health Organization (WHO).

It is known that the deep waters have higher levels of some metals such as Hg, Zn, Cd, and Pb . Many researchers have investigated the heavy metal contents in fish reared in upwelled waters (Fast, et al., 1990). They have studied the Hg, Zn, Cd, and Pb levels in the muscle of coho and chinook salmon. The average mercury concentration in the edible parts of both salmon species was 0.037 ppm which is 20 times lower than the U.S. Food and Drug Administration Action Criteria of 1.0 ppm in edible tissues. Moreover, the average level of Zn, Cd, and Pb for both salmon species were 7.64, 0.11, and 0.24 ppm respectively. The accumulation of cadmium was studied in red cray fish (*procambarus clarkii*) tissues, caught from a Spanish lake (Mayans, et al., 1986). The study suggested that Cd concentration in the tissues is a function of Cd level in the water (Mayans, et al., 1986).

Massive oil spills and oil field fires in Kuwait led petroleum hydrocarbons and trace metals to enter the Arabian Gulf as a result of Gulf War in 1991. Therefore, a survey was done after the war immediately to determine the degree and extent of these contamination (Fowler, et al., 1993). Fish were collected from Kuwait, Saudi Arabia, Bahrain, U.A.E, and Oman. The survey demonstrated that the petroleum hydrocarbon contamination and trace metal pollution in the Arabian Gulf was restricted to about 400 km from the source and the most contaminated area was found along the northern coast of Saudi Arabia (Fowler, et al., 1993). Moreover, it was reported that metals concentrations do not appear to have been measurably perturbed by the oil spill or fallout from the fires. The investigation also showed that the degree and extent of contamination resulted from war in the Arabian Gulf

region was not as high as has been popularly believed (Fowler, et al., 1993).

Recently, extensive studies have been undertaken by Kureishy (1993) to determine the levels of Hg, Cd, Pb, Cu, Co, and Ni in muscle tissue of organisms from Doha area and off Halul Island. The concentration of these ions were in the range of 0.02–0.46, 0.21–1.32, 0.67–2.47, 1.24–4.71, 0.13–0.86, and 0.58–1.73 for Hg, Cd, Pb, Cu, Co, and Ni respectively. These results do not suggest any significant increases in metal levels content due to the massive oils spills occurred in 1991 (Kureishy, 1993).

Sadiq & McCain, 1993, have reported that the mean concentrations of Cd, Cu, Ni, Pb, and V in shellfish (clams) collected from the north of the Arabian Gulf in 1991 were higher than the levels reported in 1985. The concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in clams (collected in 1991, post war) were found 0.31, 0.89, 0.61, 0.92, 55.55, 1.75, 1.25, and 4.91 ppm respectively. Several studies have indicated that the concentration of essential trace metals (Fe, Cu, Zn, and Mn) in the organs were in the order of: liver > kidney > muscle, while the concentration of non-essential metals follow the order: kidney > liver > muscle (Jaffar & Perviaz, 1989). They recommended that the liver and kidney are unsuitable for human consumption.

In Pakistan, it was reported that Mn, Zn, Fe, Cu, Cr, Ni, Pb, Hg, Cd, and As levels in the muscle of fresh water fish were in the range of 0.115–11.157, 1.875–50.65, 2.805–180.35, 0.193–7.20, 0.365–13.2, 0.628–38.8, 0.765–45.316, 0.02–26.8, 0.004–1.5, and 0.48–7.5 ppm wet weight respectively (Jaffar, et al., 1988). It was concluded that the metal

contents in the muscles were species-specific, there was no difference in their levels between large and small fish and there was a positive correlation between Zn and As levels in fish muscle and in the water quality (Jaffar, et al., 1988).

Trace metals (Cu, Mn, and Ni) in deep-sea sharks from the Rockall Trough were analysed by Vas and Gordon, 1993. The concentration ranges were <0.02–4.3; <0.02–8.64; <0.28–38 ppm for Cu, Mn, and Ni, respectively. The values were lower in the species found in deep sea due to less anthropogenic inputs in the deep waters (Vas & Gordon, 1993). The external tissues, e.g. skin and gills in all species examined had the highest metal concentrations because of direct exposure to the external environment, one of the major sources of metal exposure to the shark. The data also showed that vertebrae which is an internal tissue, have high levels of metals. Moreover, it was also found that as the fish length increases the metal concentrations decreases except in *E. princeps* species where the metal concentrations showed a general pattern of increasing levels with length (Vas & Gordon, 1993).

Ruelle, et al., 1993 reported that cadmium concentrations in kidney of *pallid sturgeon* from the upper Missouri River was very high as compared to other tissues and ranged from 0.5–1.03 ppm. Ramelow, et al., 1989, have determined the content of Cd, Ag, Pb, As, and Zn in the edible parts of several species of fish caught from Calcasieu River and Lake Louisiana. These concentrations were found in the range of 0.02–0.08, <0.01–0.3, <0.2–0.5, <0.1–0.3, and 28 ± 7 ppm for Cd, Ag, Pb, As, and Cd respectively. The order of enrichment with heavy metals in these

species was as follows: fish or shrimp muscle < mussels < zooplankton, oysters, periphyton (Ramelow, et al., 1989).

The concentration of Cd, Zn and Hg in muscle and liver of several fish species from Samborombon Bay in Argentina, were determined (Marcovecchio & Moreno, 1993). In the liver the concentration of these metals were 4.14, 68.7 and 0.20 ppm for Cd, Zn and Hg, respectively (Marcovecchio & Moreno, 1993). The distribution pattern of zinc and cadmium was almost similar, where these levels were found to be higher in liver than in muscle, while the accumulation of mercury was similar in both liver and muscle. A direct relationship between fish size and the total mercury content were noted while cadmium and zinc did not show this pattern (Marcovecchio & Moreno, 1993).

Fish of different age from Lurnice River were analyzed for Pb, Cd, and Zn (Kroupa & Hatvich, 1990). The lead concentration in roach's kidney from Kostenicky brook was 0.67 ppm, while in the Luznic roach was lower (Kroupa & Hatvich, 1990). Pb and Cd levels in liver and kidney declined with age, while lead content in muscle did not show any significant change with age (Kroupa & Hatvich, 1990). They found that the Cd and Pb levels in the bream (*Abramis brama*), which are older than ten years, increased with age and the lead content increased only in the older specimens. However Zn content in the tissue declined with increasing age and the older specimens had less manganese content in their tissue. The effect of heavy metals on fish behaviour, growth, metabolism, blood and mineral contents, hematological and physiological responses have been reported (Handy, 1992; Atchison, et al., 1987; Ghazaly, 1992).

The relation of heavy metals content with body length and age of mackerel (*Scomberomous cavella*) caught from different states of U.S.A. has been studied (Grady, et al., 1989). The maximum concentrations of Zn, Cd, Cu, and Pb were found in the young fish. A decline in metals content with age and length were also observed (Grady, et al., 1989). The effect of heavy metals on the bone characteristics and development has been reported (Hamilton & Haines, 1989; Hamilton & Reash, 1988). The toxicity of trace metal mixtures to American Flagfish (*Jordanella floridae*) has been investigated in acidified soft water (Hutchinson & Sprague, 1986; Hutchinson & Sprague, 1987).

Recently, Guerrin, et al., 1990 studied the heavy metals concentrations in *Tinca tinca* and *Scardinius erythroptalmus* fish species which were introduced four years before in a treated wastewater treatment at Realmont, France.

Liver and kidney are considered as major accumulation organs in fish (Wildlife Service, 1985). The cadmium levels in liver and kidney were 0.056 and 0.157 ppm in Rudd species while in Fench species they were 0.058 and 0.149 ppm respectively (Guerrin, et al., 1990).

Biomonitoring of heavy metal distribution in the Western Mediterranean areas has been carried out by Hernandez, et al., 1992. Mullet species was used as a bioindicator of heavy metal pollution. The highest level of Hg found in fish muscle was 460 ppb and the mean levels of Hg ranged between 100–200 ppb. High concentration of Cd found in some stations were in the range of 100–500 ppb, while Pb levels ranged from 100–400 ppb (Hernandez, et al., 1992).

Recently, Habshi, et al., 1993, have studied the levels of Hg, Pb, Ni, and V in the edible parts of different species of fish collected from the western part of ROPME Sea area [(Regional Organization for the Protection for the Marine Environment) (RSA)] i.e, from Doha (Qatar) nearshore areas along the western edge of RSA ending in Kuwait. The mercury concentrations were higher than 0.5 ppm and its concentration increased with an increase in size and age of fish. No significant difference in Hg and Pb contents between the males and females were found (Habshi, et al., 1993). The mean concentrations of Pb, Ni and V were 1.63 ppm , 0.07 ppm and 4.19 ppm, respectively (Habshi, et al., 1993). These values of Hg, Pb, Ni, V are not considered a health hazard in comparison to metal concentrations reported in other regional seas (Anderlini, et al., 1981 and Literathy, et al., 1986).

1.3 Classification of heavy metals

Trace elements may be classified into essential elements, e.g. copper, zinc, manganese, cobalt, chromium and nickel and non-essential elements, e.g. lead and cadmium (Marquis, 1989). These elements have tendency to bioaccumulate by two processes namely metabolic and biosorption (Kumar & Mathur, 1991) and are nonbiodegradable. These elements can also be classified from the environmental pollution stand point into three category: (1) noncritical, (2) toxic but not very insoluble or very rare, and (3) very toxic and relatively accessible as shown in Table 1.1 (Wood, 1974). The different factors which affect the toxicity of the trace elements in aquatic environment (Bryan, 1976) are presented in Table 1.2.

1.3.1 Essential elements

Copper

Copper is an essential element for some enzymes and glycoproteins, and is an essential micronutrient in all organisms (Sorensen, 1991). It has the ability to stabilize sulfur radicals which is its main role in the biological systems (Moore & Ramamoorthy, 1984). Copper is necessary for the synthesis of hemoglobin, where it promotes the absorption of Fe from the gastrointestinal system transports Fe from tissues into plasma. It is also important in the formation of bone and brain tissues. Cu binds α -globulin in the blood and is transported to the liver, kidney, central nervous system, heart, bone, and muscle for storage (Sorensen, 1991).

The copper contents in marine fish are higher than those in fresh water species. The maximum concentrations in muscle tissue of fish collected from polluted fresh water exceed 1 ppm wet weight and ranged from 0.5–2 ppm, in the muscle of fish collected from marine waters, the copper level may reach 3–6 ppm in case of extreme conditions of environmental contamination (Moore & Ramamoorthy, 1984).

Copper does not pose a threat to most fisheries, even those in polluted waters due to low muscle contents (Moore & Ramamoorthy, 1984). There are many factors affecting Cu level in fish. An increase in hardness, alkalinity, salinity, organic level, pH, and fish size strengthens fish resistance to Cu (Sorensen, 1991). In contrast, elevated

Table 1.1

Classification of elements according to toxicity and availability (Förstner & Wittman, 1981)

Noncritical			Toxic but insoluble or very rare		Very toxic and relatively accessible		
Na	C	F	Ti	Ga	Be	As	Au
K	P	Li	Hf	La	Co	Se	Hg
Mg	Fe	Rb	Zr	Os	Ni	Te	Tl
Ca	S	Sr	W	Rh	Cu	Pd	Pb
H	Cl	Al	Nb	Ir	Zn	Ag	Sb
O	Br	Si	Ta	Ru	Sn	Cd	Bi
N			Re	Ba		Pt	

Table 1.2

Factors influencing the toxicity of heavy metals
in aquatic environment (Bryan, 1976)

Form of metal in water	<ul style="list-style-type: none"> inorganic organic 	<ul style="list-style-type: none"> soluble particulate 	<ul style="list-style-type: none"> ion complex ion chelate ion molecule colloidal precipitated adsorbed
Presence of other metals or poisons	<ul style="list-style-type: none"> joint action no interaction antagonism 	<ul style="list-style-type: none"> more-than additive additive less-than-additive 	
Factors influencing physiology of organisms and possibly form of metal in water	<ul style="list-style-type: none"> temperature pH dissolved oxygen light salinity 		
Condition of organism	<ul style="list-style-type: none"> stage in life history (egg, larva, etc.) changes in life cycle (e.g., moulting, reproduction) age and size sex starvation activity additional protection (e.g., shell) adaptation of metals 		
Behavioral response	<ul style="list-style-type: none"> altered behavior 		

temperatures increase the toxicity of Cu (Lydy & Wissing, 1988). The levels of Cu accumulated in blood, brain, spleen, gonads, and skeletal muscle are found to be lower than those found in the liver (Cross, et al., 1973; McKim & Benoit, 1974; O'Neill, 1981; Buckley, et al., 1982).

The most important source of copper is probably the contaminated food and not water. The rate of Cu uptake is directly related to exposure time and concentration, while it is inversely related to the presence of chelators and inorganic ions in the water (Moore & Ramamoorthy, 1984). McFarlane & Franzin, 1980, indicated a consistent positive correlation between copper in pike livers and fish age, while the residues in muscle tissue decrease with age and size of fish. Some species may be affected and their survival, growth, and rate of reproduction is reduced when they are exposed to chronic or sublethal levels of copper (0.02–0.2 ppm). One of the harmful effects of copper ions is its precipitation in gill secretions leading to death by asphyxiation (Tsai, 1979). Copper is found not to be acutely toxic to human because of its intermediate coordinate characteristic between hard and soft acids. Its moderate toxicity is due to its sequestering action on and precipitating the essential carboxylic acids (Moore & Ramamoorthy, 1984).

Zinc

The vertebrate body contains a large quantity of Zn which is also an essential element. Zinc plays an important role in the biosynthesis of nucleic acids, RNA and DNA polymerases, and it is an essential part of a number of enzymes (Sorensen, 1991). A lot of physiological process such as hormone metabolism, immune response and ribosomes and

membranes stabilization need zinc as reported by Moore & Ramamoorthy, 1984.

Brown & Chow, 1977, have found that Zn concentrations in muscle of omnivorous and carnivorous fish collected from industrial and agricultural areas of Great Lakes (U.S.A) range from 16–82 ppm and 3–9 ppm wet weight, respectively. Similarly, Vinikour et al., 1980, and Adams et al., 1980 reported that the average muscle Zn burden of yellow perch, bluegill, and black crappie fish were 106, 108 and 103 ppm respectively for the ones inhabiting recreational zone rivers in the U.S.A. The zinc contents in yellow perch, bluegill and black crappie species were 100, 109, and 101 ppm respectively in an industrial zone. The residues of Zn in marine fish muscle were low. Roth & Hornung, 1977 reported that the range of Zn concentration in the fish collected from the Mediterranean coast were 0.5–33 ppm showing little evidence of contamination. Moore & Ramamoorthy, 1984, reported that the Zn residues in black marlin from Australia ranged from 5.7–14.6 ppm. Brooks & Rumsey, 1974, have reported that the average concentrations of Zn in the tissues of eight species found in New Zealand sea. The levels in muscle, liver, kidney, heart, gonad, spleen, and gills were 8, 76, 78, 24, 93, 73 and 22 ppm respectively. Similarly, it was found that the ratio of zinc in liver : muscle of black marlin fish was 5.5 : 1 (Moore & Ramamoorthy, 1984). Generally, zinc concentration was not related to feeding habits (Moore & Ramamoorthy, 1984).

No correlation was found between Zn residues in muscle and fish age/size, despite the uptake of zinc by young fish is greater than the old ones (Moore & Ramamoorthy, 1984). However, zinc accumulation was

correlated with metabolic rate. Thus, fish size/age alters Zn accumulation, where the small fish have higher metabolism (Sorensen, 1991). The zinc levels in muscle and other organs vary with seasonal variation. Badsha & Sainsbury (1978) reported that the whole body Zn residues in five-bearded rockling from the Severn Estuary (U.K) were maximum during the spring and early summer and minimum or declined in August, which possibly refers to a change in diet composition during the summer. Exposure time and concentration, fish size, water hardness, length of acclimation to test solutions, feeding level, and trophic level are the main factors affecting or altering the Zn uptake by fish (Sorensen, 1991).

Zinc plays an important role in many biological functions; however, at higher concentrations it becomes toxic. Zinc at high concentration causes mortality, growth retardation, histopathological alternations, respiratory and cardiac changes, inhabitation of spawning, dysfunction of kidney and enzymes and alteration in schooling and reproductive behaviour in fish (Moore & Ramamoorthy, 1984, and Sorensen, 1991).

Zinc often interferes with sulfur or sulfhydryl groups in human biological system, therefore it is an essential element for biosynthesis of nucleic acids and polypeptides. Moreover, the deficiency of Zn may lead to healing delay, and suppression of enzymatic activity (Moore & Ramamoorthy, 1984). In addition, inhalation of Zn fumes from galvanizing bath may produce 'zinc fever', chills, fever and nausea (Duffus, 1983).

Manganese

Manganese is an abundant metal in nature and its compounds are used in making steel alloys, electrical coils, ceramics, dry-cells, matches, glass, dyes, in fertilizers, welding rods, as oxidizing agent and as animal food additives (Amdur, et al., 1991). The respiratory system and central nervous system are affected by Manganese. Chronic manganese poisoning causes liver cirrhosis, irritability, difficulty in walking, speech disturbances, and compulsive behavior (running, fighting and singing) (Amdur, et al., 1991).

Manganese is an essential element, and acts as a cofactor for a number of enzymatic reactions, especially those involved in phosphorylation, cholesterol, and fatty acids synthesis. Manganese is transported in plasma when bound to a β^1 -globulin (Amdur, et al., 1991). The main source of the intake of manganese is from food (Amdur, et al., 1991). The daily intake of manganese ranges from 2 to 9 mg. The biological half-life in the body is 37 days (Amdur, et al., 1991). Manganese activate many enzymes in vitro. It is involved in glucose utilization (Förstner & Wittman, 1981). It acts as a cofactor for pyruvate carboxylase, oxaloacetate decarboxylase, superoxide dismutases and diamine oxidase (Kendrick, et al., 1992).

Cobalt

Cobalt is a relatively rare element produced primarily as by-product of other metals such as copper. It is essential as a component of vitamin B₁₂ which is required for production for red blood cell and prevention of anemia (Amdur, et al., 1991). Lack of cobalt or manganese

causes malformation of bones (Love, 1980). Also the insufficient levels of cobalt in the diet of ruminants cause wasting diseases and the implantation of cobalt powder causes malignant tumours in muscle (Hay, 1991). The ingestion of excessive amount of cobalt by humans and mammals causes polycythemia. Cobalt toxicity results in vomiting, diarrhea and a sensation of warmth. Oral administration in high levels produce goiter. The intravenous administration causes face flushing, blood pressure increasing, slowed respiration, dizziness, linnitus, and deafness due to nerve damage (Amdur, 1991). Also the excessive intake of cobalt lead to cardiomyopathy (Amdur, 1991).

The increase of cobalt level tend not to cause significant accumulation. It is observed that about 80% of the ingested cobalt is excreted by urine, about 15% is excreted in the feces, and the rest excreted by other secondary routes (Amdur, et al., 1991).

The largest total fraction of cobalt is found in muscle while the fat has the highest concentration. Significantly higher levels of cobalt were found in liver, heart and hair than other organs; however the concentration in these organs is relatively low (Amdur, 1991).

The total body burden has been estimated as 1.1 mg (Amdur, et al., 1991). The normal levels of cobalt in human urine and blood are 98 and 0.18 µg/litter, respectively (Amdur, et al., 1991).

Chromium

The chemistry of chromium is of considerable interest, chromium III is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism, but chromium VI is reported to be

toxic (Friman, 1978). The carcinogenicity of chromium VI is considered in terms of the uptake/reduction model. Chromium is an essential micronutrient and widely distributed element for the metabolism of fat and carbohydrates for most organisms (El-Shahawi, 1993). The chromium concentrations in fresh water fish normally fall below 0.25 ppm wet weight, while it is slightly higher in marine fish (Moore & Ramamoorthy, 1984). The chromium content in flesh, bone and gill taken from two species of Lethrinus family (*Lethrinus mahsenoides* and *Lethrinus nebulosus*) caught from the Red Sea have been measured (Abdelmoniem & El-Deck, 1992). The chromium content in various residues in wrass from the Mediterranean (Lebanon) were found 1.6 and 1 ppm wet weight for several fish species (Shiber, 1981; Roth & Hornung, 1977). Brook & Rumsey, 1974 reported that the average concentration of chromium in the muscle, liver, kidney, heart, gonad, spleen and gill of eight marine species from New Zealand were 0.02, 0.1, 0.2, 0.3, 0.2, 1.2 and 0.5 ppm, respectively.

The average concentrations of chromium in the tissues of seventeen marine species were found in the range 0.36–13.2 ppm (Jaffar, et al., 1988). The study shows no correlation between the concentration of chromium in fish muscle and in water.

The chromium concentrations in fish are often not related to feeding habits as previously reported (Moore & Ramamoorthy, 1984). Mathis & Cummings, 1973 reported that the Cr levels in omnivorous fish from Illinois River (U.S.A) were average 6.21 ppm wet weight compared to 0.12 in carnivorous fish. In the Kennebec River (U.S.A) the burdens of omnivorous white suckers ranged between ≤ 0.01 –0.22 ppm dry weight,

whereas carnivorous yellow perch and smallmouth ranged between ≤ 0.01 and $0.15\text{--}1.67$ ppm (Friant, 1979). Fish are less susceptible to the toxic effects of chromium than invertebrates. The pH, size of fish and temperature effect on the intoxication rate (Moore & Ramamoorthy, 1984). Levels of chromium in several marine organisms collected from the Castellon Coast during 1986 and 1987 were determined by Hernandez, et al., 1990.

Chromium (III) is not acutely toxic because the chromium complexes in abiotic matrices are highly stable. Since the chromium species have strong affinity for oxygen donors rather than sulfur donors that present in biomolecules (El-Shahawi, et al., 1994). It is known that Cr VI is more toxic than Cr III because the former has a high rate of absorption through intestinal tracks (Moore & Ramamoorthy, 1984). Epidemiological studies by Sittig, 1980, have shown a positive relationship between cancer incidence and occupational exposure to chromate species. Chromates also cause lung cancer, it act as irritants to the eyes, nose, throat and may cause chromosome abnormalities (Duffus, 1983).

Nickel

Nickel is less toxic element to fish compared to copper, mercury, lead, zinc, cadmium, silver, chromium and arsenic. In sea water the acute toxicity of nickel is reduced because of its competitive interactions with cations. Also the water hardness affects Ni toxicity, for, as the hardness increases the nickel toxicity decreases (Moore & Ramamoorthy, 1984).

