HEAVY METAL CONTENT IN VARIOUS TISSUES OF THE MUDSKIPPER, *BOLEOPHTHALMUS DUSSUMIERI* (CUV) AT THE MAHI ESTUARY.

CHAPTER - IV

HEAVY METAL CONTENT IN VARIOUS TISSUES OF THE MUDSKIPPER, BOLEOPHTHALMUS DUSSUMIERI (CUV) AT THE MAHI ESTUARY

The Mahi river and its tributary the Mini, which flow along the outskirts of Baroda city from northwest to south west and ultimately join the Arabian sea at the Gulf of Cambay at a distance of about 100 km from the city, has served as the most convenient receptacle of sewage and industrial waste originating from the huge industrial complex, that developed in the Nandesari-Koyli belt between 1960 and 1980. The increasing pollution load and sporadic reports of death of fishes and cattle, and human health problems, lead the state public health department to envisage the construction of a channel for conveying the industrial waste, for discharge into the Mahi estuary at the Gulf of Cambay. Ultimately, a closed conduit (with movable slabs) effluent channel with a common treatment plant at its origin was constructed in the year 1983. The channel coursing through 24 villages and a distance of about 56 Km, conveys the industrial waste of the Nandesari complex into the Mahi estuary. Prior to the constructiion of the channel, National Environmental Engineering Research Institute (NEERI) had undertaken a survey of the Mahi river and its estuary at the Gulf of Cambay, in 1975. The above study showed severe pollution of the Mahi river and its effects on the life of fishes in the river. Eleven species of fishes were identified at different sampling stations at the Mahi estuary, and the dominant fishes identified were the ones that ascend the estuary from the Gulf region to the estuarine region of the Mahi river and then return to the Gulf. During ebbing under neap tide conditions, the migrating fishes were found only upto the sill near Mohammadpura and were not found in the upstream direction beyond the sill but, during the spring tide, some of the fishes could be observed even upstream beyound the sill. Now about 12 years after the construction of the effluent channel, there is hardly any fish fauna nor any fishing activity at Sarod (the point at which the channel opens into the estuary), about 36-39 km downstream of Mohammadpura, where the earlier study had shown the pressence of fishes. Presently, most common fish that could be seen in the area around the "J" point, shiv mandir (downstream), and at Sarod (upstream) is, the Mudskipper, *B.dussumieri*. Occasionaly the flat fish, (*Synaptura*) could be seen in the early part of the present study in 1991, but never seen later in 1993. Earlier studies (Chapters- I and II) have shown increasing contamination of the Mahi estuarine waters and its sediment by heavy metals originating from the effluent channel discharge.Heavy metals are the major ingredients of industrial effluents, and are characterised by their biologically non-degradable nature and tendency for biomagnification. Generally, sediments and detritus contain the highest metal concentrations in polluted systems.Sediment and detritus feeding animals tend to accumulate higher metal concentrations than animals at higher tropic levels (Gearheart *et al.*, 1992). Since the mud skipper, *B.dussumieri,* is the most commonly found fish fauna in the study area and, forms the cheaply and easily available food of the poor coastal community, an analysis of the metal content in various tissues of the specie has been currently undertaken.

MATERIALS AND METHODS

The fishes were collected from the "J" point, Kavi (down stream of J point) and Sarod(up stream of J point). The control fishes for the estimation of background metal content were collected from Dumas in Surat (Tapi estuary) and Hansot in Bharuch (Narmada estuary). The fishes were collected during 1991-1993 and, after bringing them to the laboratory, they were sacrificed and the gill, muscle, liver, intestine, brain and gonads were dissected out and oven dried. The oven dried materials were transferred to conical flasks containing 3 ml each of sulphuric acid and nitric acid and 94 ml of distilled water. They were then kept on a hot plate for digestion till the volume was reduced to 5 ml. The flasks were then cooled and the volume was again made up to 100 ml by adding distilled water. They were then filtered through whatman filter paper No. 40, and, 10 ml samples were taken and diluted to 100 ml before aspiration in an atomic absorption spectrophotometer for analysis of various metals. The values obtained are expressed as ppm (µg/gm or mg/kg).

RESULTS

The concentration of various metals in different organs of *B.dussumieri* is shown in table 1 and, tables 2, 3 depict the relation between Water/Sediment content of metals and the amount accumulated in various organs in terms of one ppm metal contamination in the enviornment. In general, the content of various metals in tissues and organs was found to be significantly greater in fishes captured from the experimental sites than the control ones (Figs- 1-6). The background levels of Pb, Fe and Zn were quite high in fishes from the non-polluted areas. Again, fishes obtained from the "J" point had higher metal content than those captured from the down stream area. The order of accumulation in various organs are, liver- Cu>Pb>Zn>Ni>Fe>Cr>Cd, intestine- Cu>Pb>Zn>Cr>Ni>Fe>Cd, muscle- Zn>Pb>Cd>Fe>Cu>Cr, gill- Fe>Pb>Co>Cd>Ni>Cr, ovaries- Pb>Fe>Zn>Cr>Ni>Cd>Cu and brain- Zn>Ni>Cd>Fe>Pb>Cu>Cr.