Nickel play a main role in the metabolism. It interacts competitively with Ca, Co, Cu, Fe and Zn in the animals (Moore & Ramamoorthy, 1984). Few species of fresh water fish were investigated by Hutchinson et al., 1975 for Ni presence. The Ni levels were ranged from 9.5–13.8 ppm wet weight. Wright (1976) reported that the Ni level of marine fish collected from NE coast of England was ranged from 0.5–7.2 ppm. However, other studies in other areas showed that the residues are <0.1 ppm. The concentration of Ni in the muscle are generally slightly lower than in liver, kidneys, and gills (Moore & Ramamoorthy, 1984).

Nickel does not accumulate through the food chain. Mathis & Cummings, 1973, reported that the average concentrations of Ni in the sediments, invertebrates, and the muscle of omnivorous and carnivorous fish were 27 ppm dry weight, 11, 0.18 and 0.13 ppm wet weight respectively. Moreover, it is found that muscle residues of Ni may either increase or remain constant as the fish grows (Moore & Ramamoorthy, 1984). Nickel found to cause death to fish by asphyxiation and consistent with the high nickel residues in gills, because the diffusion capacity of gill is declined by Ni. Nickel also increases the lamellar membrane thickness as reported by Moore & Ramamoorthy (1984).

Nickel is a micronutrient for most organisms; however, if its amount is increased it will cause toxic effects as noted by Moore & Ramamoorthy, 1984; Duffus, 1983. The acute toxicity of nickel comes from its competitive interaction with Ca, Co, Cu, Fe and Zn. It is known that nickel is highly surface active, so it adheres to breathable air-borne particles. Thus, its inhalation may lead to nasal, laryngeal, and lung cancers. Moreover, nickel may cause teratogenic effects for mammalian

and avian embryos as reported by Gilani & Marano, 1980; Sunderman et al., 1980.

1.3.2 Non-essential elements

Lead

More than 90% of the lead under normal conditions retained in the body is in the skeleton (Sorensen, 1991). The Pb inhibits the biosynthesis of heme because of its affinity for thiol and phosphate containing ligands. Thus it affects the permeability of the membranes of kidney, liver and brain cells. Therefore, the functioning of these tissues would be reduced or completely broken down (Förstner & Wittmann, 1981). Lead tend to accumulate in tissues especially in the liver and kidney, thus it could be redistributed to the bones, teeth and brain (Duffus, 1983).

Several studies have shown that there is no relation between species feeding habits and size of fish and concentration of tetraalkyl lead in tissues (Moore & Ramamoorthy, 1984; Chau, et al., 1980). The sensitivity to Pb of smaller fish were found more than larger fish due to the higher metabolic rates of the small fish (Sorensen, 1991). Acute Pb toxicity was found inversely proportional to water harness (Sorensen, 1991). Varanasi & Gmur, 1978, reported that gills are the most efficient site of Pb uptake. Several authors have found that Pb tend to accumulate higher in kidney, gill, and liver tissues of different species during aqueous or dietary exposures (Holcombe, et al., 1976; Merlini & Pozzi, 1977; Varanasi & Gmur, 1978; Reichert, et al., 1979).

Lead concentration in skeletal muscle are lower than those of other tissues because of the low binding rate for Pb to sulfhydryl groups in muscle; also because of the low solubility and restricted relocation of Pb salts (Moore & Ramamoorthy, 1984). The toxicity of lead on fish range from mortality to subtle effects on reproduction, growth and behaviour (Sorensen, 1991).

Lead uptake and accumulation in gill, liver, kidney, erythrocyte is proportional to exposure time and concentration (Hotcombe, et al., 1976). The pH and temperature of the solution are important factors (Hotcombe, et al., 1976; Merlini & Pozzi, 1977; Somero, et al., 1977). The accumulation of Pb increases with increasing pH and temperature. Moreover, Pb accumulation is altered by salinity where fresh water species accumulate more Pb than marine species (Somere, et al., 1977).

Cadmium

Cadmium accumulates in gill, liver and kidney of fish through binding with cysteine residues of metallothionein or components of other Cd-binding proteins (Moore & Ramamoorthy, 1984; Sorensen, 1991; Woodworth, et al., 1983; Wofford & Thomas, 1984). The high affinity of Cd for sulfhydryl groups leads to an increase in the bioaccumulation and toxicity of the element (Sorensen, 1991).

Most published environmental studies indicate the Cd levels in the whole body of fish ranged from 0.2 to 8.0 ppm on dry basis. Sorensen, 1991, reported that muscles have low Cd levels because of the elevated concentration of cystine and methionine in comparison to other amino acids. The absence of sulfhydryl groups in these sulfur-rich amino acids

plays an important role in decreasing Cd binding in skeletal muscle (Sorensen, 1991). The Cd uptake is influenced by localization in sediment contact, in the benthic fish the whole body levels of Cd are higher than pelagic fish (Ney & Van Hassel, 1983). The Cd accumulation in fish is also affected by diet, i.e. food habits.

The most important route of Cd uptake is gastrointestinal tract than the gill route as the aquatic ecosystems become more contaminated with Cd (Sorensen, 1991). The gill, liver, kidney and/or gastrointestinal tract tissues are the most important organs in Cd accumulation (McFarlane & Franzin, 1980; Ney & Van Hassel, 1983; Bendell-Young, et al., 1986). Benoit, et al., 1976, have exposed 38.0 k brook trout to 3.4 ppb of Cd; they found that the kidney, liver, and gill accumulate the greatest amount of Cd. The greater levels of Cd found in kidney were more than in liver in brown trout species (Gottofrey, et al., 1988), rainbow trout (Thomas, et al., 1985), and white suckers (Bendell-Young, et al., 1986). The hepatic uptake of Cd in few cases were found to be higher than renal uptake of Cd (Bonnell, et al., 1960). It is found that Cd levels are higher in livers than skeletal muscles. In muscle Cd levels range from 0.007–1.40 ppm, dry weight (McFarlane & Franzin 1980; Bendell-Young, et al., 1986; and El Nabawi, et al., 1987). The hepatic and renal Cd concentrations provide useful information in long-term exposures because of its binding and mobilization by metallothionein (Sorensen, 1991). Liver tend to be the preferred organ for Cd accumulation in fish than kidney because of Cd releasing with urinary proteins (Fribery, et al., 1974) as well as the increasing of variability in accumulation patterns in the kidney compared with the liver (Smith, et al., 1976). The kidney tend to accumulate Cd

continuously after exposure ceases, as a result of Cd redistribution from large stores in the liver (Sorensen, 1991).

Cadmium poisoning may reach humans following their consumption of contaminated fish or water. Itai-Itai disease is an example of Cd intoxication. Residents of Toyama Prefecture (Japan) from the 1940s to the 1960s (Friberg, et al., 1974), the patients showed signs of osteomalacia in bones and calcification and pyelonephritis in kidneys, which resulted in skeletal deformation and renal dysfunction (Moore & Ramamoorthy, 1984). The Cd has a long half-life (10–30 years), therefore, the ingestion of small amount of contaminated fish over long periods, and because of Cd accumulation in organs, may lead to cadmium intoxication. So consumption of fish with residues of >0.5 ppm wet weight has been restricted by regulatory standards (Moore & Ramamoorthy, 1984). For different animals teratogenic and embryotoxic effects of cadmium have been documented (Moore & Ramamoorthy, 1984). Also cadmium may lead to cellular damage in fetal vascular endothelium, thereby decreasing utero-placental blood flow, anoxia or lack of essential nutrients may be resulted causing fetal death (Moore & Ramamoorthy, 1984). Several studies have indicated a causal relationship between exposure to cadmium and cancer incidence.

1.4 Aim of Work

Since the exploitation of the oceans as future sources of protein due to the growing world population, a greater concern must be given for metal pollution problem. The United Arab Emirates (UAE) is a coastal

country. Its shores extend along a distance of 700 km. Fishes are important for the UAE economy; they are consumed locally and exported in significant amount. The fish production in UAE in 1991 was estimated to be 92 thousand tons.

UAE is a country which has no baseline information of the maximum permissible concentrations of heavy metals in fishes. Therefore, studying the concentration of heavy metals in marine fishes is not only important but also would be used as marine pollutants indicators.

Many substances pollute the marine environment but non-biodegradable compounds are the most dangerous. Heavy metals are notable for their high toxicity. The dangers involved from the presence of heavy metals in the marine environment derived not only from their persistence and toxicity, but also the remarkable degree of concentration they undergo through the trophic chain, thus becoming a serious danger to man. These species can enter the marine media from various sources, e.g. crop spraying, rainfall, run-off from agricultural land, direct entry from industrial and sewage effluent. The detection and determination of these metals in different organs of fish are of great economic and health importance.

Information concerning levels of heavy metals in *lentjan* species [Family: Lethrinidae (Toelost)] in Ras Al-Khaima are scarce. Therefore, the main objective of present investigation was to estimate and provide information on heavy metals level (Cu, Zn, Pb, Mn, Ni, Cr, Cd, Co) that have tendency to bioaccumulate via metabolic and biosorption processes in 5 organs (muscle, skin, liver, kidney, heart) of the *Lethrinus*

lentjan species. The choice of this species was tentative as they are widely consumed. It is hoped that the application of flame atomic absorption for the determination of the tested heavy metals in certain types of fish will give enough data about the metal content in the tested fish organs and could be applied to other fishes as well.

This work was held to investigate the relationship between metal content in different tissues and length of the fish (age). Also to study the distribution of such metals in fish tissues.

One of the most important aim is to investigate the maximum amount of Sheiry fish should be consumed by U.A.E residents that will not exceed the maximum permissible levels.

CHAPTER 2
MATERIALS AND METHODS

2. Materials and Methods

2.1. Reagents and materials

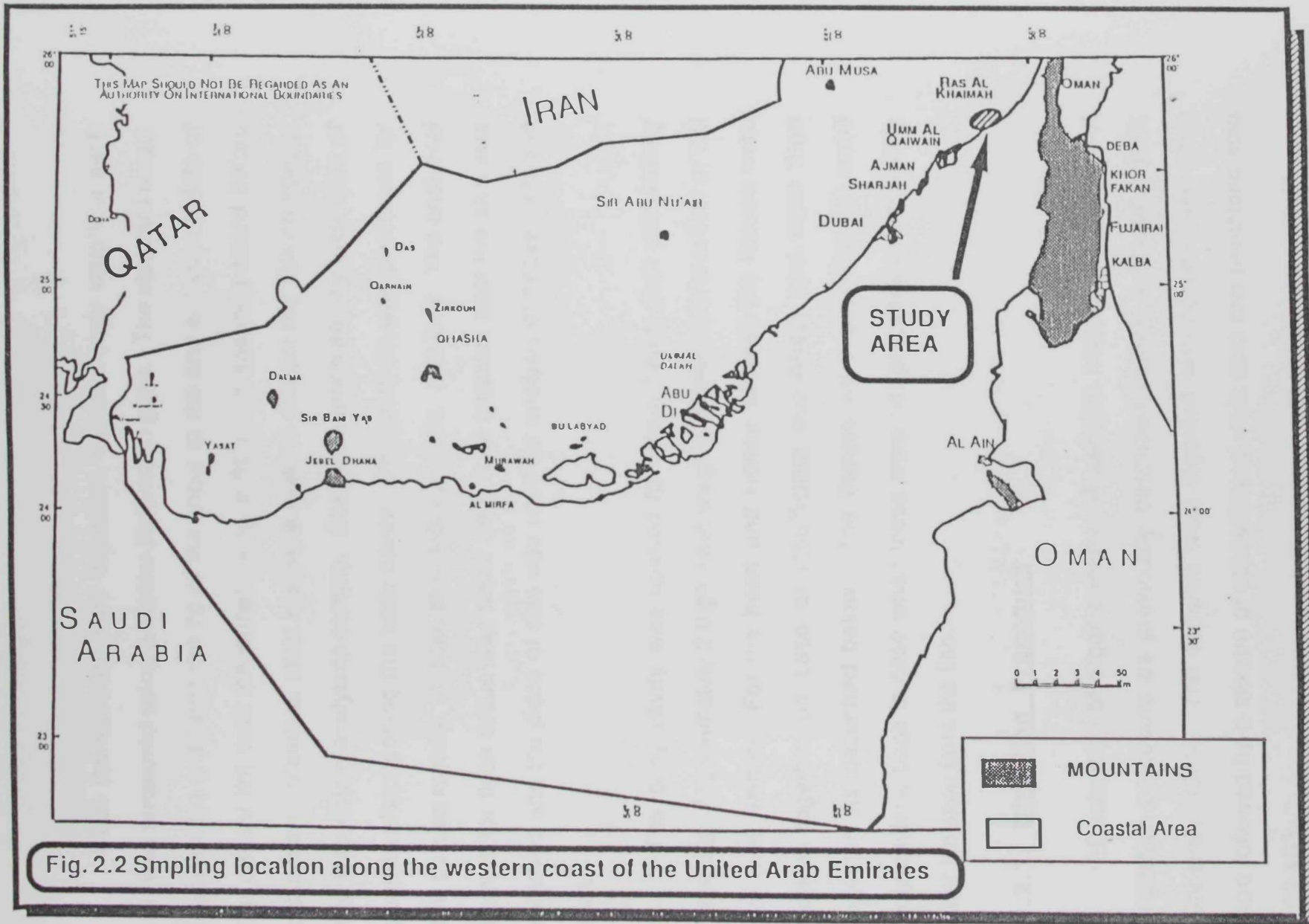
All reagents used were of analytical reagent grade: copper sulphate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; manganese sulphate MnSO_4 ; zinc chloride ZnCl_2 ; cadmium sulphate pentahydrate $\text{CdSO}_4 \cdot 5\text{H}_2\text{O}$; nitric acid HNO_3 and perchloric acid HClO_4 were of analytical reagent grade and were used without further purification. Stock solutions (1mg ml^{-1}) of these elements were prepared in double distilled water by dissolving the exact weight of each salt separately in 100 ml measuring flask and the solutions were diluted with double distilled water whenever is required.

2.2. Sampling and preparation

A total of 214 fish of *Lethrinus lentjan* (Fig. 2.1) species of both sex were collected from Ras Al-Khaimah fish market which is a market for fish catch from western coast of United Arab Emirates (Fig. 2.2). Sampling was carried out every two weeks through the period of May and June 1993. Each time about 50 samples of different sizes were collected, placed in ice box, transported to the laboratory and finally kept in freezer prior to analysis.



Fig. 2.1 *Lethrinus lentjan* fish



Once the samples were defrosted, the total body weight of each fish was measured using a Mettler Balance in gram. The standard length in millimetre unit (from the tip of the snout to the end of hypural plate of the caudal fin) was measured using a 50 cm measuring board before dissection. Stainless steel kits were used to dissect the fish on special board to obtain analytical sample. Sex was determined by inspection of gonads after opening the body cavity. The analysis was conducted for five tissues namely, muscle, skin, kidney, heart, and liver. The analytical sample for flesh tissue was taken from axial muscles after the skin was removed and the piece of skin was used for analysis of heavy metals in skin.

The body cavity was opened to obtain heart, liver and kidney samples. Approximately 2.0 gm (wet weight) of flesh, skin and liver or 0.8 gm (wet weight). For the heart and kidney samples the tissues were pooled together (in case of insufficient quantities) and were then digested as described below. The tissues were preserved in small polyethylene bags in case when these were not processed immediately after isolation from the fish.

2.2.1. Digestion Procedure

Destruction of organic matter of samples was carried out by wet digestion procedure as previously described (Barak & Mason, 1990; Christian, 1980). The samples were digested with concentrated nitric acid followed by a mixture of concentrated nitric acid and perchloric acid (4:1 v/v).

The procedure applied was as follows: In order to avoid contamination material used in analysis, all glasswares were cleaned with detergent followed by 10% HNO₃ solution and repeatedly rinsed with deionized water. Standard stock solution of 1000 ppm for each element was prepared from BDH chemicals, England. Double distilled water was used in all preparation and whenever is required.

Each thawed (previously weighed) sample was taken in 100–125 ml Erlenmeyer flask, 8 ml concentrated nitric acid 70% (Riedel–deHaën) was added. The samples were then kept on a hot plate (Nickel Electro) maintained at boiling point temperature placed in flow hood. Heating was continued, with occasional shaking till the volume of the resulting solution reduced to 1–2 ml (about $\frac{1}{2}$ –1 hour). The reaction flask were then cooled to room temperature and a 10 ml mixture of "Analar" HNO₃–HClO₄ (4:1 v/v) was added and the samples were then heated on a hot plate till the digestion completed (almost $\frac{1}{2}$ –1 hour). Heating was then continued until dryness. The residues were then diluted with water. Digestion of the sample was carried out in batches of 24–30 samples and a minimum of two reagent blanks were used with each batch which were identically treated to check for possible contamination. For the samples which could not be completely digested, further treated with 2–5 ml of the digestion mixture and one of the reagent blank was also treated as well.

In this procedure the nitric acid boils off and care must be taken to prevent evaporation of the perchloric acid to near dryness (Christian, 1980). Finally, after digestion, the samples were left to cool at room

temperature and the final solution were made up to 25 ml with deionized water.

2.2.2 Analytical determinations

Analyses for heavy metals Cu, Zn and Cd were carried out using flame atomic absorption spectrophotometers (GBC 906) equipped with background corrector, autosampler and recorder.

Multi element standards were prepared for all the elements from 1000 ppm stock solutions. Dilution of standards was carried out using deionized water for calibration the instrument.

A mean of three readings to each sample was recorded, subtracted from blank reading, then calculated using the following equation:

$$C \text{ (ppm)} = \frac{(X-B) \times V}{W}$$

C = Element Concentration (ppm)

X = Mean of three readings (ppm)

B = Blank reading (ppm)

V = Volume (ml)

W = Weight of sample (gm)

2.3. Equipment

A GBC 906 Flame Atomic Absorption Spectrometer with fuel-rich and stoichiometric air-acetylene flames were used throughout. Air was supplied through Pu 9003 air compressor, fitted with tilter and regulator, moisture trap, quite running and oil free pumps; acetylene was delivered

from cylinders after passing through concentrated sulphuric acid for purification. The optimum conditions of copper (II), manganese (II), zinc (II) and cadmium (II) are tabulated in Table 2.1.

Parameter	Optimum Value	Range	Unit
Flow rate	1.0	0.5 - 1.5	L/min
Loop diameter	1.0	0.5 - 1.5	cm
Flow rate of reagent	1.0	0.5 - 1.5	L/min
Reagent concentration	1.0	0.5 - 1.5	mg/L
Sample concentration	1.0	0.5 - 1.5	mg/L
Sample flow rate	1.0	0.5 - 1.5	L/min
As flow rate	1.0	0.5 - 1.5	L/min
Sample pressure	1.0	0.5 - 1.5	atm
Flow rate of reagent	1.0	0.5 - 1.5	L/min
Reagent concentration	1.0	0.5 - 1.5	mg/L
Sample concentration	1.0	0.5 - 1.5	mg/L
Sample flow rate	1.0	0.5 - 1.5	L/min
As flow rate	1.0	0.5 - 1.5	L/min
Sample pressure	1.0	0.5 - 1.5	atm

Table 2.1.

The optimum instrumental parameters for determination of copper (II), zinc (II), manganese (II), and cadmium (II) by atomic absorption spectrometry.

	Cu	Zn	Mn	Cd
<u>* Instrument Parameters</u>				
System Type	Flame	Flame	Flame	Flame
Matrix	Acidic Water	Acidic Water	Acidic Water	Acidic Water
Lamp Current (mA)	4.0	5.0	5.0	3.0
Wave length (nm)	324.7	213.9	279.5	228.8
Slit Width (nm)	0.5	0.5	0.2	0.2
Slit Height	Normal	Normal	Normal	Normal
Instrument Mode	Absolute BC off	Absolute BC off	Absolute BC off	Absolute BC off
Sampling Mode	Auto sampling	Auto sampling	Auto sampling	Auto sampling
<u>* Gas Parameter</u>				
Flame Type	Air-Acetylene	Air-Acetylene	Air-Acetylene	Air-Acetylene
Acetylene Flow	1.51	1.28	1.61	1.20
Air Flow	10.3	10.0	10.0	10.0
<u>* Sampling Parameters</u>				
Delay Time(s)	2	2	2	2
Rinse Time(s)	5	5	5	5
Recalibration Rate	30	30	30	30
Rescale Rate	15	15	15	15
Rescale Std. No.	1	1	1	1
<u>* Data Collection Parameters</u>				
Read Time(s)	3	3	3	3
Expansion factor	1	1	1	1

CHAPTER 3

RESULTS

3. Results

Heavy metals are potentially harmful in traces to man and his living resources. With increased industrialization and urbanization a whole gamut of these inorganic water pollutants have found their way to fresh water through natural run off, thus disturbing the delicate balance of the aquatic ecosystem resulting in several irregularities in fish physiology (Swain & Sinclair, 1994). As fish are located on the end of the aquatic food chain, they may clearly reflect the status of water quality and may act as an indicator of water pollution in terms of heavy metals content (Bryan, 1984). Thus pollution resulting from the uptake, concentration and retention of the heavy metals by fish may be monitored through fish analysis and potential health hazards for the consumer may be averted. Therefore, it is important to study the contents of the toxic elements in marine fishes and organisms because these are often used as indicators of marine pollution (Marce, 1987) and in addition to monitor the source points and sites of dumping ground.

Several investigations related to the heavy metal distribution in the aquatic organisms have been undertaken (Jaffar, et al., 1988). Heavy metals when present beyond traces are toxic to humans since they may combine with the proteins and may not cause any poisoning, but when their concentrations exceeds the tolerance limit, they become a real health concern. Heavy metals such as chromium, nickel, cadmium, arsenic, mercury and lead are toxic pollutants of the aquatic environment.

Some other elements such as zinc produce acute toxicity to fresh water fish and invertebrates (Eaton, et al., 1980).

In aquatic systems the availability of a metal to organisms depend on many physico-chemical as well as biological factors (Dallinger, et al., 1987). Availability is influenced by the chemical speciation of ionic metal forms, the chemistry of water and the relative distribution of metal between soluble and particulate fractions. It has been reported by Dallinger, et al., 1987, that the metal uptake as well as the toxicity of heavy metal may substantially depend on the chemical species involved. Thus, the study reported here embraces the above cited objectives through the following considerations: Firstly, it presents the first comparative data on the heavy metal contents in local fresh water fish and relevant waters; secondly, it attempts to establish a correlation between the heavy trace metal contents in the local water and relevant water so that a background enrichment ratio could be defined for pollution free area of catch; thirdly to determine whether these levels of heavy metals constitute a health hazard for the consumers; and finally, the results obtained were reviewed from the view point of trace essential metals content including zinc, cobalt, copper, nickel, chromium and manganese and non-essential metals lead and cadmium in five organs namely muscle, liver, kidney, heart and skin of *Lethrinidae* family fish. The choice of these species was tentative as they are widely consumed in the United Arab Emirates and some of them are currently under study for expression of our export market. Attempts were also made to study the distribution and bioaccumulation of the tested metals in the various tissues and correlate tissue levels with the age and sex of fish (*Lethrinus*

lentjan) if possible. Thus it became imperative to estimate the heavy metal contents from a nutritional and a health hazard point of view.

The analysis of 214 *Lethrinus Lentjan* fishes for copper, zinc, manganese, nickel, cobalt, chromium, lead and cadmium in their muscle, liver, skin, kidney and heart were carried out for female, male and not determined sex (N) fish at different ages. In order to avoid contamination, material used in analysis were pyrex and polyethylene. Glass material was subject to an ordinary wash and subsequently treated with HNO₃ 1:1 for 4 hours and repeatedly rinsed with distilled and deionized water.

3.1. Distribution of essential elements in the different fish tissues

The analyses of the tested essential metals namely copper, zinc, manganese, cobalt, chromium and nickel were carried out in the organs muscle, liver, skin, kidney and heart of *Lethrinus Lentjan* species.

Distribution of copper

Copper ions are able to accumulate into most of the fish organs from natural fresh water or from any other sources. A majority of studies related to copper ions concentrations in aquatic organisms emphasize bioaccumulation (the ability of an organism to concentrate an element above abiotic environmental levels) or biomagnification (the tendency for elements to be concentrated with tropic level) transfer (Vinikour, et al., 1980). The uptake of copper in the various fish organs is critically examined. The accumulation patterns of copper in liver, skin and muscle of female and male is summarized in Fig. 3.1 and Table 3.1. It can be

Table 3.1

Mean (\pm SD) heavy metal concentration in *Lethrinus Lentjan* [female, male and neutral (not determined sex — N)] tissues (ppm) collected from Ras Al Khaima (U.A.E coast water)*

Tissue	Sex	No. **	Cu	Zn	Mn	Cd
Liver	Female	140	5.61 \pm 1.97	70.08 \pm 38.62	1.35 \pm 0.2	0.78 \pm 0.33
	Male	22	3.52 \pm 0.25	34.1 \pm 4.7	0.97 \pm 0.21	0.63 \pm 0.12
	N	29	4.43 \pm 0.58	39.54 \pm 2.78	1.15—0.05	0.51—0.2
		191	x 4.88 \pm 1.71	55.3 \pm 32.98	1.22 \pm 0.23	0.66 \pm 0.28
Skin	Female	139	0.28 \pm 0.08	42.28 \pm 8.51	0.12 \pm 0.03	0.08 \pm 0.03
	Male	22	0.4 \pm 0.18	31.42 \pm 2.95	0.11 \pm 0.2	0.06 \pm 0.07
	N	39	0.35 \pm 0.14	37.75 \pm 8.1	0.27 \pm 0.12	0.11 \pm 0.08
		200	x 0.33 \pm 0.13	38.59 \pm 8.35	0.16 \pm 0.11	0.08 \pm 0.06
Muscle	Female	150	0.17 \pm 0.06	3.3 \pm 0.28	0.1 \pm 0.02	0.12 \pm 0.02
	Male	21	0.16 \pm 0.02	2.82 \pm 0.15	0.08 \pm 0.02	0.09 \pm 0.01
	N	43	0.18 \pm 0.11	3.61 \pm 0.45	0.13 \pm 0.02	0.11 \pm 0.04
		214	x 0.17 \pm 0.06	3.31 \pm 0.39	0.11 \pm 0.02	0.11 \pm 0.02

* *x* is the average concentration of the element in female, male and N tissues.

* ND = Not detected

** Number of fish sample

seen that the accumulation of copper in muscle, skin and liver follow the order:

liver > skin > muscle

and the highest values of copper in liver were found in female as compared to male.

The copper content in male and female in the different fish organs, e.g. liver, skin and muscle were found to depend on the fish size. The results obtained are summarized in Figs. 3.2—3.4. The average copper concentration (*Table 3.1*) in skin and muscle for female were found to be 0.28 ± 0.08 and 0.17 ± 0.03 ppm, while in male fish the mean concentration of copper were found to be 0.40 ± 0.18 and 0.16 ± 0.02 ppm, respectively. In liver (*Table 3.1*) the mean concentration of copper in female and male were found to be 5.61 ± 1.97 and 3.52 ± 0.25 ppm, respectively. In the muscle tissues (*Fig. 3.4*) the highest copper concentration were found higher in smaller fish size than large fish size and attained a constant value at large fish size. A clear decline in the copper content in the fish muscle were observed at 16 cm fish length. The accumulation of copper concentration in the fish liver is dependent on the fish length (*Fig. 3.2*). The accumulation pattern of copper in liver and the different sex follow the order:

male < female

at moderate fish length (17—21 cm). In the fish skin (*Fig. 3.3*) the copper concentration decreases at small fish size and increases with increasing fish length up to 24 cm.

The mean concentration of copper in the heart and kidney (*Table 3.2*) were found to be 3.87 ± 1.26 and 3.25 ± 1.52 ppm, respectively. Standard deviation and standard error in both heart and kidney are also given in *Table 3.2*.

Distribution of zinc

The bioaccumulation of zinc in liver, skin and muscle organs for female and male of *Lethrinus lentjan* fish is summarized in *Fig. 3.5*. The results obtained from the analyses of fish in female and male follow the sequence of order:

liver > skin > muscle

The mean concentration of zinc in the muscle, skin and liver was found 3.31 ± 0.39 , 55.3 ± 32.98 and 38.59 ± 8.35 , respectively (*Table 3.1*).

The accumulation of zinc in liver and skin was found slightly depend on the fish size. The obtainable results are shown in *Figs. 3.6—3.8*. Slightly increase in zinc content in liver and skin was found at large fish size as compared to small fish size (*Fig. 3.6*). The accumulation of zinc in liver fish of female (*Fig. 3.7b*) was found higher than in male (17—20 cm). More or less similar behaviour was also obtained in the zinc content in female skin as compared to male at moderate fish size (17—20 cm) as shown in *Fig. 3.8b*.

The relationship between the zinc content in fish muscle and the fish size was also investigated. The results obtained are given in *Fig. 3.9*. The zinc concentration is slightly decreases with increasing fish size

Table 3.2

Levels of heavy metals in *Lethrinus lantjan* heart and kidney in pooled samples*

Element	Kidney x	Std. Dev.	Std. Error	Heart x	Std. Dev.	Std. Error
Cu	3.25	1.53	0.22	3.87	1.26	0.18
Zn	43.26	16.87	2.46	32.38	10.19	1.47
Mn	0.64	0.24	0.04	0.31	0.17	0.03
Co	0.61	0.4	0.06	0.91	0.73	0.12
Cr	0.28	0.18	0.03	0.38	0.29	0.06
Ni	0.88	0.62	0.1	0.97	0.74	0.14
Pb	1.83	1.51	0.26	2.64	2.06	0.34
Cd	0.3	0.14	0.02	0.34	0.23	0.04

* x represent the mean of n = 5 measurements.

up to 20 cm (*Fig. 3.9a*). The sequences of zinc content in female and male fish (*Fig. 3.9b*) follow the order:

female > male.

The distribution of zinc content in fish heart and in kidney was also investigated and the results obtained are given in Table 3.2. The mean concentration of zinc in heart and kidney was found to be 32.38 ± 10.19 and 43.26 ± 16.87 , ppm, respectively.

Distribution of manganese

Many substances pollute the marine environment, but non-biodegradable compounds are the most dangerous (Bryan, 1984). Manganese is notable for its toxicity and the dangers involved from its occurrence in the marine environment derive not only from its persistence and toxicity but also the remarkable degree of concentration. Manganese species undergo through the trophic chain, thus becoming a serious danger to man. The bioaccumulation of manganese in marine organisms, e.g. fish depends on exposure time and metal concentration in the water (Bryan, 1984; Marce, 1987). Therefore, metal levels in marine fish can be reached much higher values than those in the sea water (Bryan, 1984). Other factors affecting bioaccumulation of manganese in fish are physiological conditions, growth, salinity and temperature, age, position relative to shoreline and water depth and pollutant interactions (Hernandez, et al., 1990). On the other hand the manganese toxicity for the marine organisms in particular fish depends also on factors such as temperature, hardness and salinity.

The analyses of manganese in fish liver, skin and muscle were carried out for female and male fish. Fig. 3.10 shows the average concentration of manganese in the three organs. The accumulation pattern of manganese in the liver, skin and muscle follow the order:

liver > skin > muscle

and the average concentration of manganese was found 0.11 ± 0.02 , 0.16 ± 0.11 , 1.22 ± 0.233 ppm in muscle, skin and liver, respectively.

The bioaccumulation of manganese in liver was found to depend on fish size and sex. The results obtained are summarized in Fig. 3.11. It can be noticed that the accumulation pattern of manganese attained a constant value around 1.3 ppm in the range 14—22 cm fish size in fish liver and slightly decreases at large fish size (≥ 23 cm). The average concentration of manganese in fish liver of female was found high as compared to male fish at moderate fish size 17–20 cm while at small fish size (≤ 17 cm) no differences in manganese content in female fish was determined. The manganese content in fish liver of female (*Fig. 3.11b*) increases with increasing fish size.

The accumulation of manganese in fish skin and muscle were found to depend on fish size and sex. The obtainable results are given in Figs. 3.12 and 3.13. In fish skin (*Fig. 3.12*) the distribution of manganese was found high for small fish size 12–13 cm (approximately 0.32 ppm). The concentration patterns of manganese in fish muscle were found high for small fish size and decreases with increasing fish size (*Fig.*

3.13). The distribution of manganese in the muscle for male and female fish follow the order (*Fig. 3.13*):

female > male

at fish size 18—20 cm.

The accumulation of manganese in fish kidney and fish heart was also investigated (*Table 3.2*). The concentration of manganese in fish heart was found to be 0.31 ± 0.17 ppm while for fish the kidney was found equal to 0.64 ± 0.24 .

3.2. Distribution of non-essential elements

The non-essential elements cadmium and lead have been shown to exert a wide range of effects on fish from metabolic and physiological to behavioral and ecological (Forstner & Wittmann, 1981). The effects observed include disturbances in osmoregulation, respiration, tissue damage, reduced energetic resources and poor performance (Ghazaly, 1992). The extent of such effects depends on the inherent toxicity of the metal, its concentration, its chemical form, the species affected, the animal condition and the characteristic of the milieu.

Distribution of cadmium

Cadmium is the most serious metallic contaminant which man has to deal in the latter part of the twentieth century. Cadmium frequently present in discharges from industrial processes is of great importance to those concerned with the suitability of water for aquatic life, especially fish because of the relatively high toxicity. Cadmium has been shown to

exert a wide range of effects on fish, from metabolic and physiological to behavioral and ecological. Thus, cadmium has been considered one of the most hazardous environmental contaminants resulting from modern industrialization and subsequently it has been the subject of many studies related to its human health effects. Thus, the purpose of this study has been focussed on the quantitative measurements of cadmium in the different fish organs for male, female.

Cadmium levels in the fish liver, skin and muscle are presented in Fig. 3.14. The accumulation pattern of cadmium in liver, skin and muscle follow the order:

liver > muscle > skin.

In fish liver (*Fig. 3.35*), the concentration of cadmium was found to depend on fish size and sex.

The data indicated that the cadmium level increases with increasing fish size (*Fig. 3.15a*) and the accumulation behaviour follow the order:

female > male

as shown in Figure 3.15b except at fish size 18 cm. In contrary, the cadmium level in fish skin and fish muscle at different fish size (*Fig. 3.16*) is high at small fish size as compared to large fish size with few exceptions at 18 and 19 cm fish length.

The distribution of cadmium in fish skin at different fish size for the different sex is given in Fig. 3.37. It is clear that cadmium concentration in fish skin decreases as the fish length increases up to 17 cm with

exception at fish length 18 and 19 cm as shown in Figure 3.17a. The concentration pattern of cadmium in the different sex at various fish size follow the order:

female > male

at fish size 17–20 cm and female fish attained a constant value at fish length 14–17 cm and 19–23 cm (*Fig. 3.17b*).

The distribution of cadmium in fish muscle of different fish sex at different fish length is summarized in Fig. 3.38. At small fish size the concentration of cadmium in muscle is slightly higher than large fish size fish (*Fig. 3.18a*). The cadmium level in female (*Fig. 38b*) is noticed higher than male.

The cadmium level in fish kidney is found lower than Cd level in fish heart. The average concentration in heart was found 0.34 ± 0.25 ppm and in kidney it was found equal to 0.3 ± 0.14 ppm as shown in Table 3.2.

3.3 Distribution of essential and non-essential elements in the different fish organs

It is known that trace elements exert positive or negative influence on plants, animals and human beings. Some of these elements are essential to sustain biological life, and also they are essential for optimal human growth, development, achievement and reproduction (Fôrster & Wittman, 1981). Other elements are nonessential (e.g. Cd, Pb, Hg, Bi, etc), since they are not serving a beneficial biological function (Fôrster & Wittman, 1981).

3.3.1 Distribution of essential elements

Copper, manganese, cobalt, zinc, chromium and nickel are well known to be essential elements (Marquis, 1989). Therefore, a detailed investigation of these elements are critically investigated.

The concentration behaviour of the tested essential elements in fish liver at different fish sizes is summarized in Figure 3.19. The copper concentration in fish liver was found to be the highest as compared to Mn at all fish sizes, while the zinc content in fish liver (*Table 3.1*) was found high as compared to other tested elements.

In fish skin (*Fig. 3.20*) at fish size 17–24 cm, the concentration of copper was found high as compared to other essential elements except zinc (*Fig. 3.6*). The concentration pattern follow the order:

$$\text{Zn} > \text{Cu}$$

In fish muscle (*Fig. 3.21*) the concentration of the elements is decreased slightly with increasing fish size. The concentrations of the elements in the fish muscle follow the order:

$$\text{Zn} > \text{Cu} > \text{Mn}$$

It can be noticed that chromium (*Table 3.1*) in the different fish organs namely liver, skin and muscle have the lowest concentration in all these tissues, while zinc have the highest accumulation.

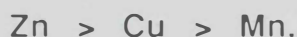
In the different fish organs the concentrations pattern of Zn, Cu, and Mn follow the order:

$$\text{liver} > \text{skin} > \text{muscle}$$

The distribution patterns of the different essential elements in kidney and heart are summarized in Table 3.2 and Fig. 3.22. The accumulation pattern in kidney follow the order:



while in heart it follows the order:



3.3.2 Accumulation behaviour of essential and nonessential elements in the different fish organs

The distribution behaviour of the tested elements in liver, skin and muscle are summarized in Figs. 3.46 – 3.48 and Table 3.1. In liver tissue (*Fig. 3.23*) the accumulation pattern of the investigated elements follow the sequence:



Also in skin tissue (*Fig. 3.47*) the sequence of the metals follow the order:



In muscle tissue (*Fig. 3.25*) the order of accumulation behaviour of the different elements follow the order:



The distribution behaviour of the different elements in the fish kidney and heart are given in Fig. 3.22 and Table 3.2. In the kidney it can

be noticed that the accumulation of the tested elements follow the sequence:



However in the fish heart the sequence



was achieved.

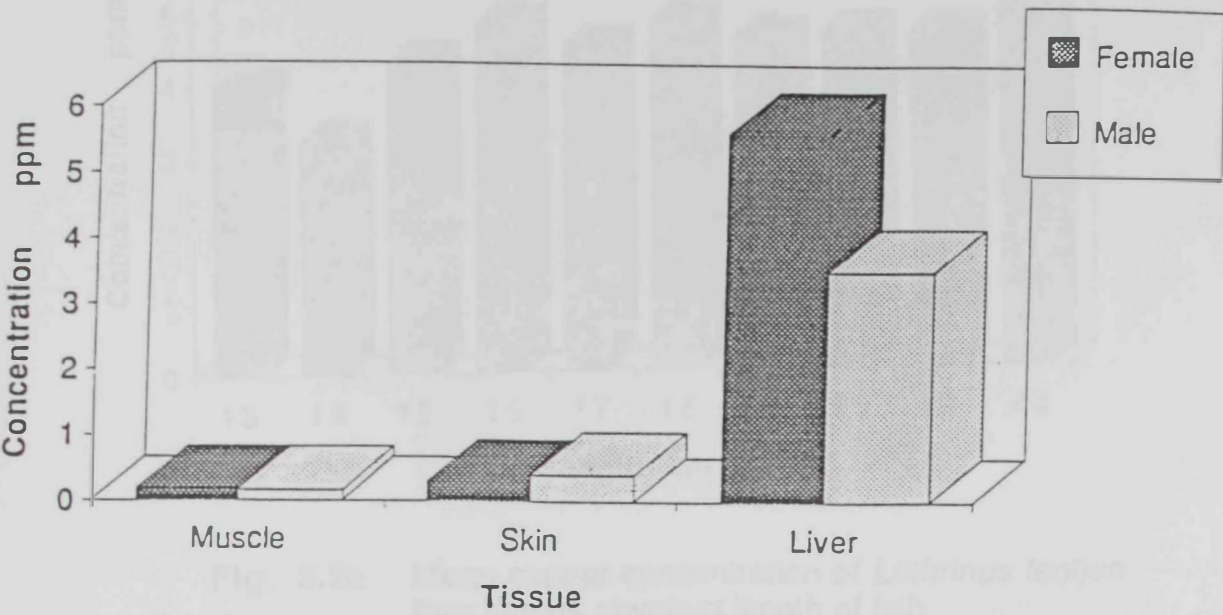


Fig. 3.1. Mean copper concentration in muscle, skin and liver in female and male *Lethrinus lentjan*

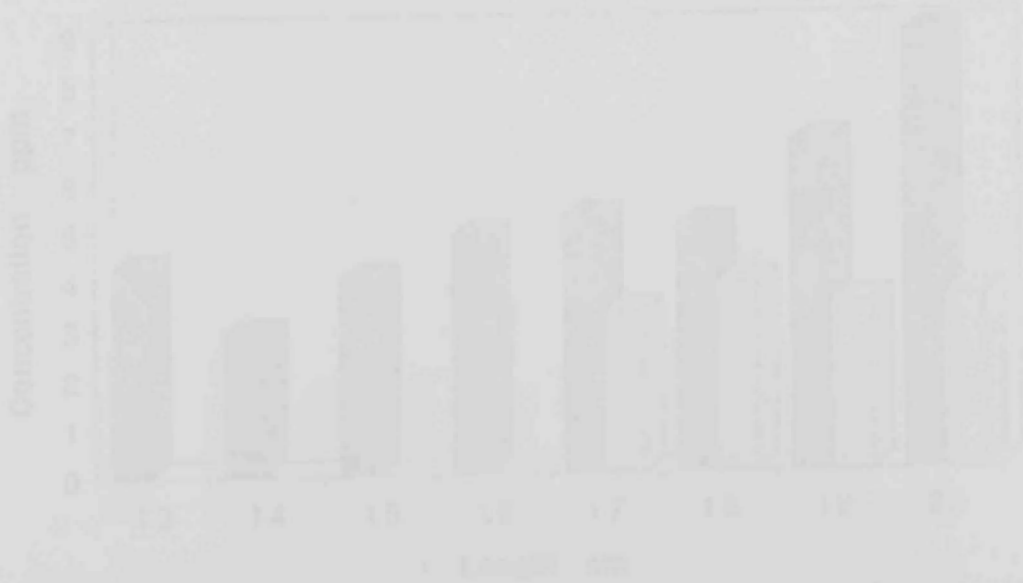


Fig. 3.2b. Mean copper concentration in liver in female and male *Lethrinus lentjan* length (cm)

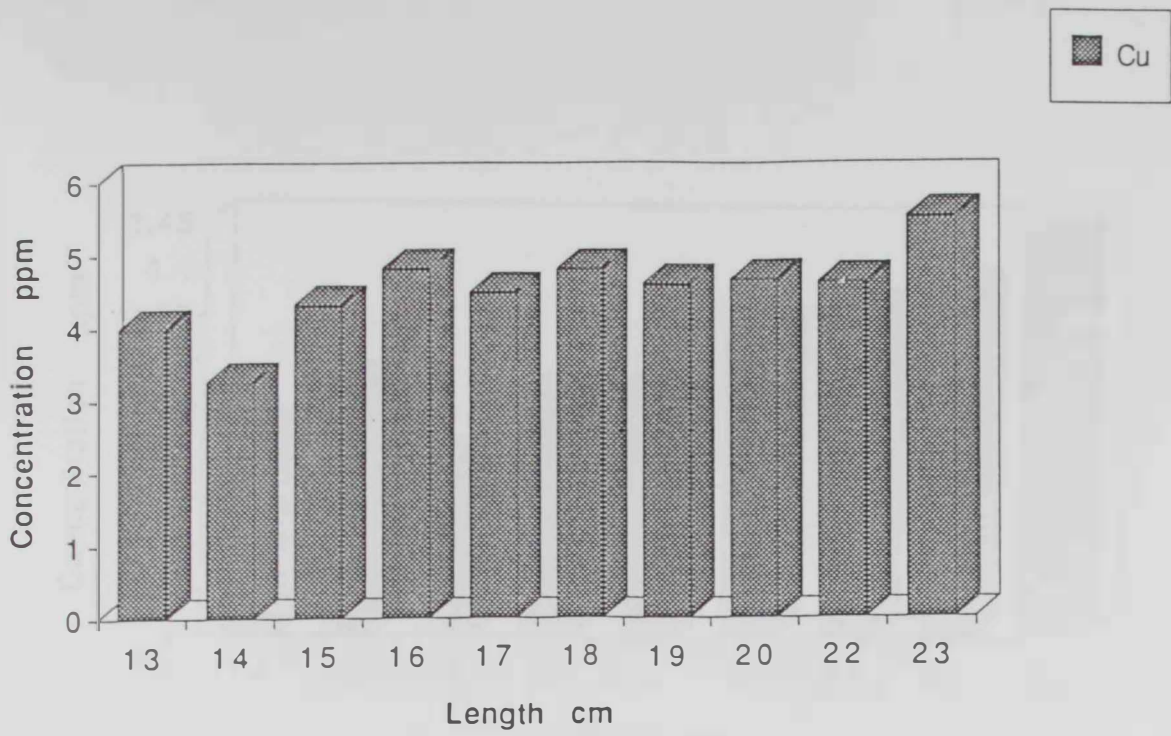


Fig. 3.2a. Mean copper concentration of *Lethrinus lentjan* liver versus standard length of fish