TABLE 1: MEAN METAL CONTENT (mg/kg) IN TISSUES OF B.dussumieri

SR. NO	TISSUE	PLACE	Cr	Zn	Ni	Pb	Cd	Fe	Cu
1	LIVER	DUMAS	2.4	6.2	1.9	20.2	2.1	27.7	2.6
2		BHARUCH	1.7	4.8	1.9	19.0	1.5	8.1	2.0
3		(Hansot)							
4		Shiv Temple	3.3	44.5	4.2	35.2	3.0	11.4	34.7
5		"J"Point	3.3	54.0	25.5	61.7	3.2	14.8	109.9
1	INTESTINE	Dumas	2.6	2.4	2.4	26.4	1.9	3.4	2.6
2		Bharuch	4.9	5.9	2.3	16.2	1.8	4.2	3.2
3		(Hansot)							
4		Shiv Temple	4.4	21.8	4.3	30.8	2.2	8.6	60.5
5		"J"Point	31.5	52.9	21.8	60.6	5.1	12.8	126.9
1	MUSCLE	DUMAS	1.4	3.1	2.1	2.1	1.1	2.1	1.7
2		BHARUCH	1.4	4.4	1.4	2.00	1.5	1.9	1.3
3		(Hansot)							
4		Shiv Templ	1.3	52.8	1.7	4.6	3.3	2.1	4.3
5		"J"Point	2.4	75.3	3.8	23.6	11.8	3.9	7.7
1	BRAIN	DUMAS	1.0	26.0	1.4	4.1	6.3	3.9	1.1
2		BHARUCH	1.3	11.6	1.0	4.3	2.5	2.7	1.2
3		(Hansot)							
4		Shiv Temple	29.0	47.2	44.2	48.6	48.5	30.3	28.0
5		"J"Point	39.1	100.1	86.0	46.0	62.9	48.8	44.0
1	GILL	DUMAS	2.4	2.1	4.1	5.2	3.6	24.2	2.7
2		BHARUCH	2.1	1.1	8.2	5.6	5.0	19.7	4.2
3		(Hansot)							
4		Shiv Temple	5.3	1.3	11.5	5.3	5.3	38.9	12.7
5		"J"Point	13.4	14.4	22.4	48.1	12.6	49.7	19.6
1	OVARY	DUMAS	3.7	4.0	1.4	3.6	2.6	4.2	2.1
2		BHARUCH	3.1	4.2	1.4	3.6	2.5	5.7	2.1
3		(Hansot)							
4		Shiv Temple	3.9	5.2	2.2	4.1	3.3	5.3	2.1
5		"J"Point	4.9	6.2	4.1	6.2	4.1	5.7	3.2

TABLE 2: SHOWING THE ABSOLUTE CAPACITY FOR ACCUMULATION OF VARIOUS METALS BY TISSUES OF *B.dussumieri* AS A PROPORTION OF UNIT CONTENT OF WATER (1ppm - mg/1)

SR. NO.	TISSUE	Cr	Zn	Ni	Pb	Cd	Fe	Cu
1	LIVER	22.92	120.50	138.24	149.51	122.04	38.19	552.26
2	INTESTINE	221.09	118.16	118.32	146.85	193.82	33.03	637.68
3	MUSCLE	16.63	168.26	20.46	57.19	446.08	9.94	38.59
4	BRAIN	275.01	223.59	466.78	111.47	2379.71	125.94	221.11
5	GILL	93.92	32.05	121.58	116.56	475.11	128.15	98.24
6	OVARY	34.52	11.64	22.31	15.02	154.60	14.74	16.08

TABLE 3: SHOWING THE ABSOLUTE CAPACITY FOR ACCUMULATION OF VARIOUS METALS BY TISSUES OF B.dussumieri AS A PROPORTION OF UNIT CONTENT SEDIMENT (1ppm - mg/l)

SR. NO.	TISSUE	Cr	Zn	Ni	Pb	Cd	Fe	Cu
1	LIVER	0.005	0.027	0.051	0.091	0.011	0.015	0.368
2	INTESTINE	0.051	0.027	0.043	0.089	0.017	0.013	0.425
3	MUSCLE	0.039	0.038	0.007	0.035	0.039	0.004	0.026
4	BRAIN	0.064	0.504	0.017	0.068	0.210	0.050	0.147
5	GILL	0.022	0.007	0.044	0.071	0.042	0.051	0.065
6	OVARY	0.008	0.003	0.008	0.009	0.037	0.006	0.011

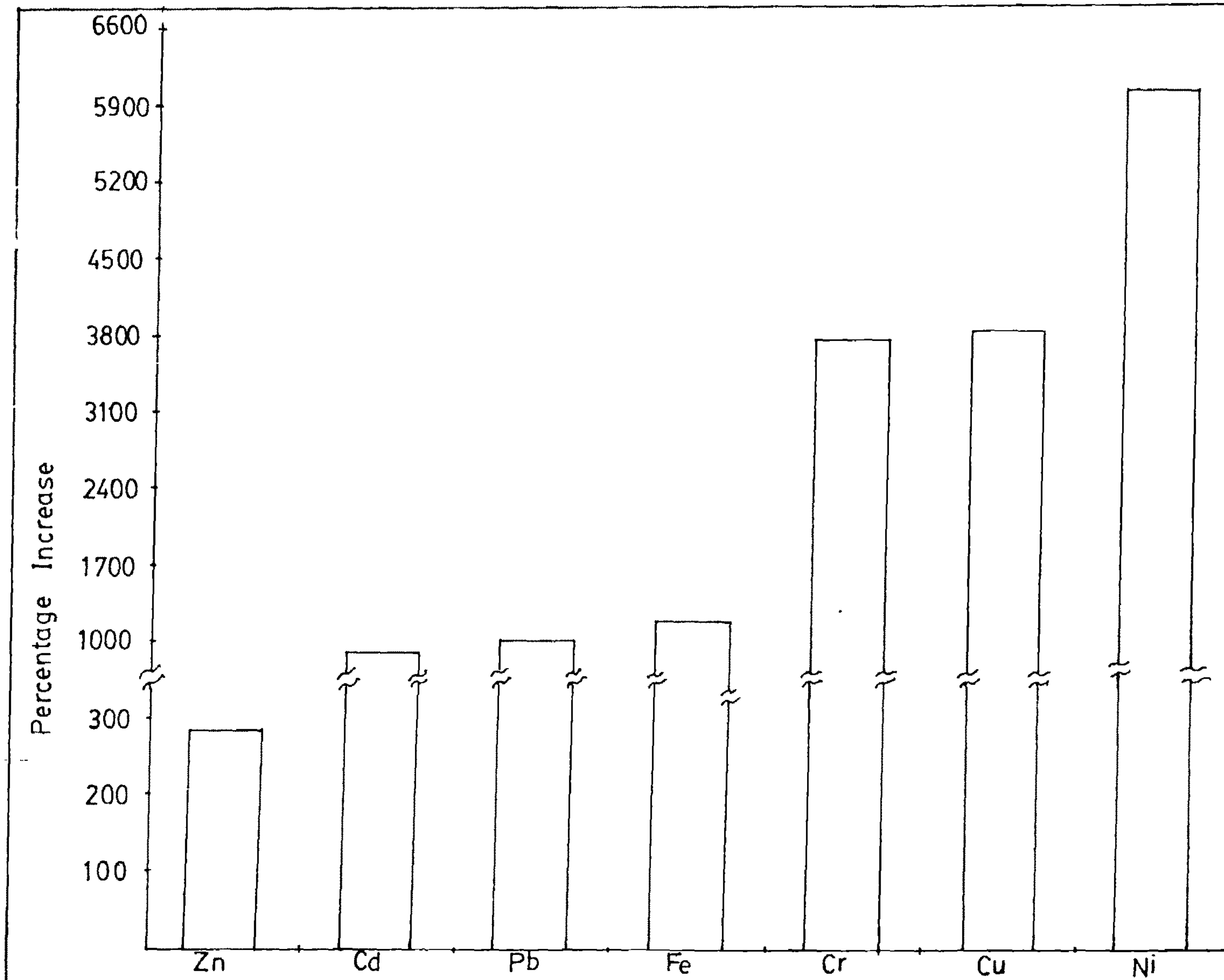

Fig.1-Percentage increase of various metals in the brain of mud skipper from the Mahi estuary.

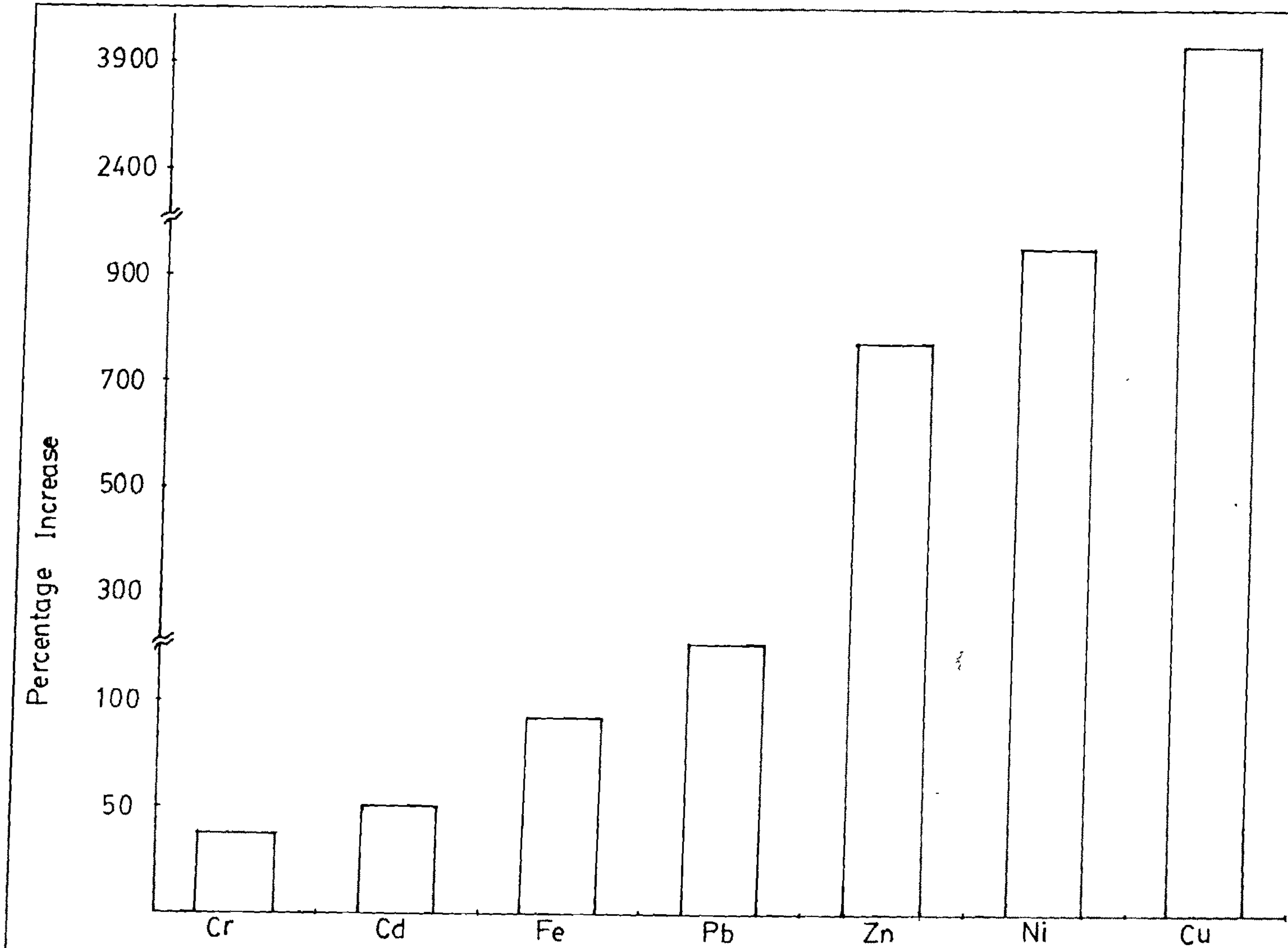

Fig.2 Percentage increase of various metals in the liver of mud skipper from the Mahi estuary.