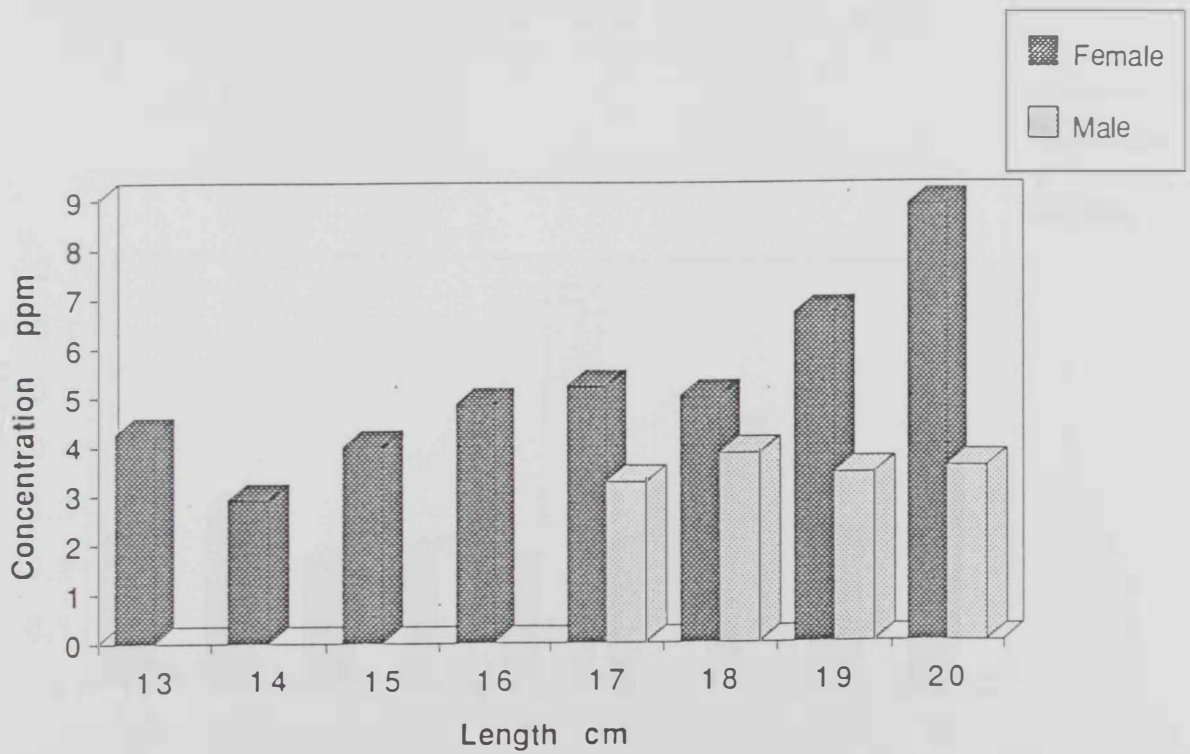


Fig. 3.2b. Mean copper concentration of *Lethrinus lentjan* liver in female and male versus standard length of fish

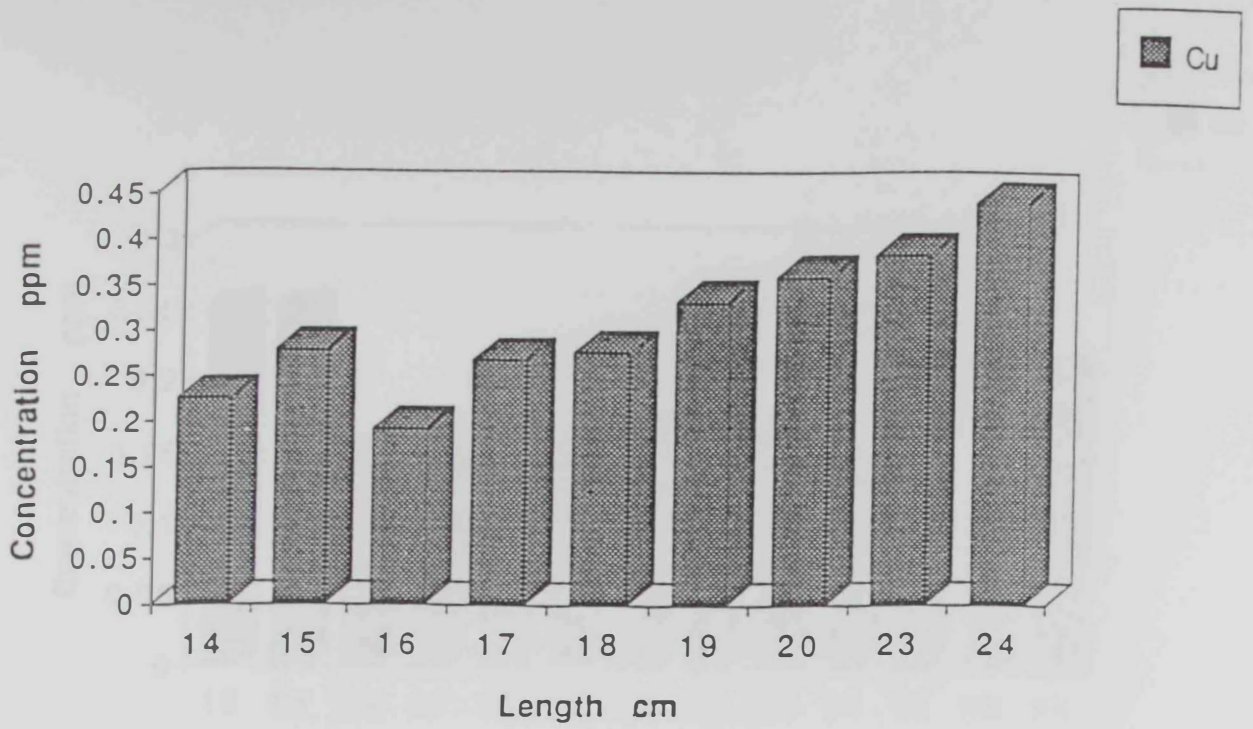


Fig. 3.3a. Mean copper concentration of *Lethrinus lentjan* skin versus standard length of fish

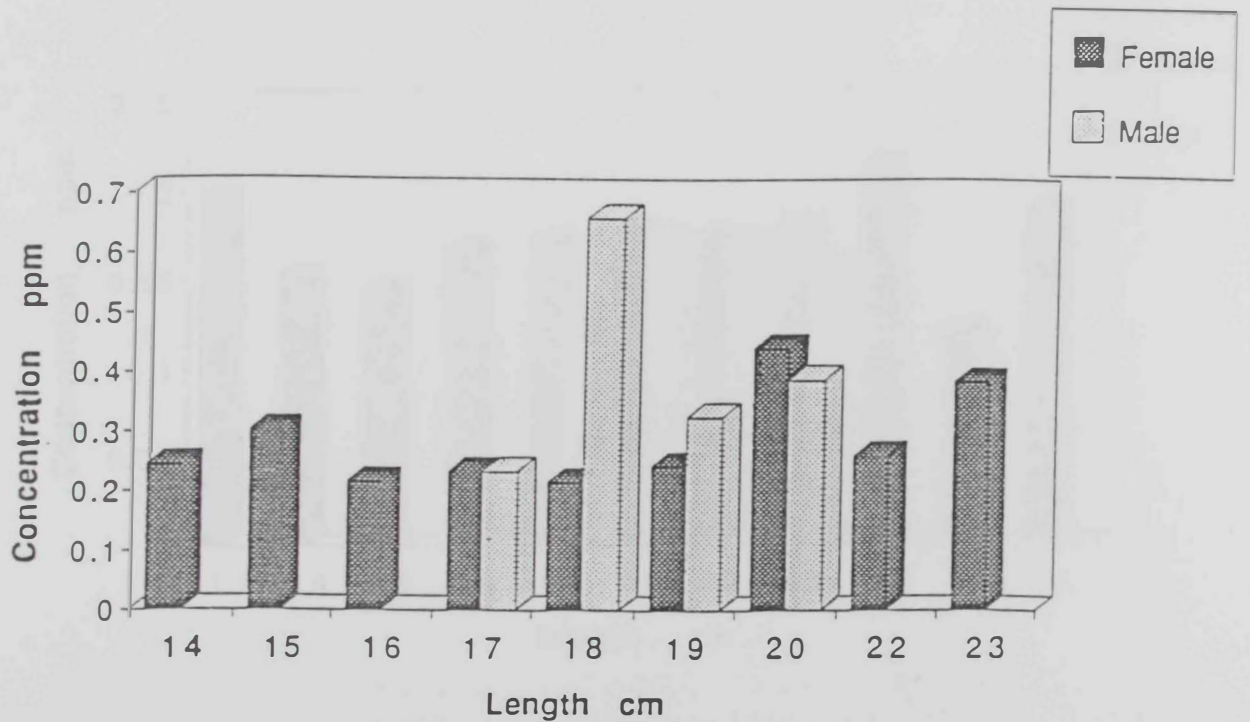


Fig. 3.3b. Mean copper concentration of *Lethrinus lentjan* skin in female and male versus standard length of fish

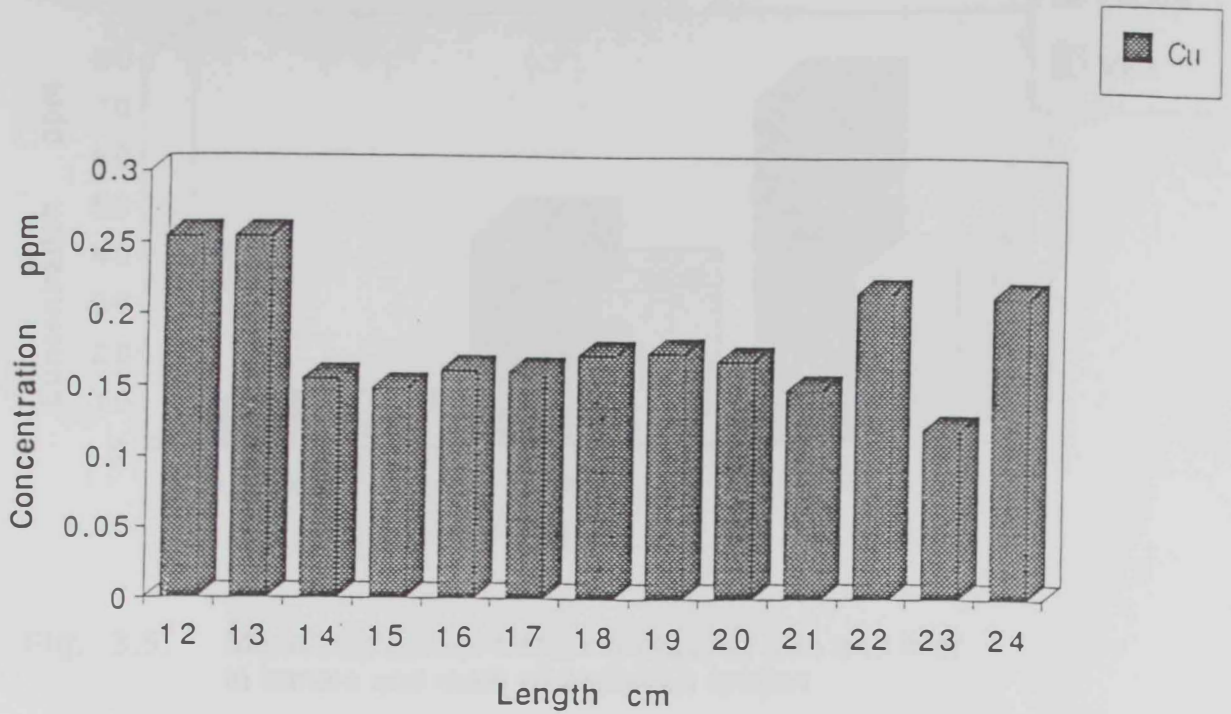


Fig. 3.4a. Mean copper concentration of *Lethrinus lentjan* muscle versus standard length of fish

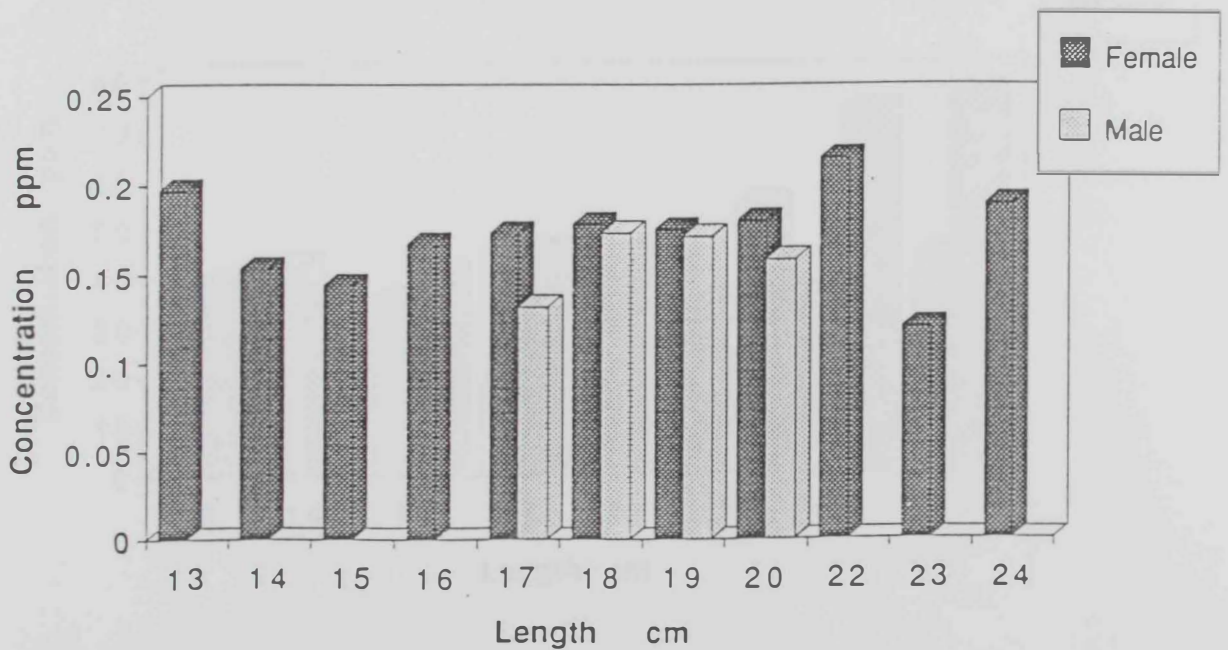


Fig. 3.4b. Mean copper concentration of *Lethrinus lentjan* muscle in female and male versus standard length of fish

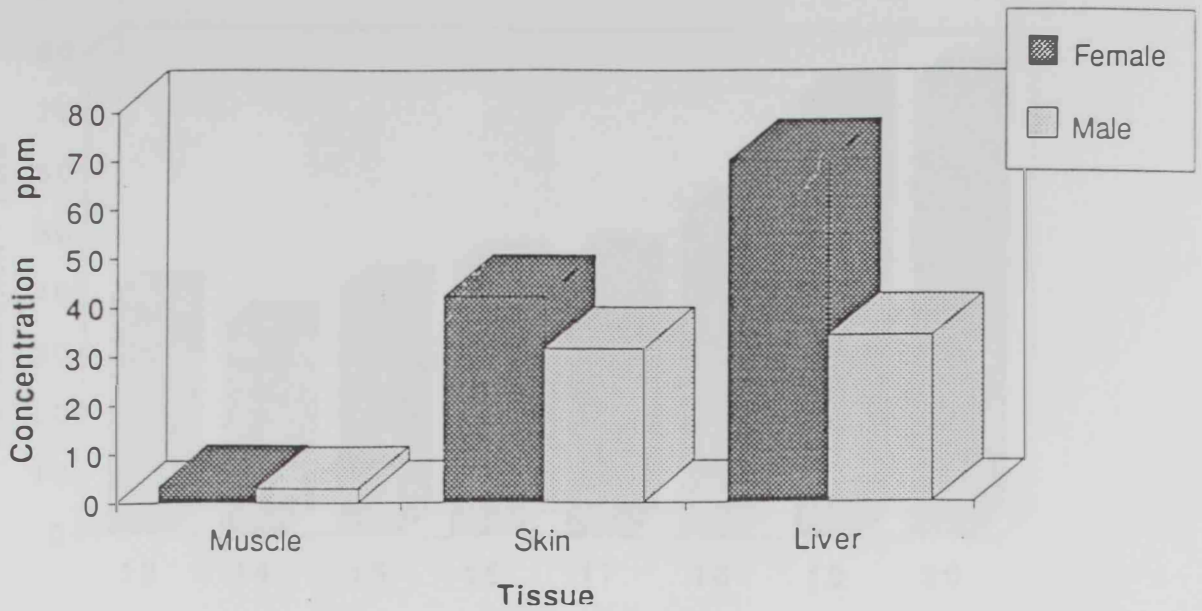


Fig. 3.5. Mean zinc concentration in muscle, skin and liver in female and male of *Lethrinus lentjan*

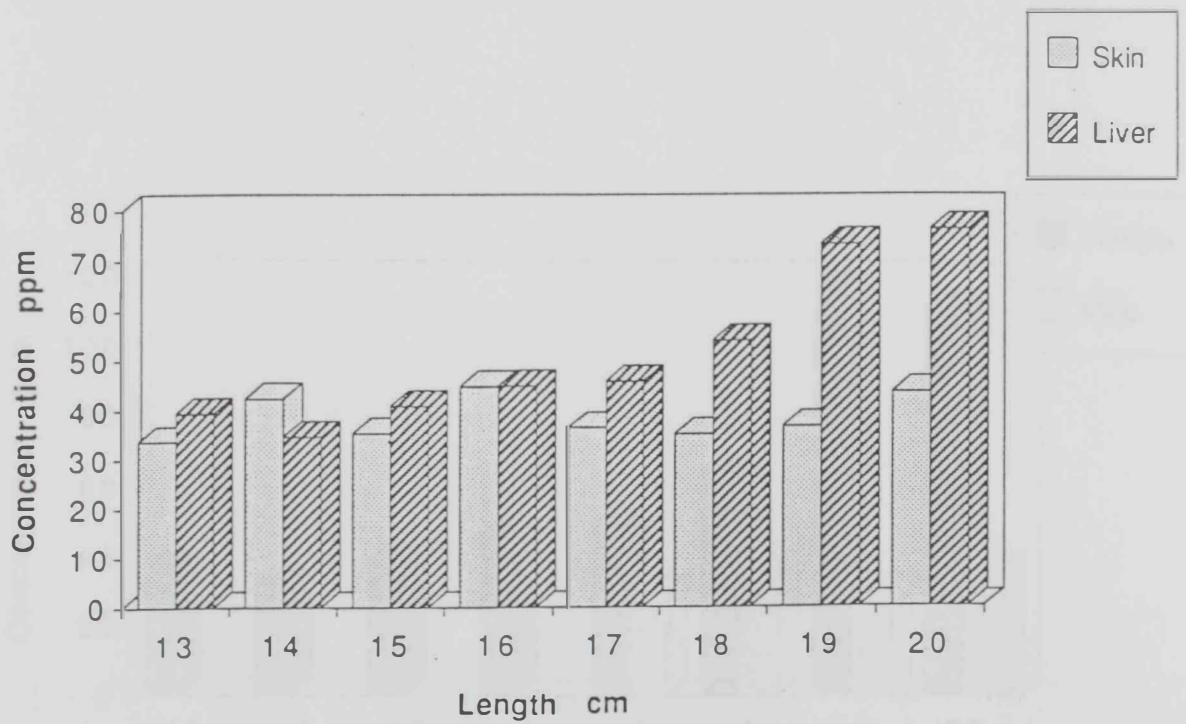


Fig. 3.6. Mean concentration of zinc in *Lethrinus lentjan* in skin and liver versus standard length of fish

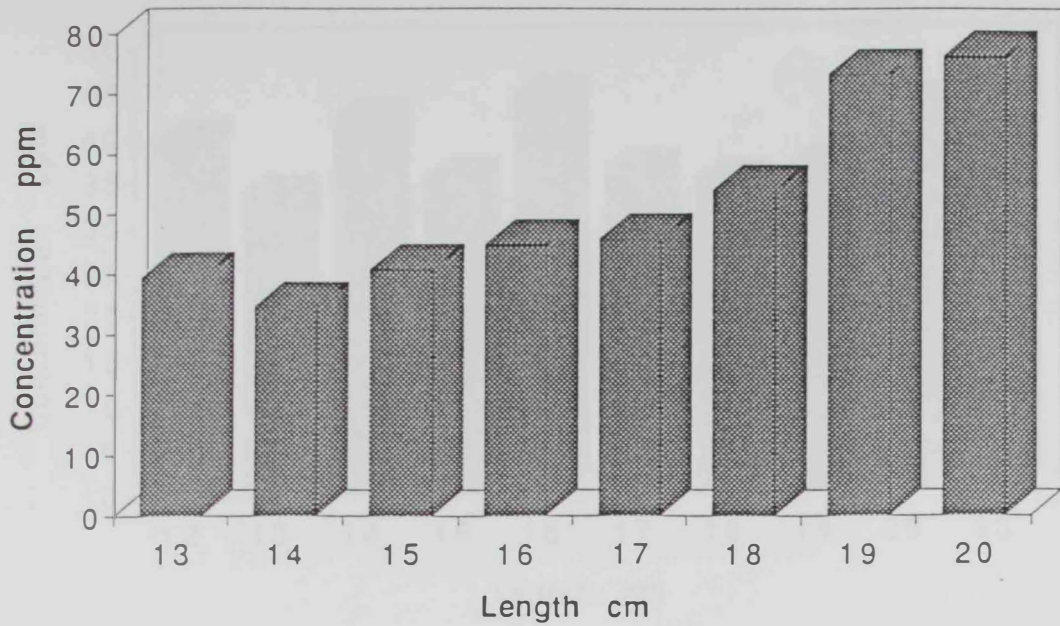


Fig. 3.7a. Mean zinc concentration of *Lethrinus lentjan* liver in female and male versus standard length of fish