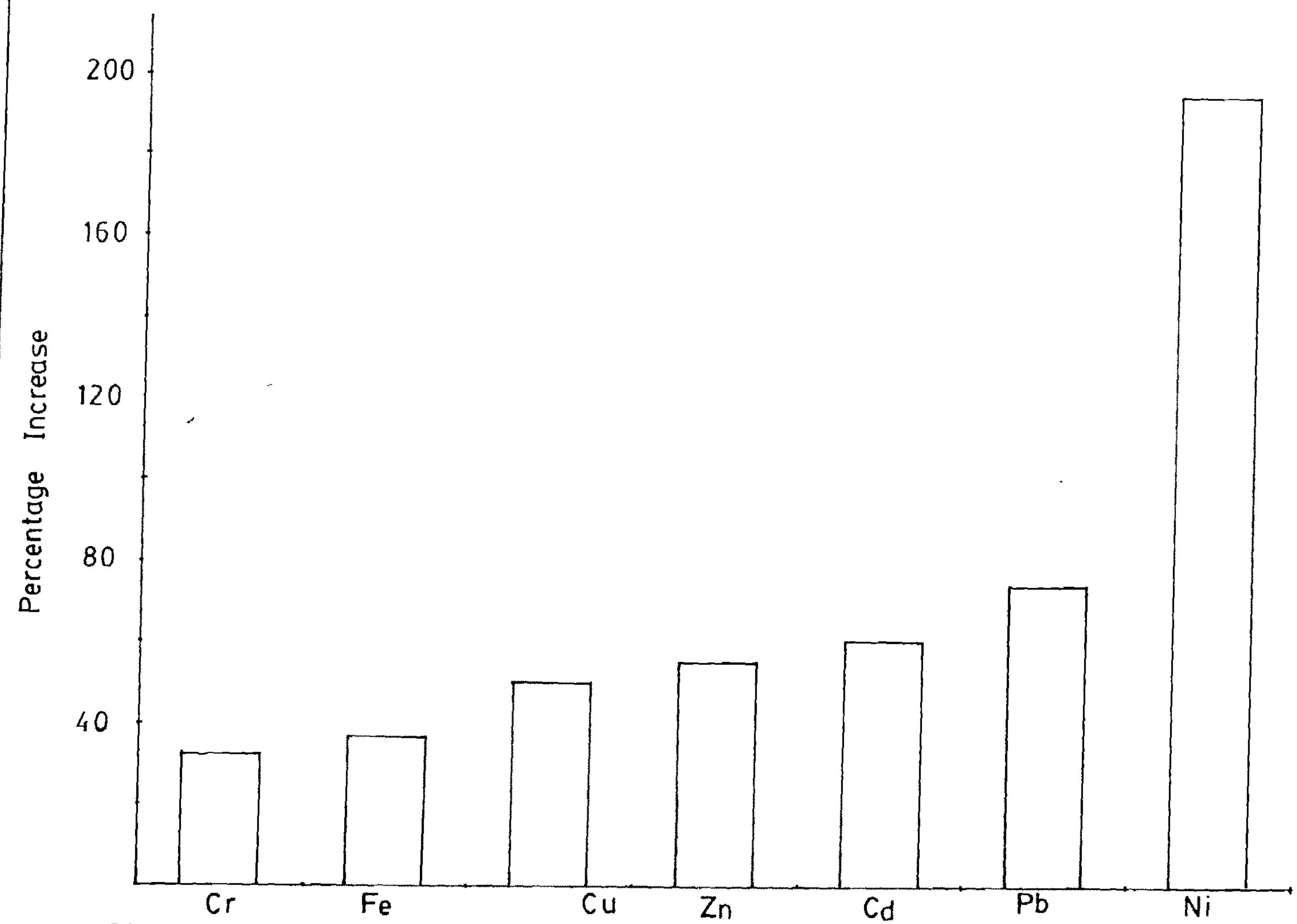

Fig.3 Percentage increase of various metals in the ovary of mud skipper from the Mahi estuary.