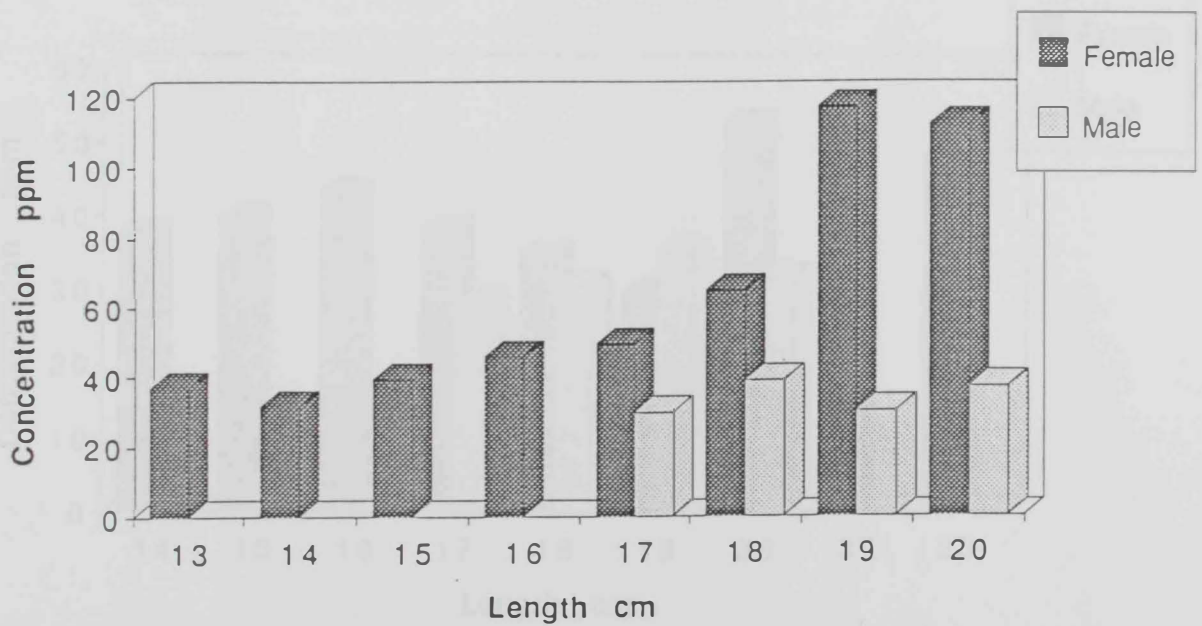


Fig. 3.7b. Mean zinc concentration of *Lethrinus lentjan* liver in female and male versus standard length of fish

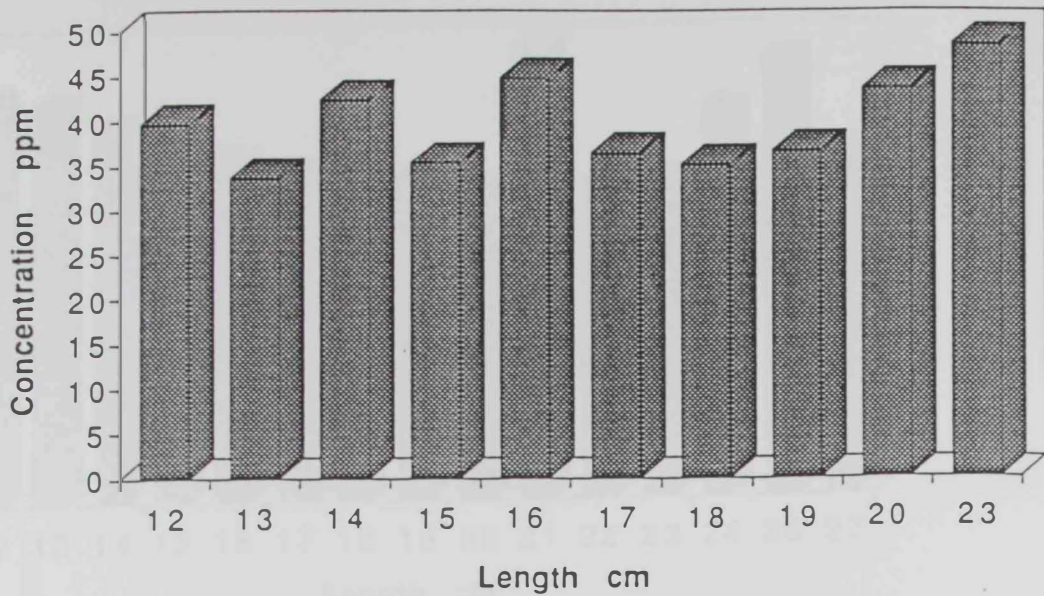


Fig. 3.8a. Mean zinc concentration of *Lethrinus lentjan* skin versus standard length of fish

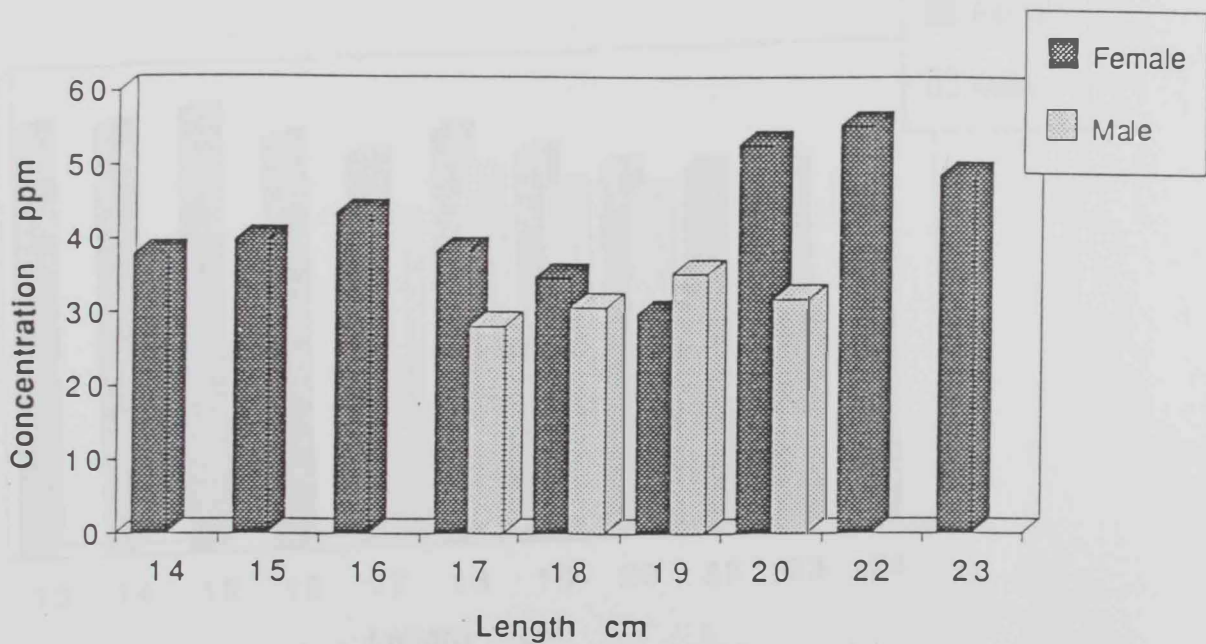


Fig. 3.8b. Mean zinc concentration of *Lethrinus lentjan* skin in female and male versus standard length of fish

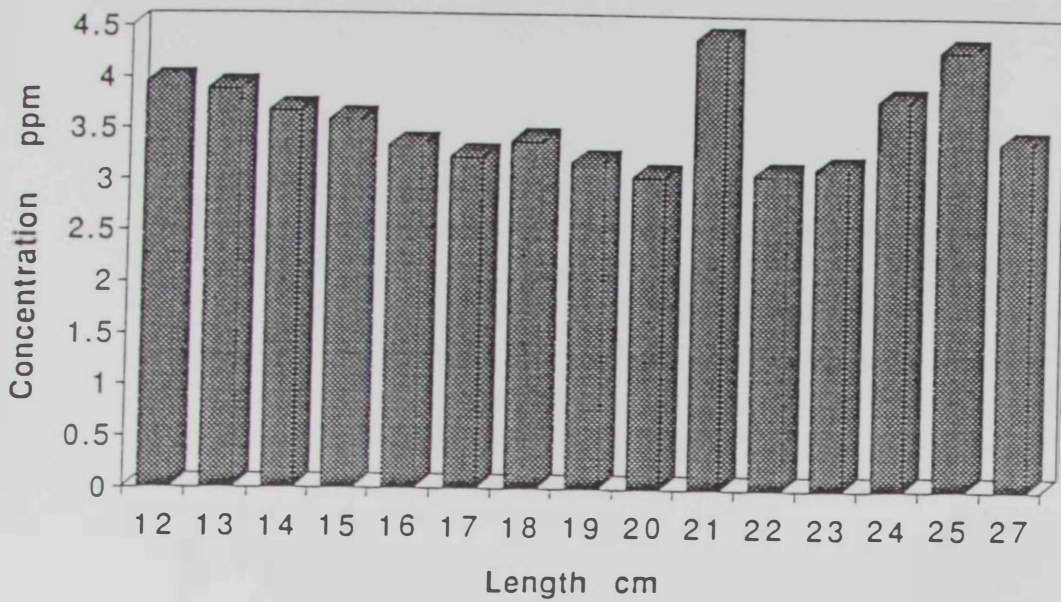


Fig. 3.9a. Mean zinc concentration of *Lethrinus lentjan* muscle versus standard length of fish

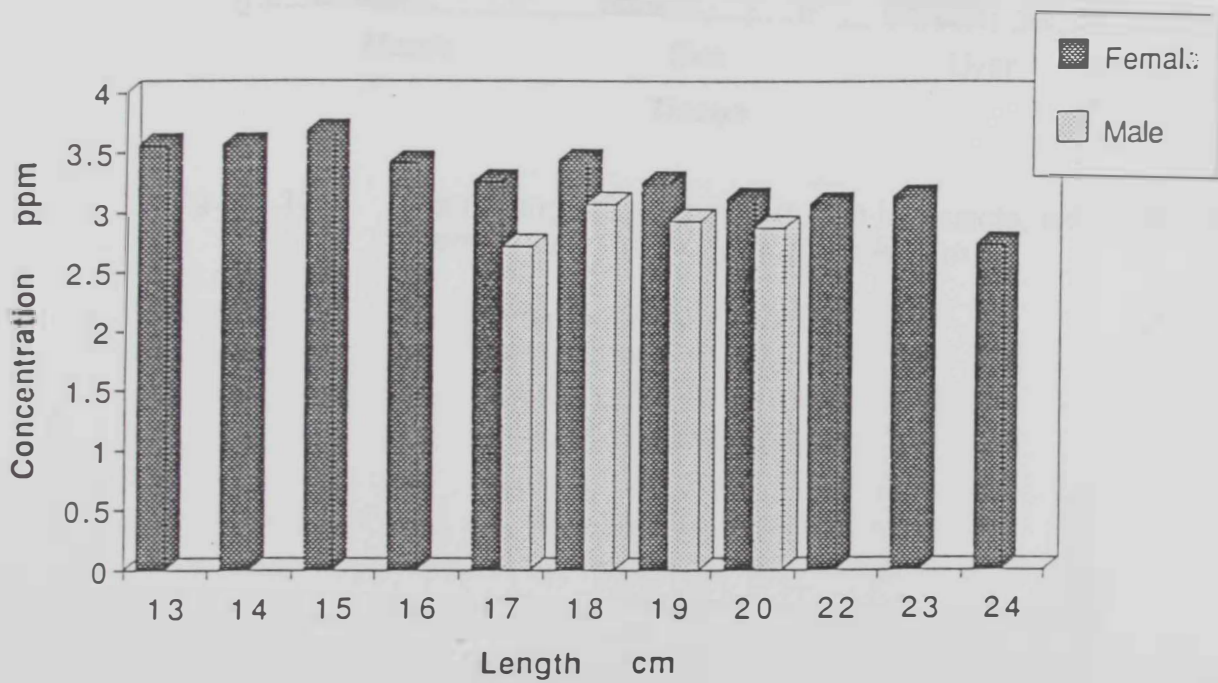


Fig. 3.9b. Mean zinc concentration of *Lethrinus lentjan* muscle in female and male versus standard length of fish

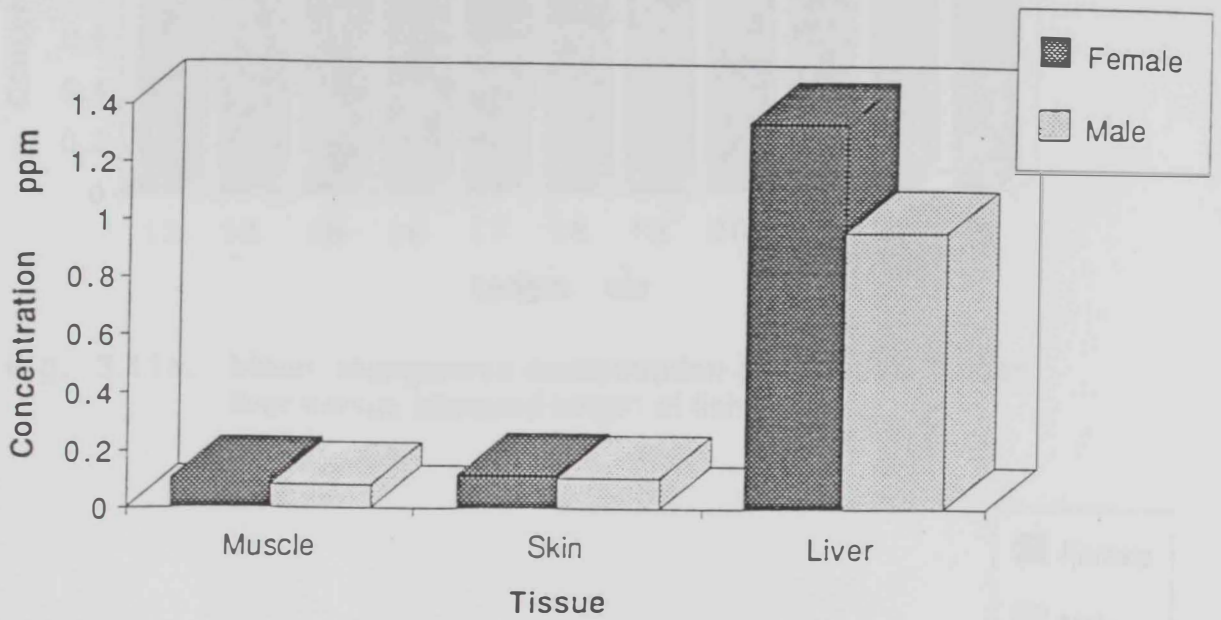


Fig. 3.10. Mean manganese concentration in muscle, skin and liver in female and male of *Lethrinus lentjan*

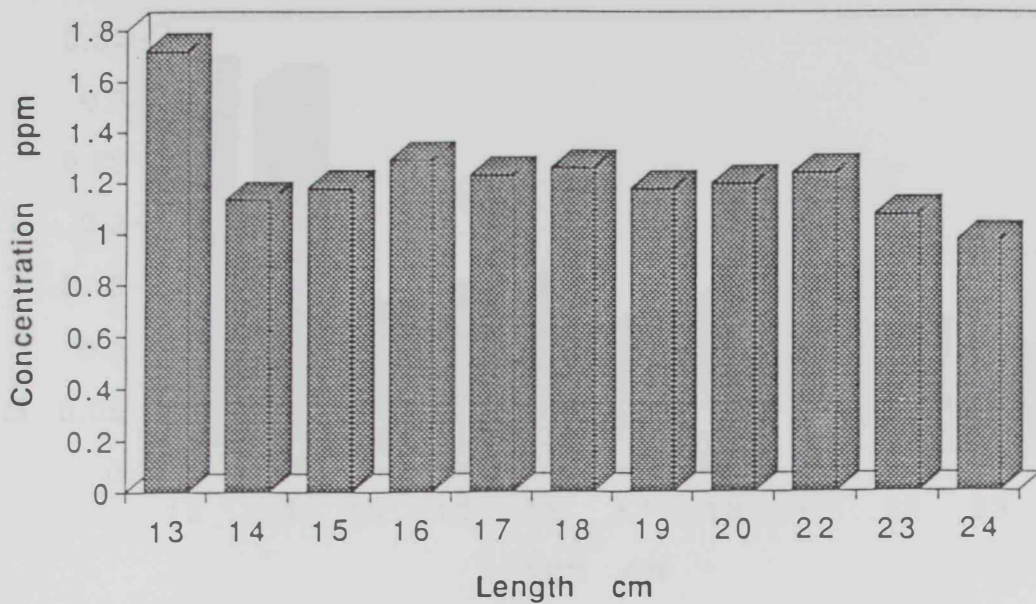


Fig. 3.11a. Mean manganese concentration of *Lethrinus lentjan* liver versus standard length of fish

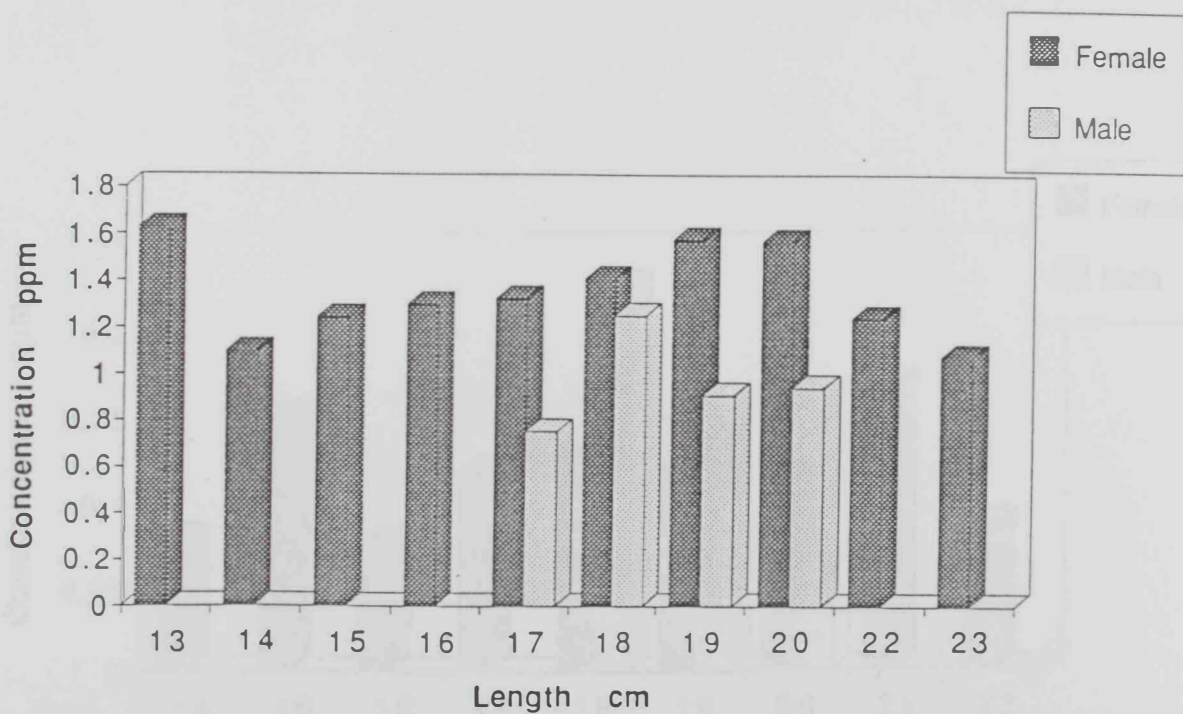


Fig. 3.11b. Mean manganese concentration of *Lethrinus lentjan* liver in female and male versus standard length of fish

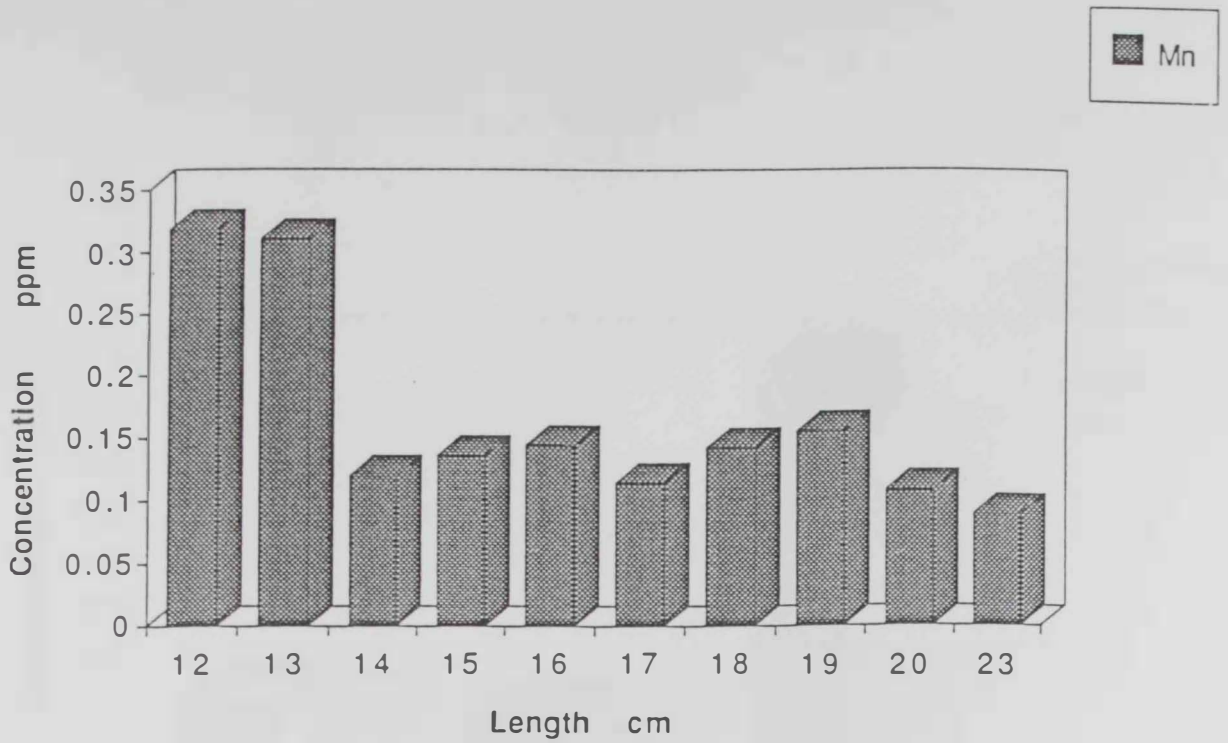


Fig. 3.12a. Mean manganese concentration of *Lethrinus lentjan* skin versus standard length of fish