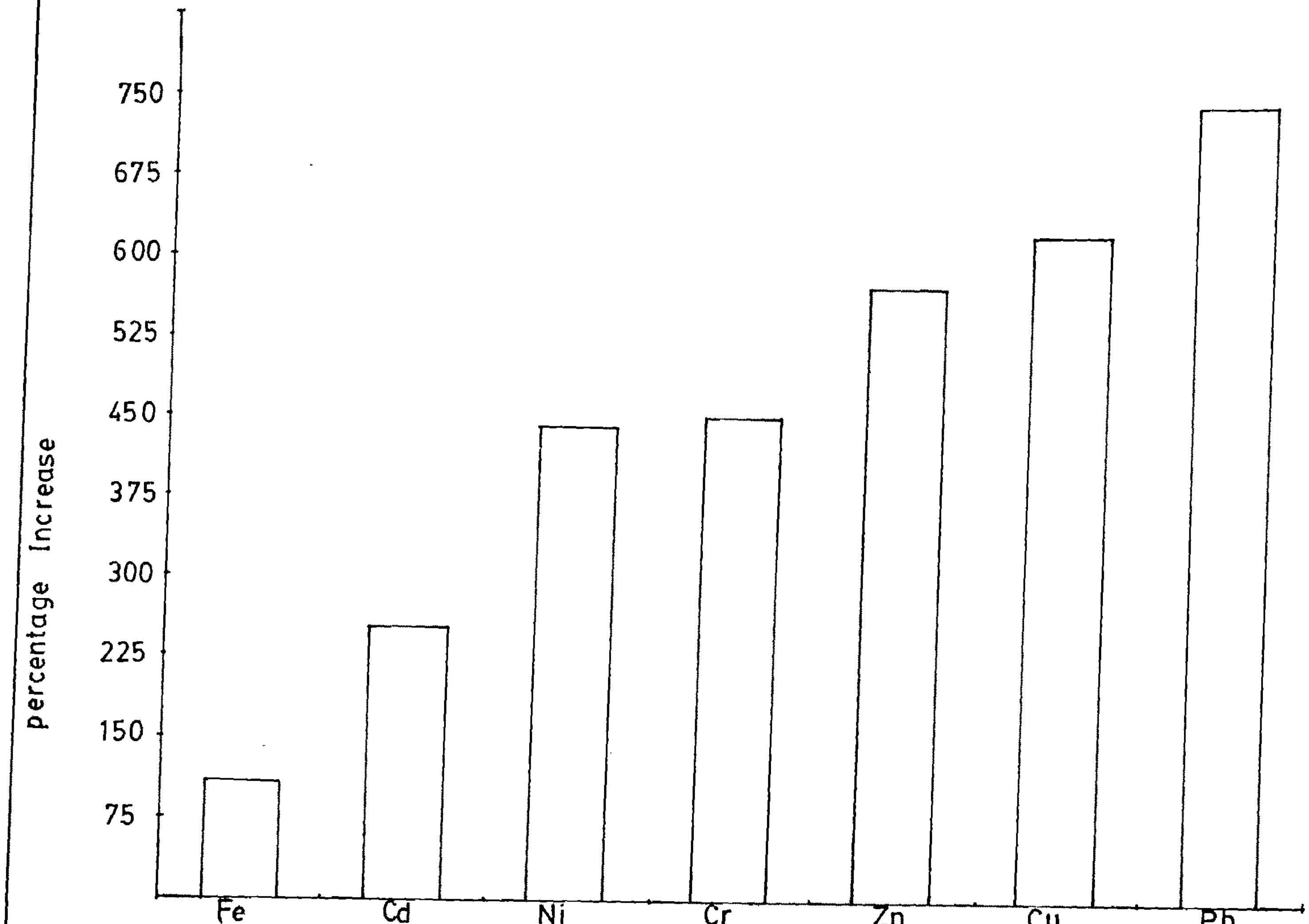

Fig4 percentage increase of various metals in the gill of mud Skipper from the Mahi estuary.

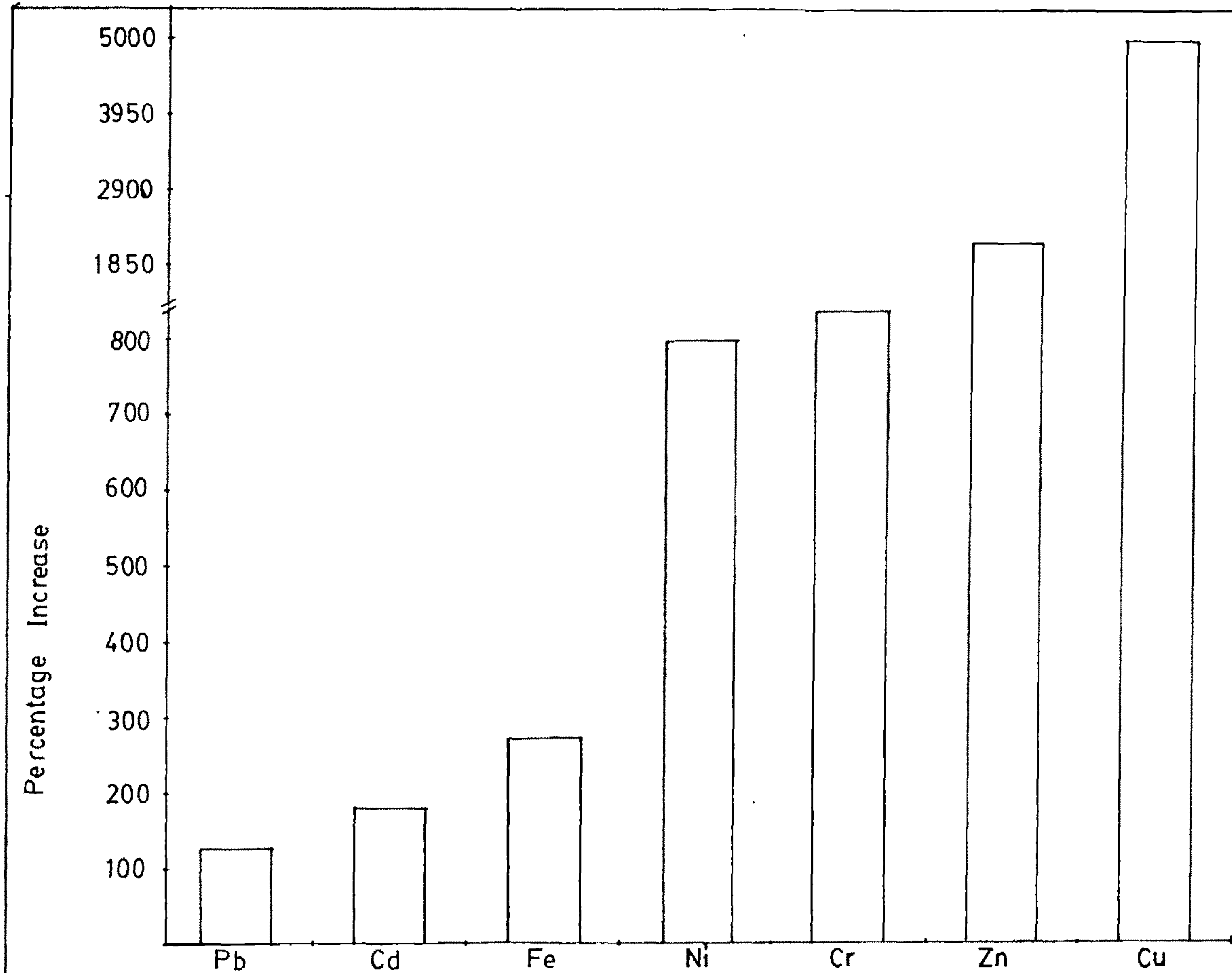

Fig.5 Percentage increase of various metals in the intestine of mud skipper from the Mahi estuary.