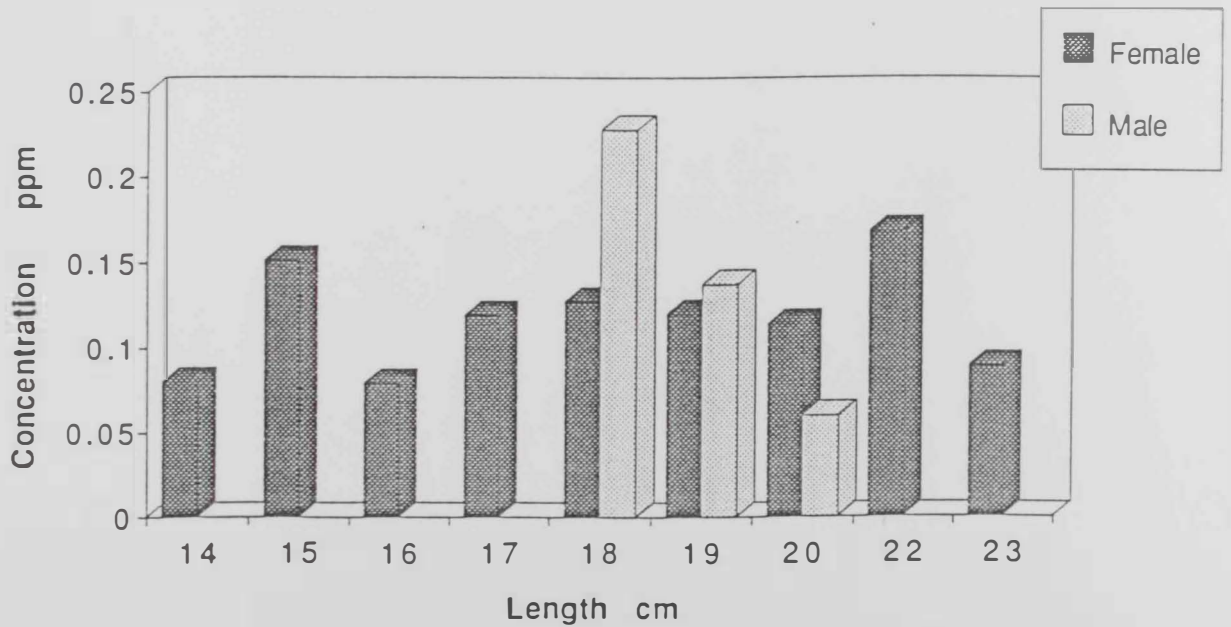


Fig. 3.12b. Mean manganese concentration of *Lethrinus lentjan* skin in female and male versus standard length of fish

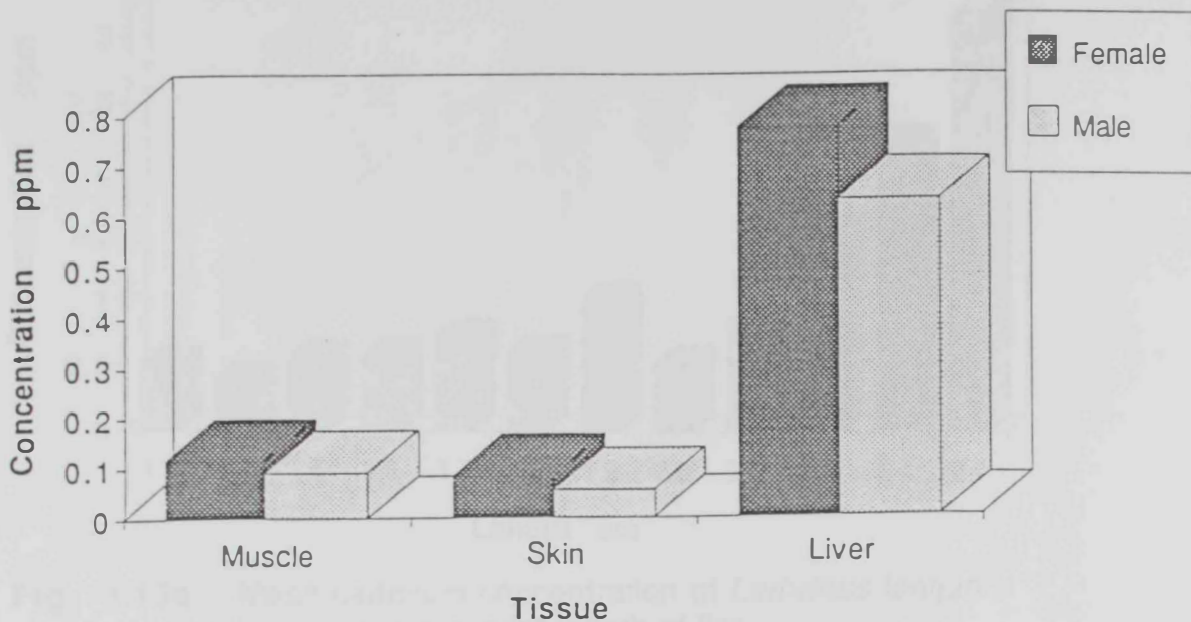


Fig. 3.14. Mean cadmium concentration in muscle, skin and liver in female and male of *Lethrinus lentjan*



Fig. 3.15. Mean cadmium concentration in muscle, skin and liver versus standard length of fish

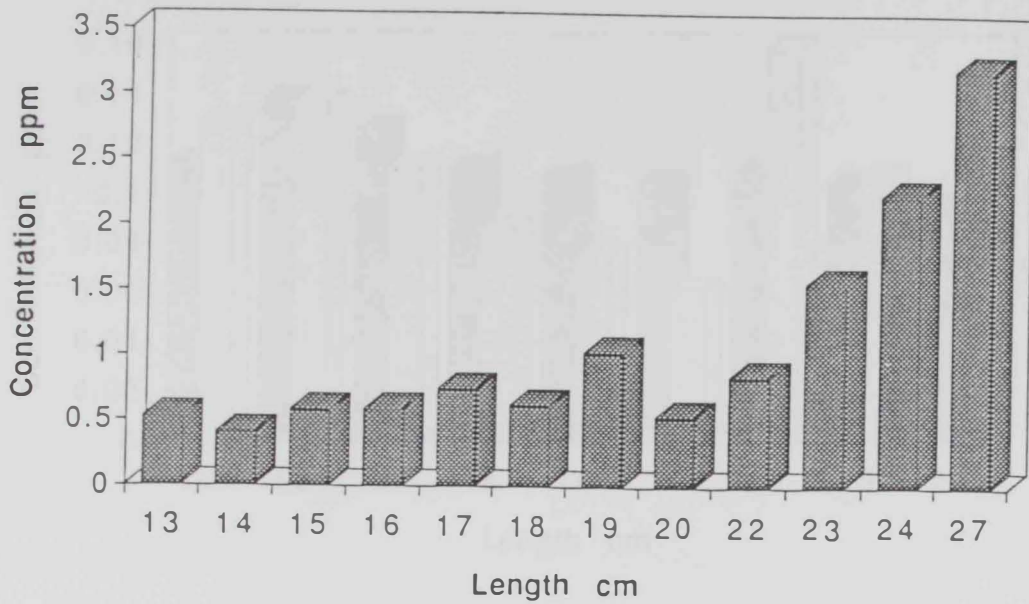


Fig. 3.15a. Mean cadmium concentration of *Lethrinus lentjan* liver versus standard length of fish

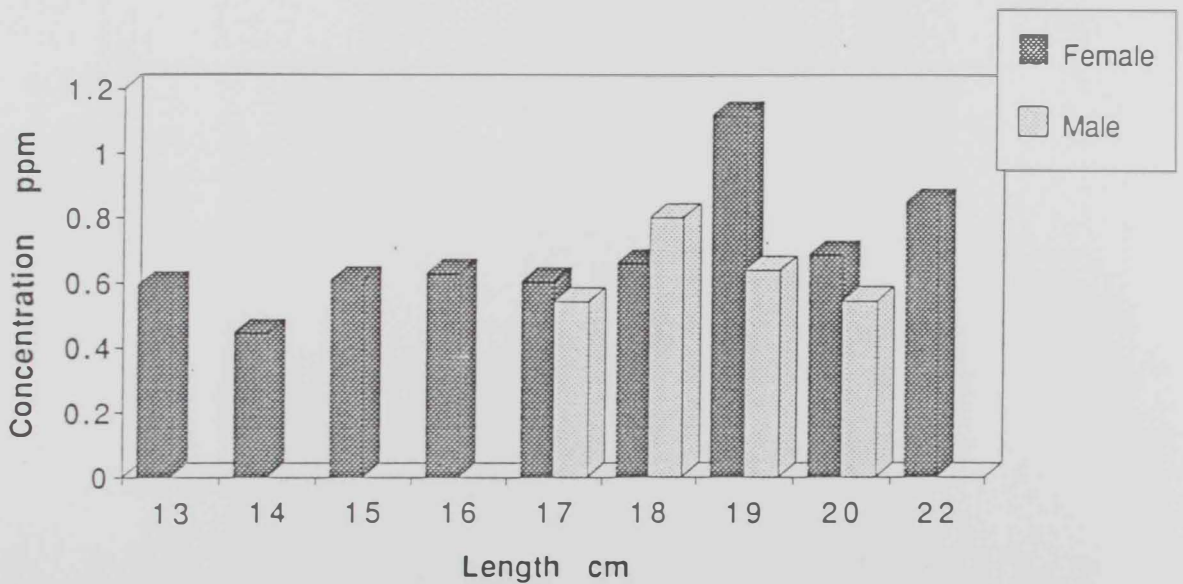


Fig. 3.15b. Mean cadmium concentration of *Lethrinus lentjan* liver in female and male versus standard length of fish

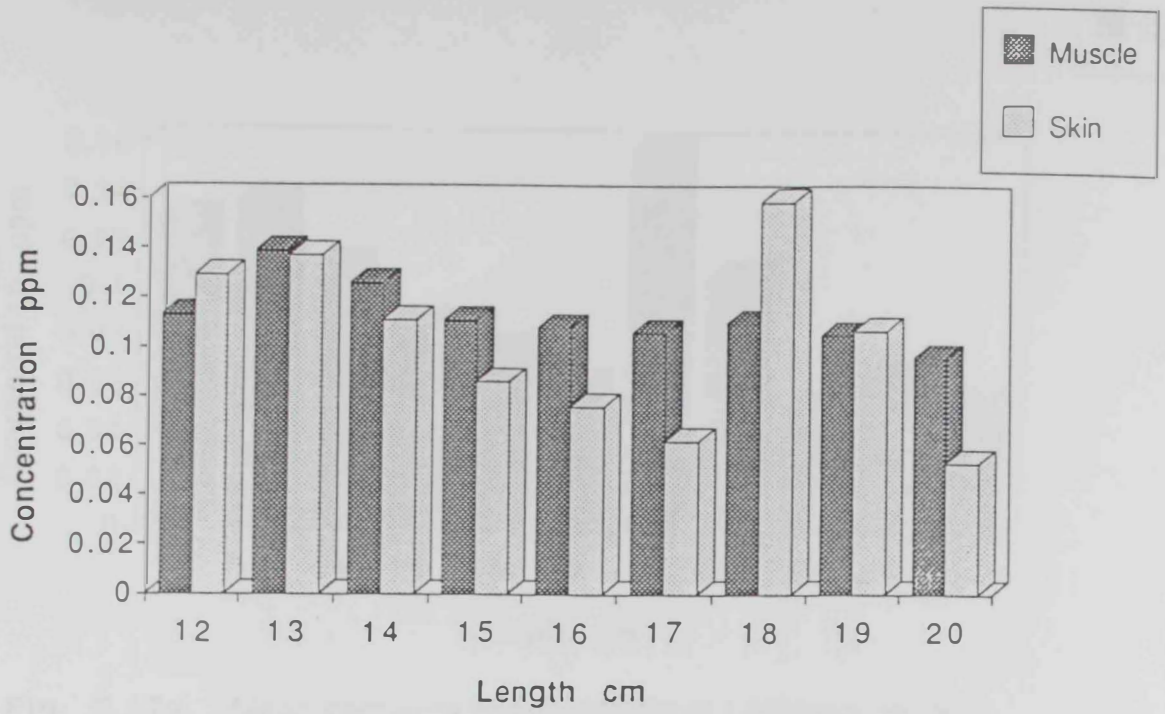


Fig. 3.16. Mean concentration of cadmium in *Lethrinus lentjan* muscle and skin versus standard length of fish

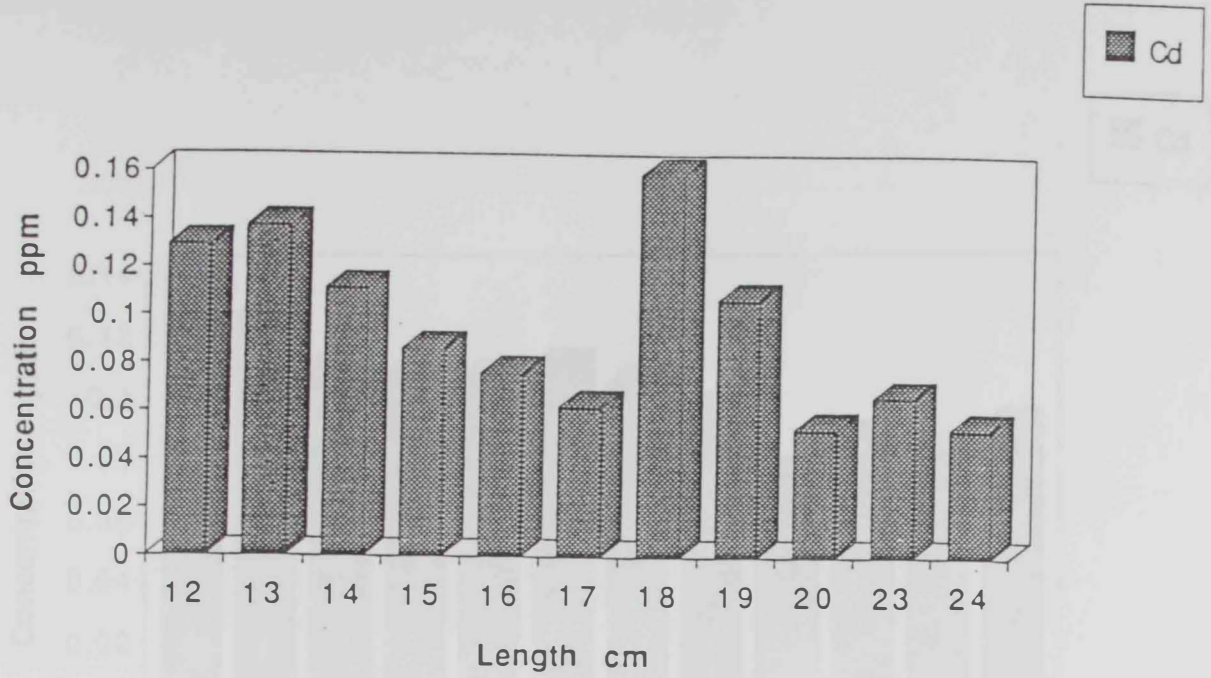


Fig. 3.17a. Mean cadmium concentration of *Lethrinus lentjan* skin versus standard length of fish

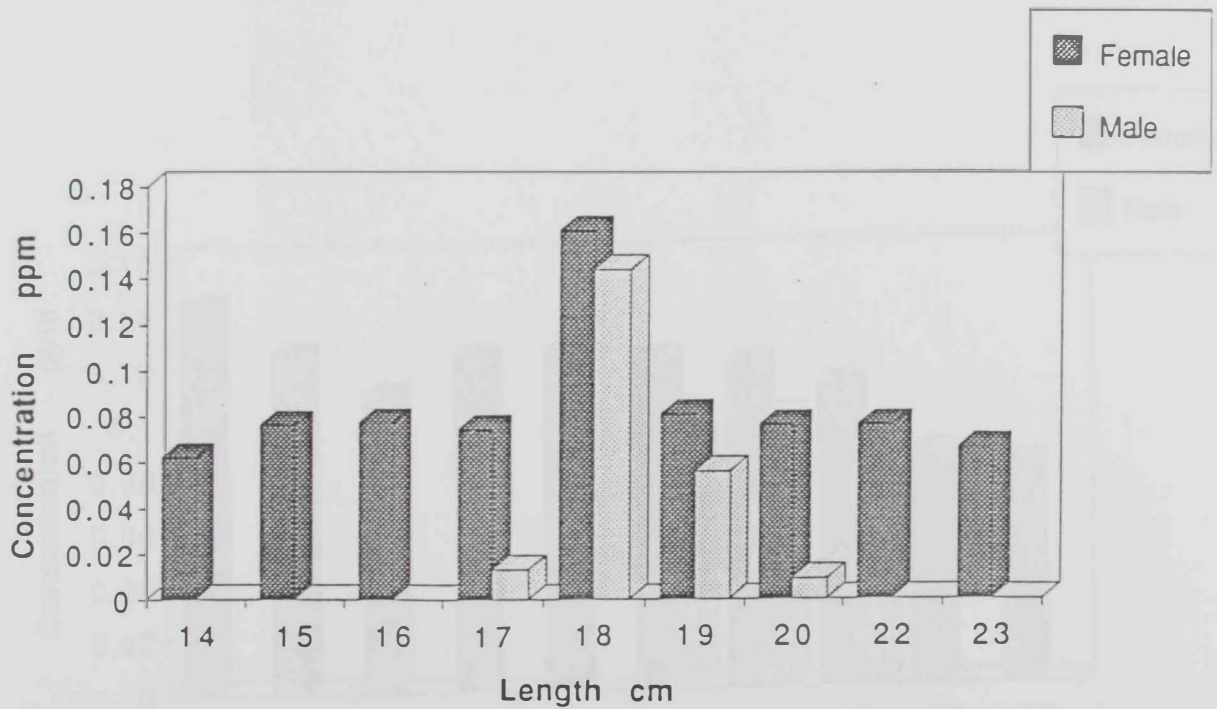


Fig. 3.17b. Mean cadmium concentration of *Lethrinus lentjan* skin in female and male versus standard length of fish

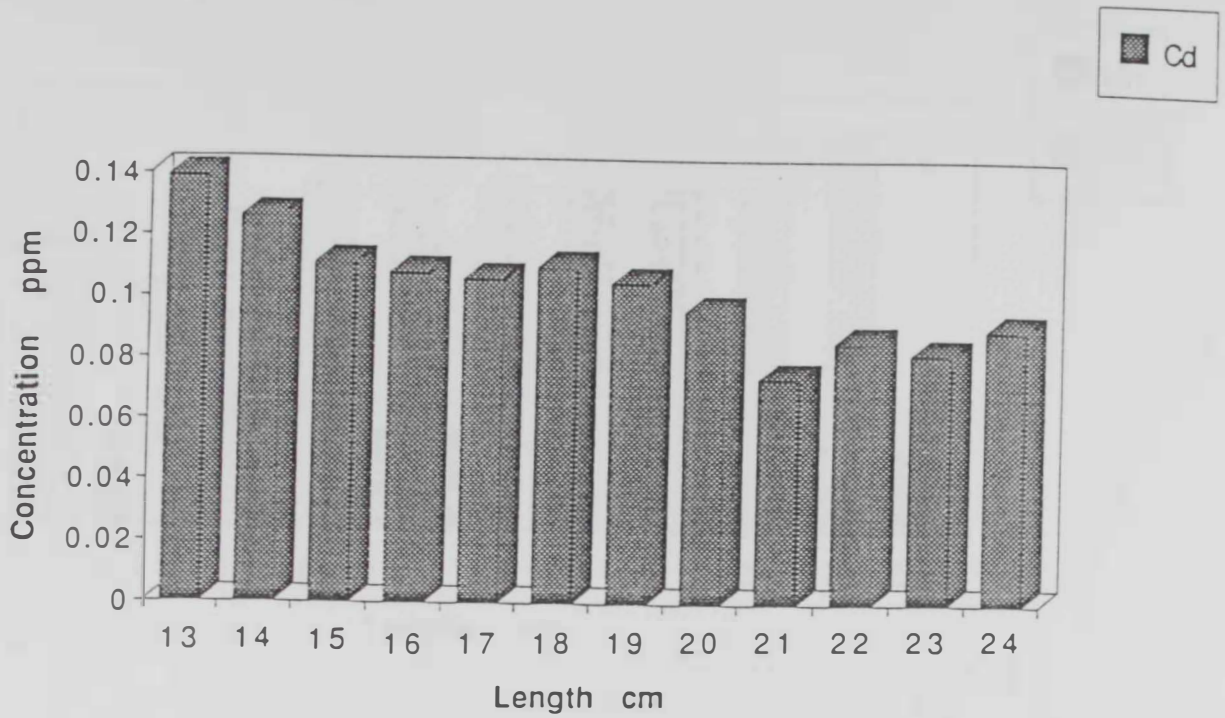


Fig. 3.18a. Mean cadmium concentration of *Lethrinus lentjan* muscle versus standard length of fish