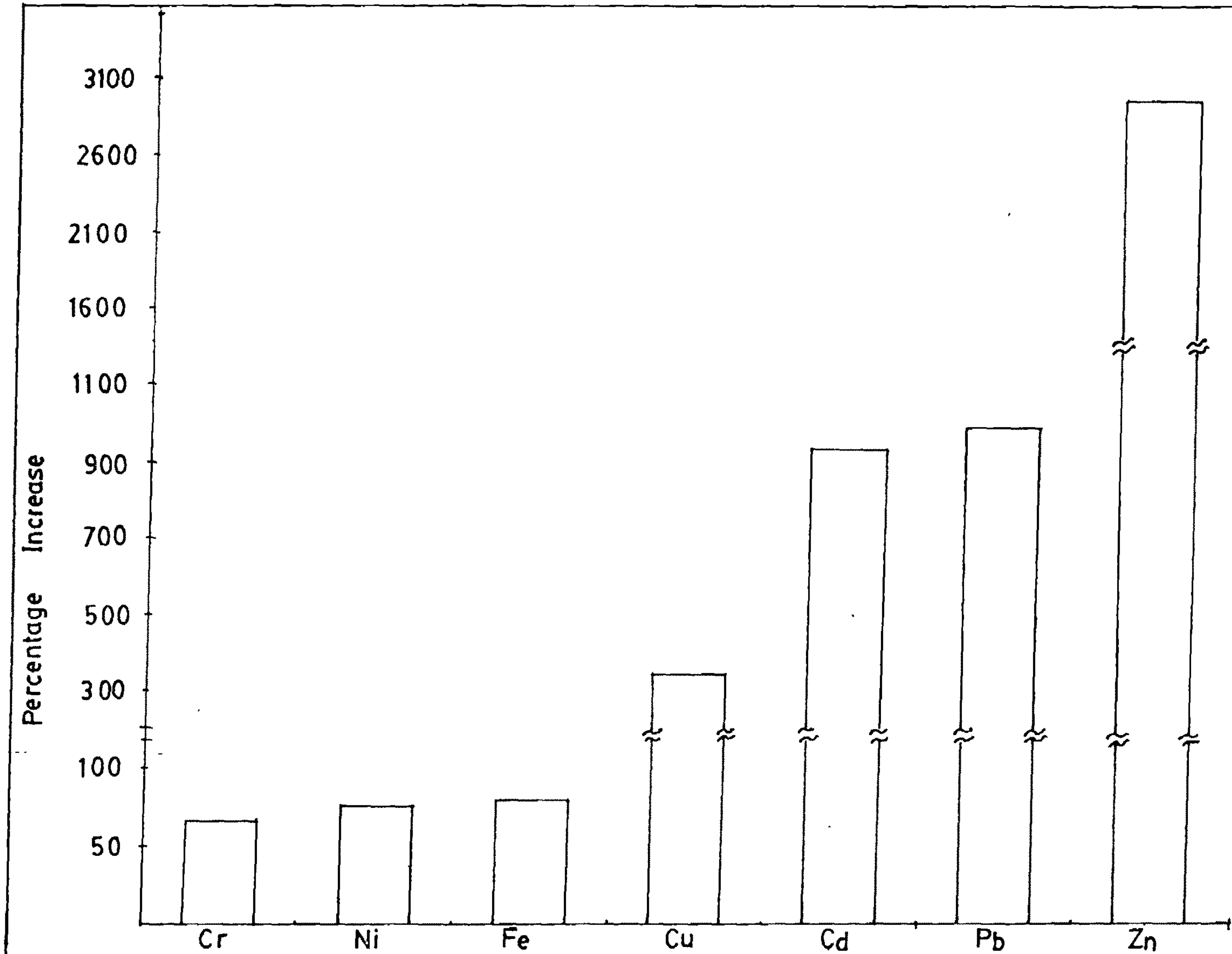

Fig.6 Percentage. Increase of various metals in the muscle of mud skipper from the Mahi estuary.

The relative content of various metals in different organs in terms of unit content of the metals (1ppm) in the estuarine water, shows accumulation of Cd to be the greatest, followed by Cu, Ni, Zn Cr Pb and Fe in that order (table 2). The relative content of various metals in different organs in terms of unit content of the metals (1ppm), in the sediments, shows accumulation of Cu to be greatest followed by Pb, Cd, Ni, Cr, Zn and Fe (Figs- 7-13).

DISCUSSION

Many metals are essential in small amounts for plant and animal life, but optimum concentration ranges are frequently very narrow. In these cases, the difference between the concentration of a metal necessary for best growth and survival, and concentration resulting in toxic or adverse effects can be surprisingly small. Non-optimal concentrations of essential metals are commonly found in nature and, in an ecosystem, species differ in their response to metal concentration (i.e., species have differing survival potential in environments of different metal forms and concentrations). Carpenter (1924) was among the first to provide scientific observations of the reduction in flora and fauna in Pb and Zn polluted rivers of West Wales. Metals which are essential/beneficial for plant or animal in small

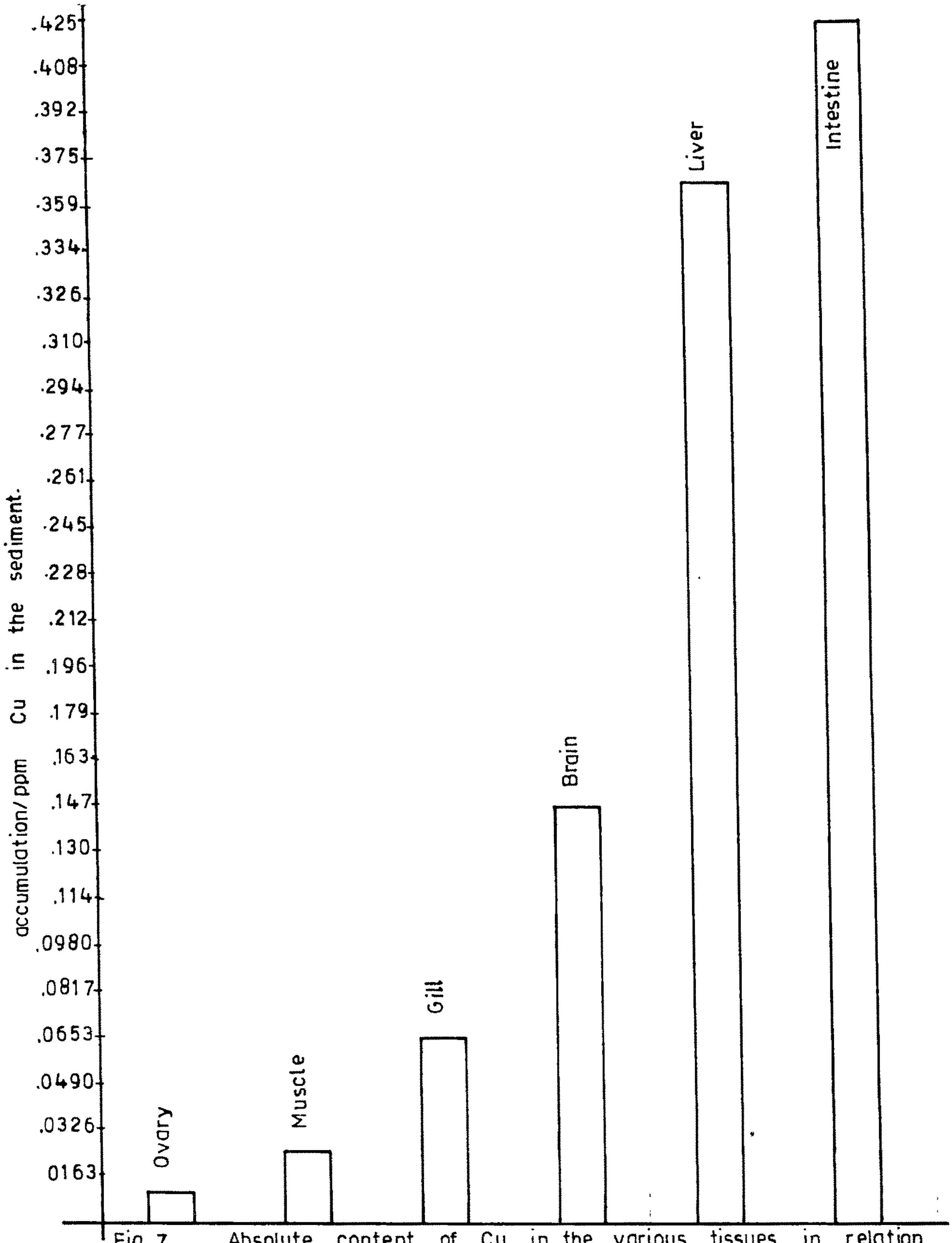

Fig 7 Absolute content of Cu in the various tissues in relation unit content (1ppm; mg/kg) in the sediment.