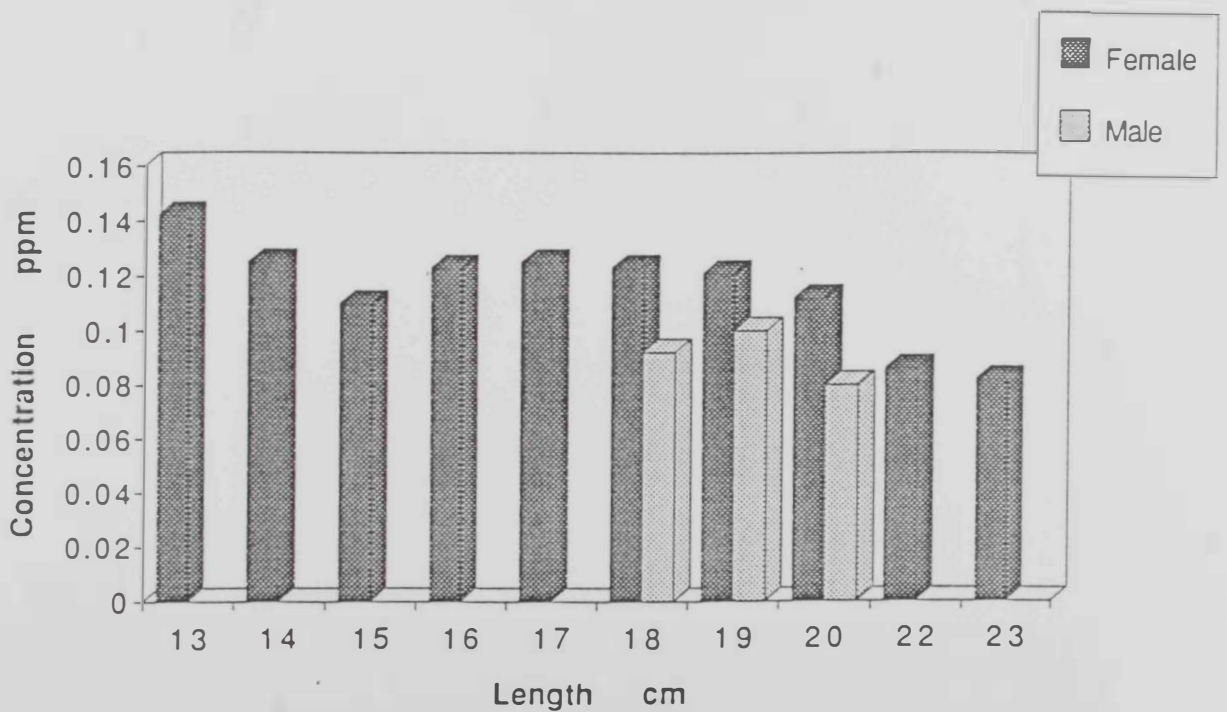


Fig. 3.18b. Mean cadmium concentration of *Lethrinus lentjan* muscle in female and male versus standard length of fish

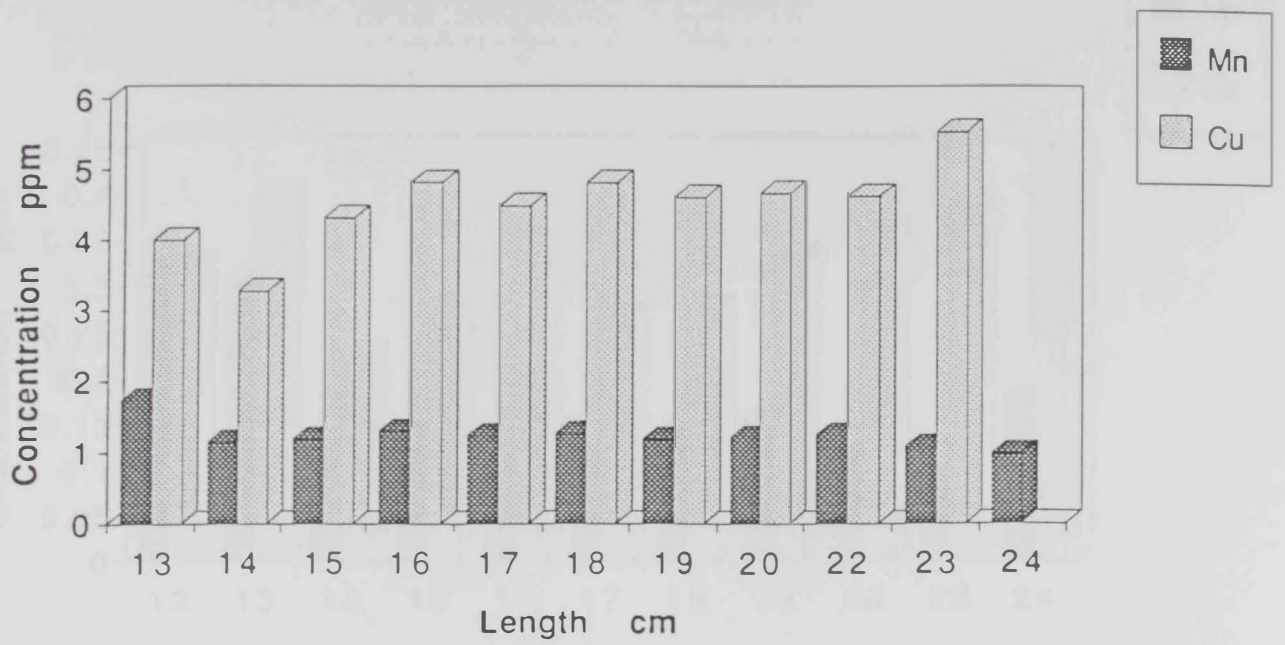


Fig. 3.19 Mean concentration of essential elements in *Lethrinus lentjan* liver versus standard length of fish

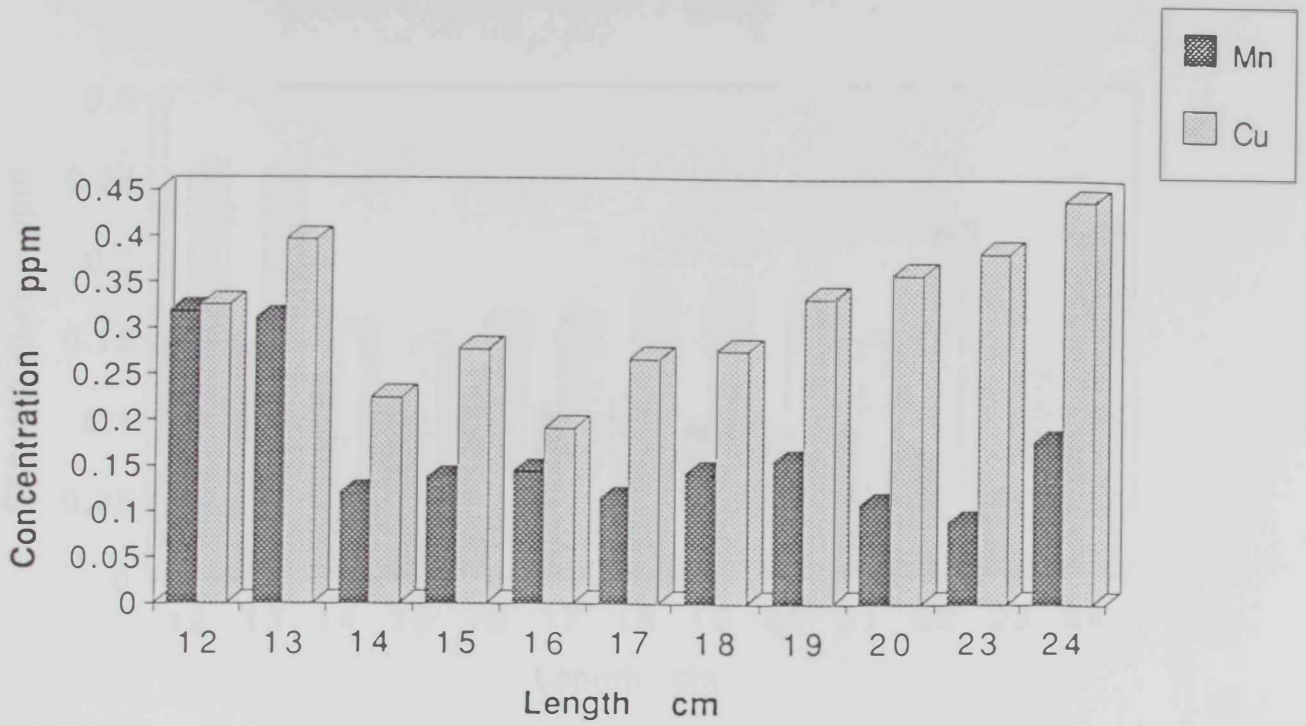


Fig. 3.20 Mean concentration of essential elements in *Lethrinus lentjan* skin versus standard length of fish

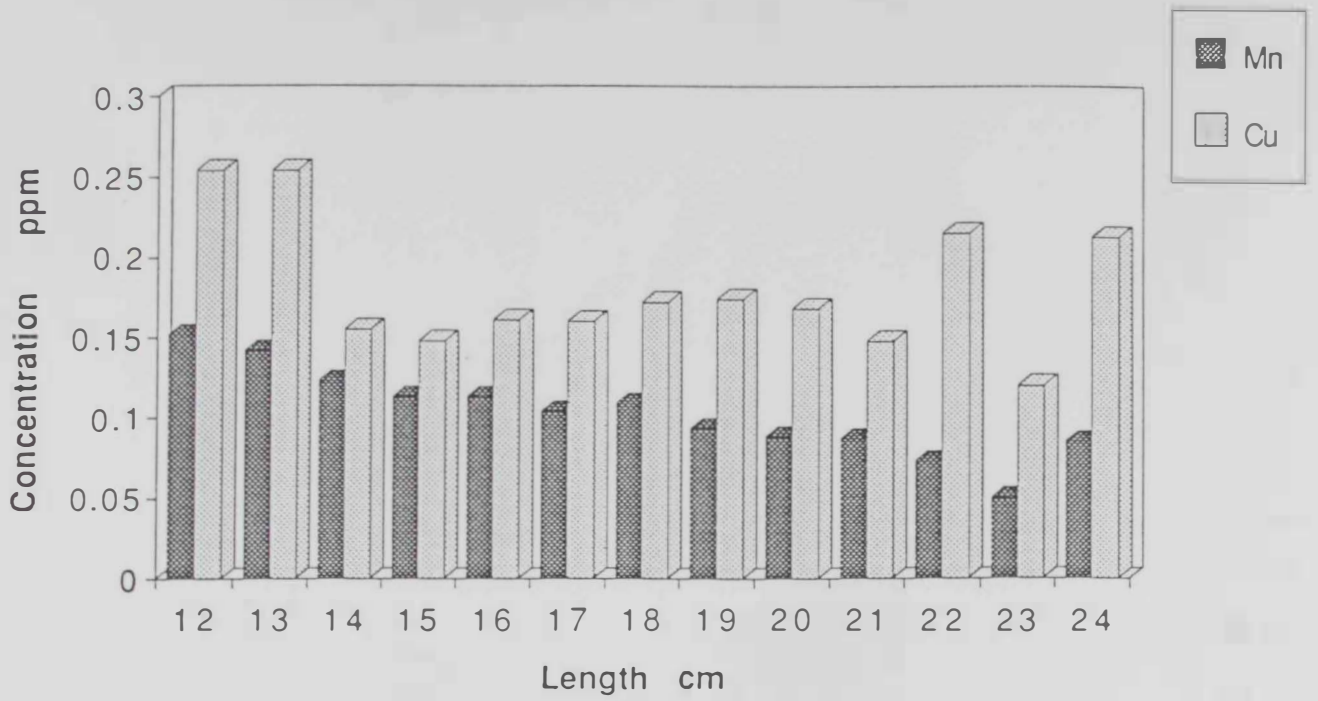


Fig. 3.21 Mean concentration of essential elements in *Lethrinus lentjan* muscle versus standard length of fish

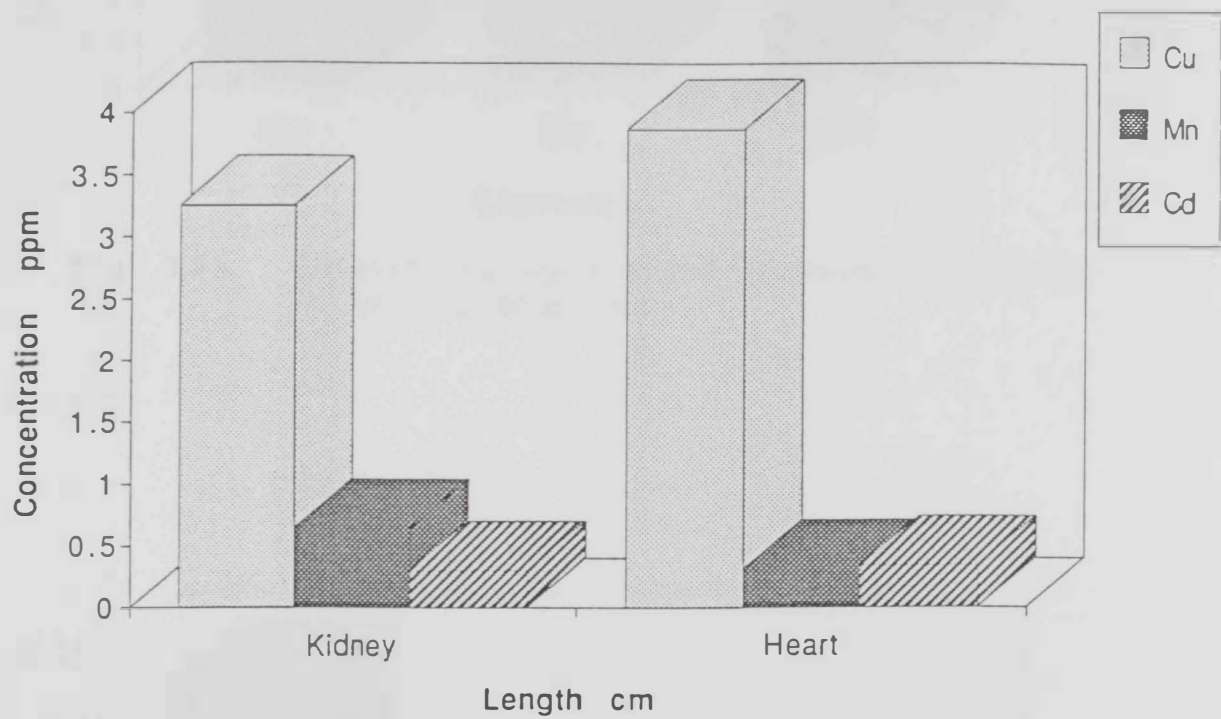


Fig. 3.22. Distribution of essential and non-essential elements in *Lethrinus lentjan* heart and kidney

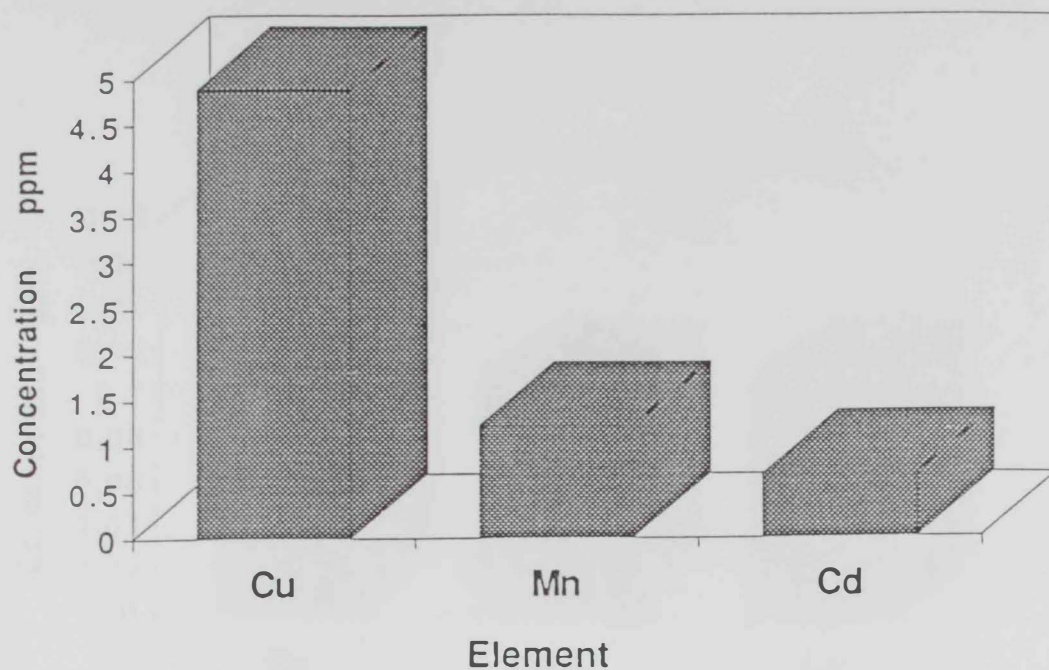


Fig. 3.23. Distribution of essential and non-essential elements in *Lethrinus lentjan* liver

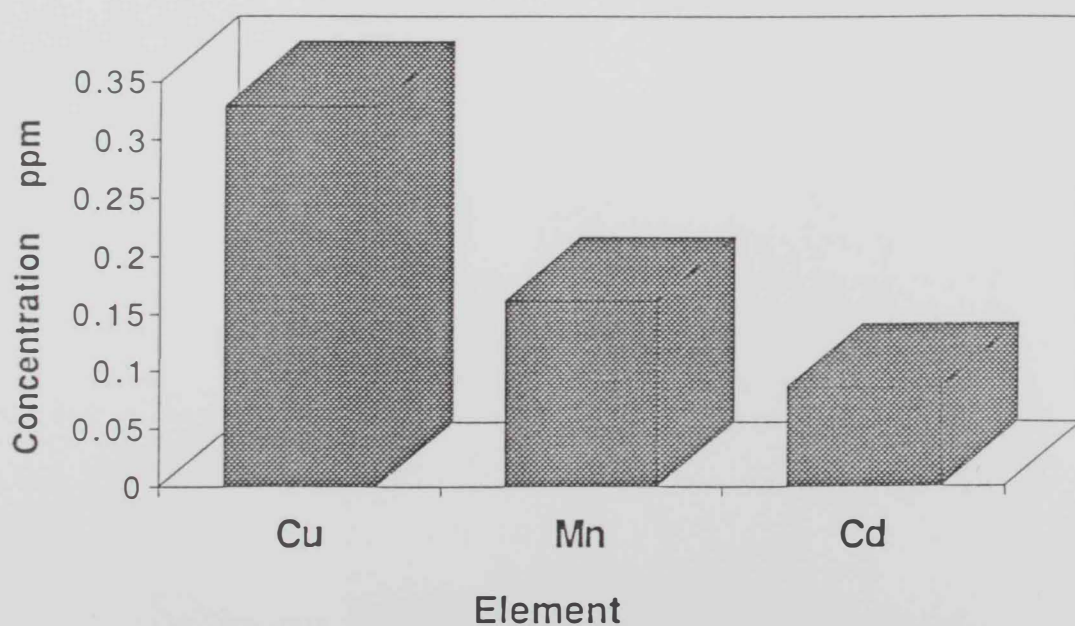


Fig. 3.24. Distribution of essential and non-essential elements in *Lethrinus lentjan* skin

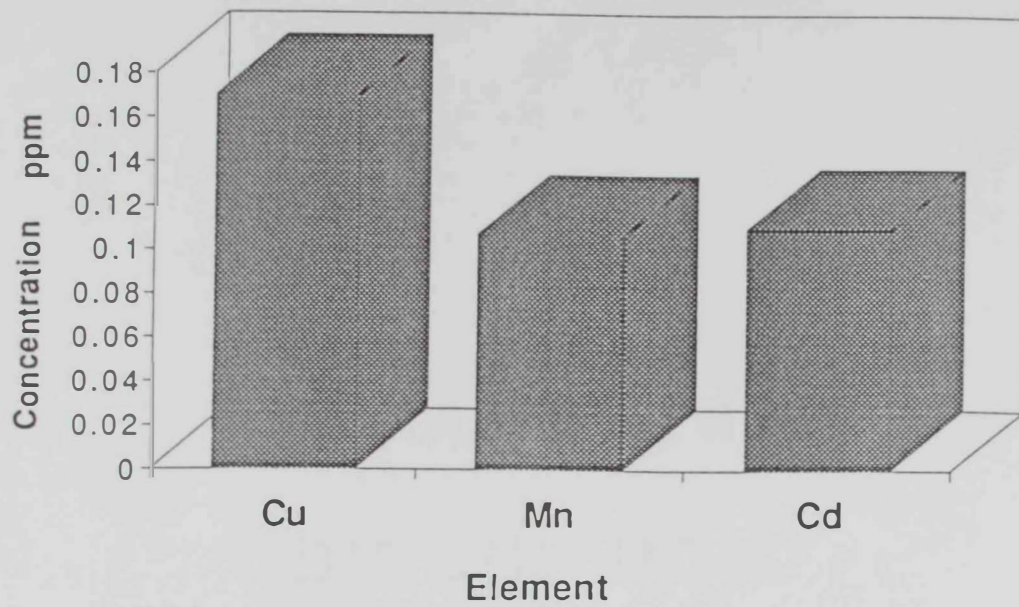


Fig. 3.25. Distribution of essential and non-essential elements in *Lethrinus lentjan* muscle

CHAPTER 4
DISCUSSION

4. Discussion

Heavy metals released both naturally and through human activities may accumulate in aquatic environment. Organisms living in contact with sediment where metals accumulate are known to concentrate trace metals in their body tissues. Because of their tendency to concentrate pollutants of various kinds from their environment, certain animals, e.g. fish have been found useful as indicator organisms (Schuhmacher, et al, 1992). Therefore, trace metal concentrations in stationary fish could be possible indicators in areas affected by human activities. The use of fish for monitoring trends of trace metals has been recommended by ICES (International Council for Exploration of the Sea). OSPARCOM (Oslo and Paris Commission, 1991) has also agreed upon using trace metals in fish as a monitoring technique in their programs for assessing the efficiency of control measures (Jargensen & Pedersen, 1994).

A majority of studies related to heavy metal concentrations in aquatic organisms emphasis bioaccumulation or biomagnification. Thus the present study aimed to determine if bioconcentration pattern between three essential elements Cu, Zn, Mn and one of the non-essential trace elements namely Cd. These elements were selected because most studies of heavy metal in fish have examined one or more of these elements. Also these metals are often closely associated with each other as natural impurities (Vinikour, et al., 1980) or as alloys (McKee & Wolf, 1973).

4.1 Accumulation of essential elements

The tested essential elements Cu, Zn, Mn, Co, Ni and Cr have the ability to form stable coordinate bonds to fixed active sites in the immobile protein molecules (Kendrick, et al., 1992). Most of these metal chelates act mainly as catalysts; therefore they induce the enzymatic activity (Fôrstner & Wittman, 1980). manganese is involved in glucose utilization, copper is found in enzymes capable of carrying oxygen as hemoglobin dose, cobalt is required to form hemoglobin, zinc is an essential constituent of enzymes and nickel at high concentration is well known to cause death to fish by asphyxiation and its inhalation lead to lung cancers as previously reported (Fôrstner & Wittman, 1981). The biological role of chromium (III) as an essential trace element was proposed when it was found that rats fed a chromium-deficient diet developed an impaired tolerance towards glucose and a significant relationship was found between the alcohol—extractable chromium content of food stuff and biological activity (Hay, 1991; Kendrick, et al., 1992).

Recently, Fôrstner & Wittman, 1981 have been reported that if the nutritional supply of trace essential elements exceed a certain limit (oversupply), these elements become toxic and cause elthality. Deficiency may occur when the trace element concentration is undersupply. A schematic relationship between yield growth and trace essential element concentration is given in Fig. 4.1 (Fôrstner & Wittman, 1981). Thus, the levels of the tested trace elements in Sheary fish commonly consumed by the population of Northern Coast of United Arab

Emirates was examined to determine whether these levels constitute a health hazard for the consumers.

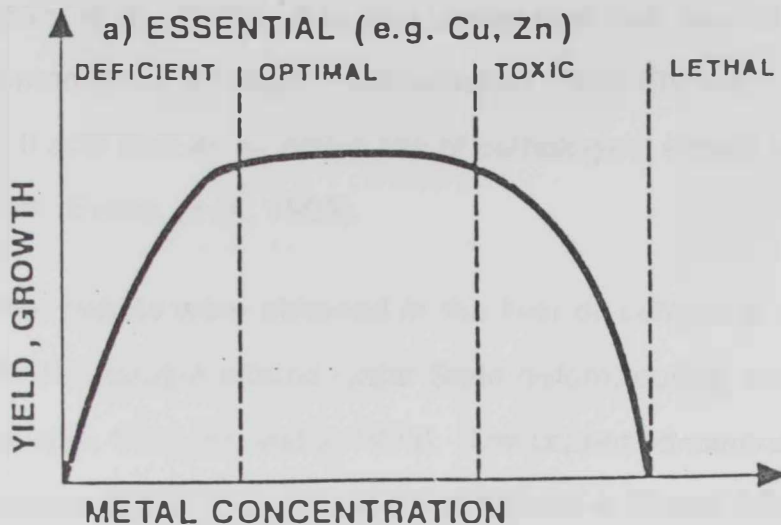


Fig. 4.1 Deficiency and oversupply of essential trace elements (Förstner & Wittman, 1981)

Distribution of Copper:

Fig. 3.1 shows the levels of copper in liver, skin and muscle for male and female fish. In liver the copper content was found high (4.88 ± 1.71 ppm) while in skin and muscle have very low concentrations 0.33 ± 0.13 and 0.17 ± 0.06 ppm, respectively. This behavior could certainly attributed to the fact that most of the copper element is stored in the liver to form metallothionein complex species (Amdur, et al., 1991) and metallo-enzymes (Vinikour, et al., 1980). Metallothionein is a kind of protein found in liver and kidney with high molecular weight (6000–7000). This protein can combine with trace divalent metalions, e.g. Cu, Zn, Cd and Pb to form tetrahedral or square planer stable five or six membered ring metal chelates (Schriver, 1990 and Collon & Wilkinson, 1988). Thus, the liver tissues in fish is often recommended as indicator

organisms because of its tendency to concentrate pollutants of various kinds at higher levels from their environment (Galindo, et al., 1986; Schuhmacher, et al., 1992). It is well known that liver has an important role in contaminant storage, redistribution, detoxification or transformation. It acts also as an active site of pathological effects induced by contaminants (Evans, et al., 1993).

Similar results were obtained in the liver of *Lethrinus nebulosus* and *lentjan* fish caught around Qatar State before, during and after the Gulf War oil spill, 1991 (Kureishy, 1993). The copper concentration in the liver and muscle of nebulous species was around 4.17 and 2.38 ppm dry weight, while in *lentjan* caught the copper level in liver and muscle was 2.79 and 2.32 ppm, respectively. Our data of copper concentration in liver are also quite close to the data reported by Harrison & Klaverkamp, 1990.

The distribution of copper in liver and muscle (*Fig. 3.1*) follow the sequence:

liver > muscle

This behavior is in good agreement with the published work by Jaffar & Pervaiz, 1989. The reason for this behavior is possibly attributed to the specific metabolism process and enzyme-catalyzed reaction involving copper taking place in the liver (Jaffar & Pervaiz, 1989). It may also be due to the fact that copper granules in the cellular organelles may be sequestered in the lysosomes (a process which protects the cell from injury) as reported by Abu Damir, et al., 1993. The data in *Fig. 3.1* also shows difference between copper concentration in female and male fish

in liver, while in skin and muscle no significant differences was observed ($P > 0.05$).

Figures 3.2–3.4 show the trends of copper concentration in liver, skin and muscle with fish size (or age), respectively. In liver and skin (Figs. 3.2 and 3.3) a positive correlation was observed between the copper concentration and fish length (Size) ($R = 0.76$ and $R = 0.9$, respectively). This behavior is possibly due to the slow excretion of copper and it is also accumulated at a rate greater than the rate of tissue growth during much of the life time of the fish as reported previously (Bryan, 1984). In muscle (Fig. 3.4) the copper concentration decrease slightly with increasing fish size, then attained a semiconstant value at 10–17 cm length. These data are in good agreement with to the data reported by Vas & Gordon, 1993. This is possibly attributed to the fact that muscle tissues are not considered to be specific physiological sites for copper storage (Zia & Khan, 1989).

The copper concentration in liver, skin and muscle tissue of individual *Lethrinus nebulosus* fish of the Arabian Gulf region following the Gulf War, 1991 was found in the range 0.6–4.4 ppm (Fowler, et al., 1993). These data are higher than the data reported in our study. The copper level in muscle determined in this study is of a similar range compared to published results for other fish species of Lake Murray (Currey, et al., 1992) and the data reported on *Lethrinus nebulosus* species from Qatar (Kureishy, 1993) and in disagreement with the reported results by Tarique, et al., 1993, Sharif, et al., 1991 and Ramelow, 1989 for different species of different regions and fall within the

ranges of concentration reported by Szefer & Falandysz, 1985 for Cod species from the Southern Baltic Sea.

The mean concentration of copper in muscle tissue of *Lethrinus lentjan* in the present study are found lower than the data reported for the *Lethrinus mahsenoides* (0.34 ppm) and *Lethrinus nebulosus* (0.45 ppm) species of the same family and caught from the Red Sea, respectively (Abdelmoniem & El-Deek, 1992).

The concentration of copper in kidney (3.25 ± 1.53 ppm) was found low as compared to heart (0.39 ± 1.26) as given in Table 3.1. The reason for this behavior could be based on changes in composition of target organ or tissue and the enzyme-catalyzed reactions involving copper in both organs. Translocation of copper in both organs, the nature and the number of the coordinating site in the fibrous protein structure of the kidney may be different from that present in heart and spawning are other possibilities (Kendrick, et al., 1992).

Distribution of zinc:

Fig. 3.5 shows the levels of zinc in liver, skin and muscle. The high concentration of zinc in liver is possibly explained by the fact that zinc is an essential element bound to metallothionein protein and is required for metalloenzymes as a cofactor (Amdur, et al., 1991). Many explanations have been offered for the observed trends, e.g. specific metabolism process and enzyme-catalyzed reaction taking place in the liver (Jaffar & Pervaiz, 1989; Galind, et al., 1986). In their study zinc concentration were found 74.15 ppm in Rohu fish. This value is close to the zinc concentration in female fish of *Lethrinus lentjan* (70.1 ± 38.62

ppm) in the present study. The average zinc concentration in female fish (*Fig. 3.5*) follow the sequence:

liver > skin > muscle

and the average zinc concentration (*Table 3.1*) was found to depend on sex and the following sequence:

female > male

in liver, and skin ($P < 0.05$) was achieved.

Similar accumulation behavior of zinc in female and male have been reported by Khan & Weis, 1993. This sequence is possibly attributed to the fact in female and male fish the types of hormones are different and the number of coordinating site in their protein structure may be different and contain optically active ligands of nitrogen, oxygen and/or sulphur sites which favourable formations of tetrahedral species of zinc chelates (Kendrick, et al., 1992).

The zinc concentration in liver and skin (*Figs. 3.6–3.8*) increase with increasing fish size and strong correlation was found in liver ($R = 0.92$). These results are in good agreement with the data reported by Evans, et al., 1993 and Singh, et al., 1991 and indicated that there is a strong correlation between the zinc content in liver with the fish size. Zinc is an essential element and usually does not increase in concentration with age or size because it is thought to be under homostatic control (Thompson, 1990). Exposure to different metal concentrations over time dietary shifts, differences in the uptake, assimilation and excretion rates of zinc with age may account for the observed trend (Evans, et al., 1993).

The mean concentration of zinc in muscle was found 3.30 ± 0.28 ppm. This value is lower than the data reported of *Lethrinus mahsenoides* (4.81 ppm) and *Lethrinus nebulosus* (6.87 ppm) species from Red Sea and Arabian Gulf region following the Gulf War (Abdelmoniem & El-Deek, 1992; Fowler, et al., 1993) and is quite close to the data reported by Harrison & Klaverkamp, 1990 for other fish species in other locations.

The uptake of zinc showed no clear distribution pattern between fish size and its concentration in muscle (*Fig. 3.9*). The value of correlation coefficient was found very weak 0.07. Zinc seemed to accumulate upto a certain level then the concentration appeared to remain constant. This behavior is due to several mechanisms which may regulate the content of the metals in fish (Marco Vecchio & Moreno, 1993; Vinikour, et al., 1980). Moreover, Guns, et al., 1988 reported that no significant differences was observed between zinc concentration and length.

The accumulation patterns of the elements are related to interdependency of uptake and domination rates of elements (Vinikour, et al., 1980). When sufficient levels of the element essential for metabolism is sequestered in the body and equilibrium is established between the body burden of the element and environment concentrations. After that, the body burden may remain relatively stable or decrease with increasing the size or age of the fish (Vinikour, et al., 1980).

The accumulation of zinc in kidney (43.26 ± 16.87 ppm) was found high as compared to heart tissue (32.38 ± 10.19 ppm). The reason for this behavior is possibly attributed to the fact that the number of α -hydroxy acids and amino acid containing sulphur are possibly high in kidney tissue as compared to heart tissue. This behavior is related to the fact that kidney tissues are covered with mucous membrane which enhance the chelatin with zinc (Sorensen, 1991) The possibility of occurrence of enzymes bound zinc in kidney also could account for this trend.

Distribution of manganese:

It is known that manganese is one of the essential elements which play an important role as a cofactor for a number of enzymatic reaction especially those involved in phosphorylation, cholesterol and fatty acid synthesis (Hay, 1991; Kendrick, et al., 1992).

It is observed that manganese (*Fig. 3.10*) have greater tendency to accumulate in liver rather in skin and muscle and the accumulation pattern of the average manganese (*Table 3.1*) follow the sequence:

liver > skin > muscle

This behavior is possibly attributed to the ability of the manganese to concentrate in mitochondria, where liver, pancreas and intestines tissue are rich in these organelles (Amdur, 1991). Another reason for this behavior may be based on the specific metabolism process and enzyme-catalyzed reaction involving manganese taking place in liver (Jaffar & Pervaiz, 1989).

It can also be noticed that (*Fig. 3.10*) there is a significant difference ($P < 0.05$) between the manganese levels in male and female fish where the sequence follow the order:

female > male

In muscle and skin (*Fig. 3.10*) the differences in manganese content in female and male is not significant where the $P > 0.05$.

Fig. 3.11 shows no difference in manganese content in fish liver and fish size and the correlation ($R = 0.636$) with exception at fish size 13 cm where the manganese content was found high. The reason for this behavior at small fish size is possibly related to the high metabolism rate and the increase in the uptake at the early growth of fish as reported by Evans, et al., 1993.

The mean concentration of Mn in fish liver was found 1.22 ± 0.23 ppm. This value is lower than the value reported by Jaffer & Pervaiz, 1989 [4.71 ppm in Salmon sole fish and 4.38 ppm in Rohu (*Labeo rohito*)], while it fall within the range of Mn concentration reported by Vas & Gordon, 1993 in deep-sea shark liver from the Rockall Trough.

Manganese concentration in skin shows higher concentration in younger fish than older fish (*Fig. 3.12a*) and a negative correlation was found between concentration and fish length ($R = -0.72$). This behavior could be due to change in the uptake rate of manganese with age (Vas, et al., 1990).

A strong correlation between the rate of uptake and the rate of growth (*Fig. 3.12a*) in skin was achieved. Thus the faster growth rates

the more accumulation of metals in younger fish than the older fish where the growth rate is slow (Vas, et al., 1990). It may be also due to changes in relative organ size with growth (Vas, et al., 1990; Milner, 1979) or changes in composition of the target organ or tissue with growth, e.g. lipid content (Nicholson, et al., 1991; Girmas, et al., 1985). Translocation of manganese among tissues and spawning are other possibilities (Evans, et al., 1993) for this behavior.

The manganese concentration in fish muscle was found 0.17 ± 0.06 (Table 3.1). This value falls within the ranges of concentrations for other published results for other species in other locations by Schuhmacher, et al., 1992; Jaffer, et al., 1988; Vas & Gordon, 1993.

It is worth mentioning to note that the mean concentration of Mn in fish muscle was slightly lower than those reported by Fowler, et al., 1993 on *Lethrinus nebulosus* species caught from Bahrain, Saudi Arabia, Dubai, Oman after the Gulf War, 1991 where the manganese concentration in muscle was in the range 0.19–0.4 ppm for individual fish (Fowler, et al., 1993). Abdelmoniem & El-Deek, 1992 reported that the average concentrations in *Lethrinus mahsenoides* muscle was 0.32 ppm while for *Lethrinus nebulosus* muscle was 1.13 ppm.

The relationship between manganese concentration and fish size in muscle (Fig. 3.13) is very strong inverse relationship ($R = -0.967$). The content of manganese increased with increasing growth rate at small fish size suggesting a metabolic regulation of manganese content as previously reported by Ronnberg, et al., 1990. Manganese as an essential element usually does not increase in concentration with age or

size since it could be present under homeostatic control (Thomson, 1990).

The accumulation of manganese in kidney and heart is given in Table 3.1. The distribution follows the order:

kidney > heart

This behavior is attributed to the difference in the protein structure of both organs, the number of coordinating and active sites and the types of enzymes, coenzymes and hormones involved in both tissues (Kendrick, et al., 1992). Manganese is found in a variety of enzymes such as pyruvate carboxylase, oxaloacetate decarboxylase and superoxide dismutases and manganese porphyrin complexes which are normally accumulated in kidney at high level as compared to heart as reported by Kendrick, et al., 1992.

4.2 Accumulation of non-essential elements

There has been an increasing concern over environmental lead and cadmium pollution and the subsequent effect of these toxic metals (not serving as beneficial biological function). With the industrial and technological revolutions, the intensified use of lead and cadmium poses a serious threat to human health (Sharif, et al., 1993). These elements tend to accumulate in bottom sediments from which they may be released by various processes of remobilization and— in changing form— can move up the food chain, thereby reaching man where they could produce chronic and acute ailments. The deficiency and oversupply of these elements are given in Fig. 4.2 (Förstner & Wittman, 1981).

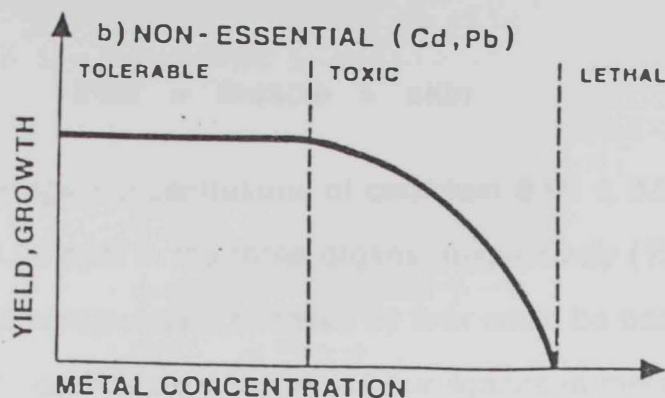


Fig. 4.2 Deficiency and oversupply of nonessential trace elements (Förstner & Wittman, 1981)

The targets of the toxic metals are specific biochemical processes and/or membranes of cells and organelles. The toxic effect of these elements occur due to the similarity of their metabolism with other essential elements metabolism in the central nervous system (Amdur, et al., 1991). Other reason for the element toxicity that these elements attack the gastrointestinal, liver, or renal tubular cells which are particularly susceptible to toxicity (Amdur, et al., 1991).

Accumulation of cadmium:

Cadmium is a ubiquitous, non-essential element which possess high toxicity to both humans and aquatic organisms (Diaz-Mayans, et al., 1986). Cadmium and cadmium compounds have been used extensively by various industries and this has produced sharp increases in contamination of water. Cadmium is widespread in the biosphere which is accumulated by animals and fish (Diaz-Mayans, et al., 1986).

The accumulation behavior of cadmium (*Fig. 3.14*) in fish liver, skin and muscle follow the sequence:

liver > muscle > skin

with an average concentrations of cadmium 0.66 ± 0.28 , 0.11 ± 0.02 and 0.08 ± 0.06 ppm in the three organs, respectively (*Table 3.1*). The reason for this accumulation behavior by liver could be based on the greater tendency to coordinate with the sulphur ligands in metallothionein protein present in liver. Metallothionein is primarily a tissue protein contains 61 amino acids and 21 of them are cysteine which have greater tendency to form stable five or six-membered ring chelates with cadmium via the carboxylate, amino and mercapto groups (Amdur, 1991). The fact that metallothionein is ubiquitous in most organs but is in highest concentration in liver and kidney (Amdur, 1991). Therefore cadmium accumulates highly in liver.

The accumulation of cadmium in the three organs in female and male fish follow the order:

female > male

and the differences between female and male in cadmium accumulation in muscle and skin is not significant ($P > 0.05$). It can be inferred from the distribution of cadmium in these organs that female fish have great tendency to accumulate cadmium. It seems likely that all three organs in female fish contains large number of specific active sites and hormones which have greater tendency to accumulate cadmium.

Fig. 3.15 shows the accumulation of cadmium in fish liver with fish age (or size). The concentration of cadmium in liver increases with fish length. This behavior is common for non-essential elements (Evans, et

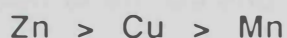
al., 1993) because it is thought that excretion of Cd is very slow and it accumulated at a rate greater than the rate of tissue growth during fish life time and the correlation is very strong ($R = 0.857$).

The distributions of cadmium in skin and muscle with fish size are summarized in Figs. 3.16–3.18. A decrease in cadmium concentration with size is observed for both organs. The correlation coefficients of fish skin and fish muscle were found -0.598 and -0.896 suggesting weak and strong correlation in both organs, respectively. A primary reason for a decrease in metal concentration is related to new tissues being incorporated at a greater rate than metals can be actively transported into the tissues to establish a steady-state concentration (dilution by growth) as previously reported by Vinikour, et al., 1980.

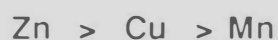
The accumulation of cadmium in kidney and heart is summarized in Table 3.2. Many explanations have been offered for the observed trend where metallothionein tissue protein is ubiquitous in most fish organs and is highest concentration in kidney (Amdur, 1991). This protein structure is able to form stable cadmium chelate via sulphur ligands. Also, cadmium is less well regulated in fish body and it can enter fish through food chain and accumulate in kidney as organometallic compounds as solid granules which are then stored or excreted (Amdur, 1991).

4.3 Accumulation behavior of essential and non-essential elements in the different fish organs

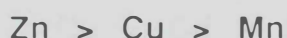
In liver (*Figs. 3.5 and 3.19*) the accumulation behavior of the tested essential elements followed the sequence:



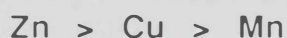
at all fish sizes. In skin (*Figs. 3.5 and 3.20*) the uptake trend of the elements followed the order:



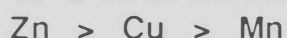
In muscle (*Figs. 3.5 and 3.21*) the following sequence:



In heart (*Fig. 3.22*) the order of sequence:



and in kidney (*Fig. 3.22*) the following order:



were achieved.

The high accumulation of zinc is attributed to the fact that in biological systems there are about 18 zinc metalloenzymes and about 15 Zn²⁺ ion-protonated enzymes. Zinc also acts as a catalyst in metallobiomolecules bound to amino acid side chains containing N, O or S donor ligands (Kendrick et al., 1992) to form tetrahedral zinc metalloproteins and metalloenzymes.

The accumulation behavior of the tested elements in liver (*Fig. 3.23 and Table 3.1*) followed the order:



The high concentration of Zn, Cu and Mn could be related to the occurrence of these elements in many enzymatic reactions in liver as previously mentioned. In skin (*Fig. 3.24*) the order:



was achieved. In muscle (*Fig. 3.24 and Table 3.1*) the accumulation behavior followed the sequence:



while in kidney and heart (*Fig. 3.22 and Table 3.2*), it can be noticed that the accumulation order in kidney followed the order:



and in the heart the sequence followed the order:



Different factors, e.g. excretion rate, the binding rate of sulphydryl groups, number of coordinating sites, the solubility of metal salts, the restricted relocation of the different elements in the tested fish organs, the nature of the enzymes available in each tissues and the affinity of each trace element to form stable chelates with the available active sites in each fish organs are possibly participating factor in these trends.

**CONCLUSION
AND
RECOMMENDATIONS**

4.4 Conclusion and Recommendations

The results of this study indicate that:

1. The accumulation of Cu, Cd, Zn and Mn were greatest in liver tissues as compared to skin and muscle.
2. Most of the tested metals are highly accumulated in female tissues as compared to male tissues.
3. Most of the tested elements were within the permissible limits for human consumption. Therefore consuming *Lethrinus lentjan* (Sheary) fish from U.A.E region does not pose a health hazard, but protection of the aquatic environment is warranted to preserve this important part of the traditional diet.
4. Most of the elements are highly accumulated in fish liver, as compared to muscle; therefore it is recommended to discard the liver and eat only the muscle.
5. According to the recommendations of various international agencies as cited by Sharif, et al., 1993, the provincial tolerable intake of Cd by human beings is ($1-1.2\mu\text{g kg}^{-1}$ body wt day⁻¹). According to our results for average intake to reach this limit, a person will require to consume about 800 gm of fish flesh (*Lethrinus lentjan*) per day, which is far more than the average consumption of fish by a normal person per day.

As a result, we can conclude that *Lethrinus lentjan* fish of the western coast of U.A.E (Ras Al-Khaima) is safe for human consumption which reflect as well that the area is free of heavy metals pollution.

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REFERENCES

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