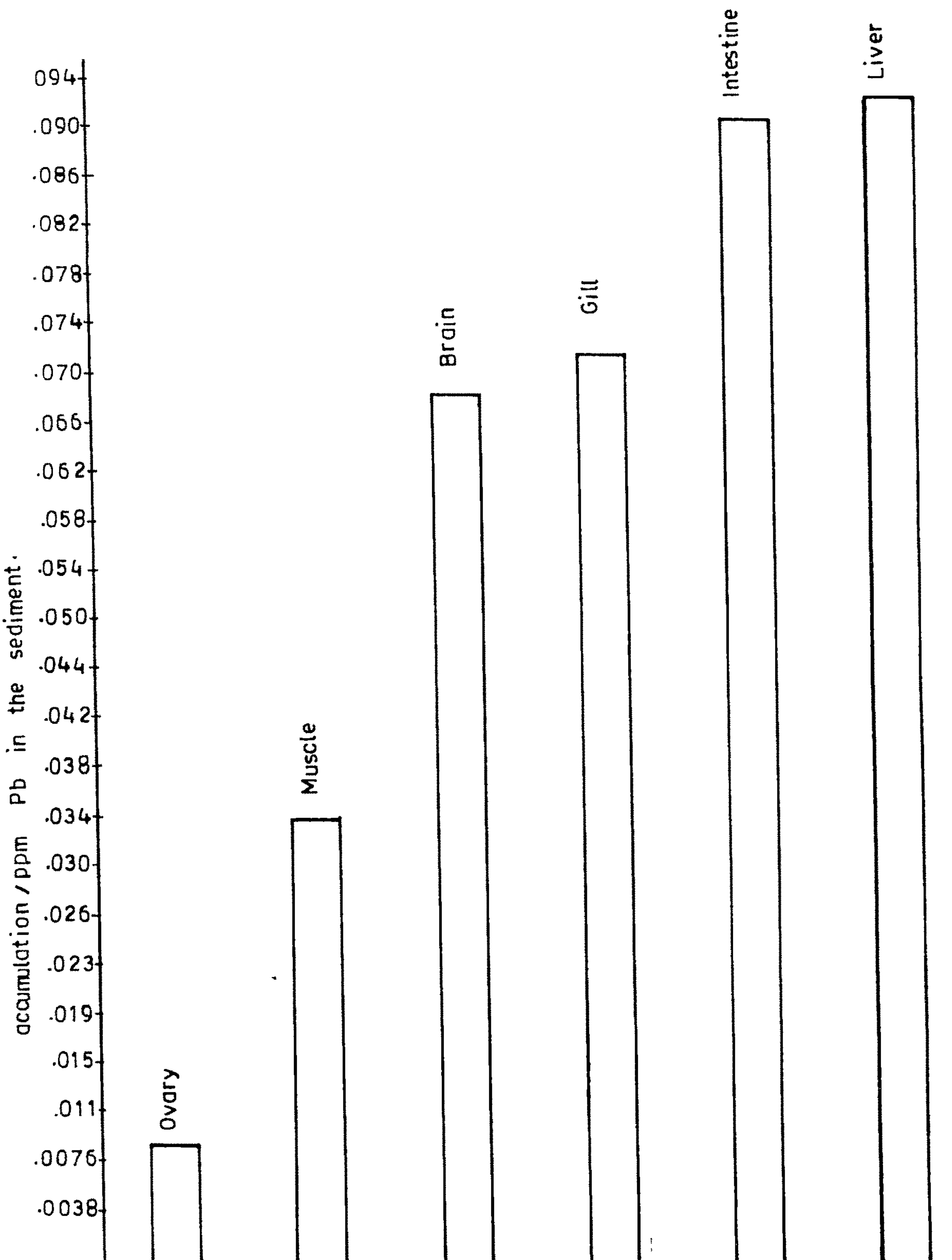

Fig 8 Absolute content of Pb in various tissues in relation to unit (1ppm; mg/kg) in the sediment.

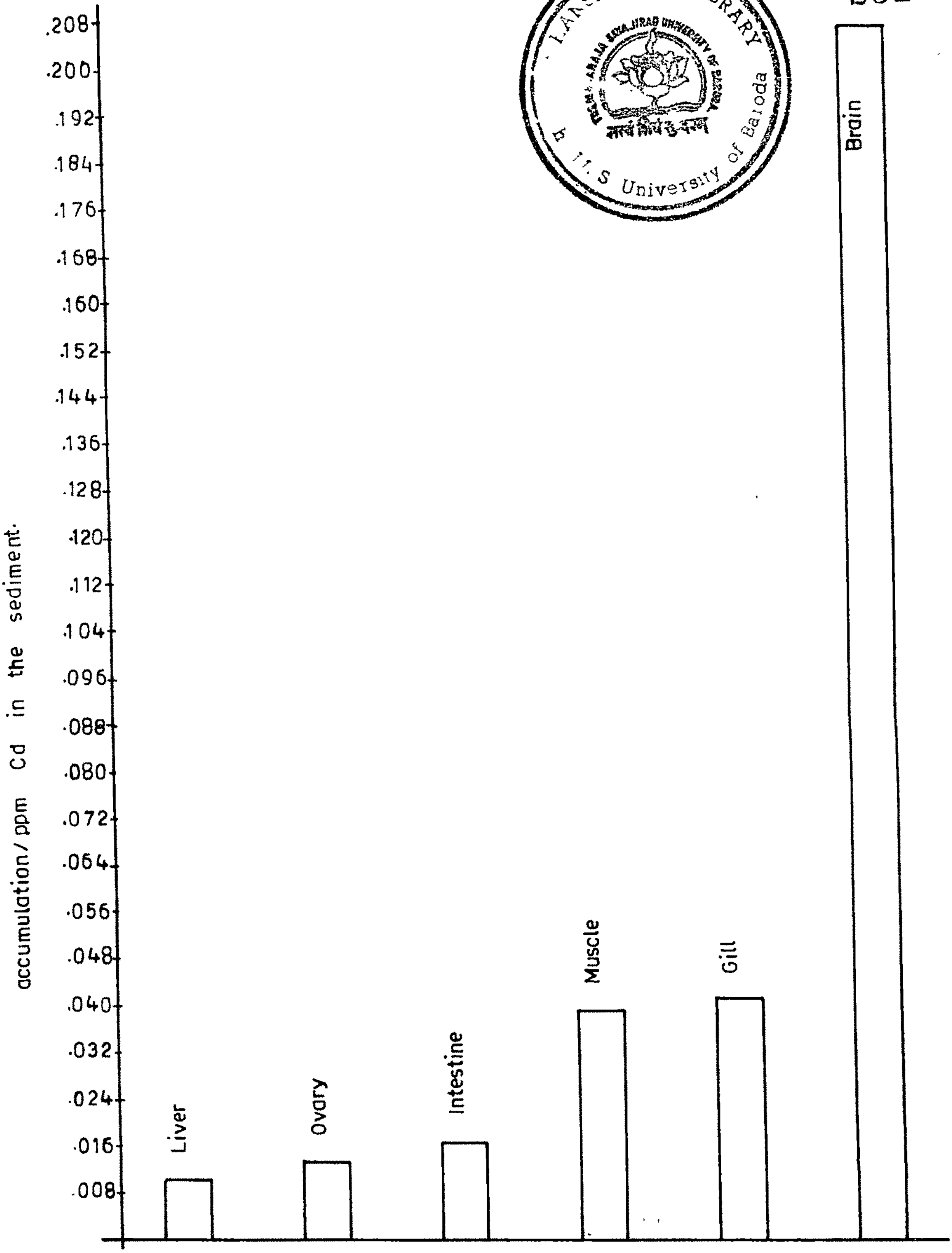

Fig 9 Absolute content of Cd in the various tissues in relation to unit content (1 ppm; mg/kg) in the sediment.

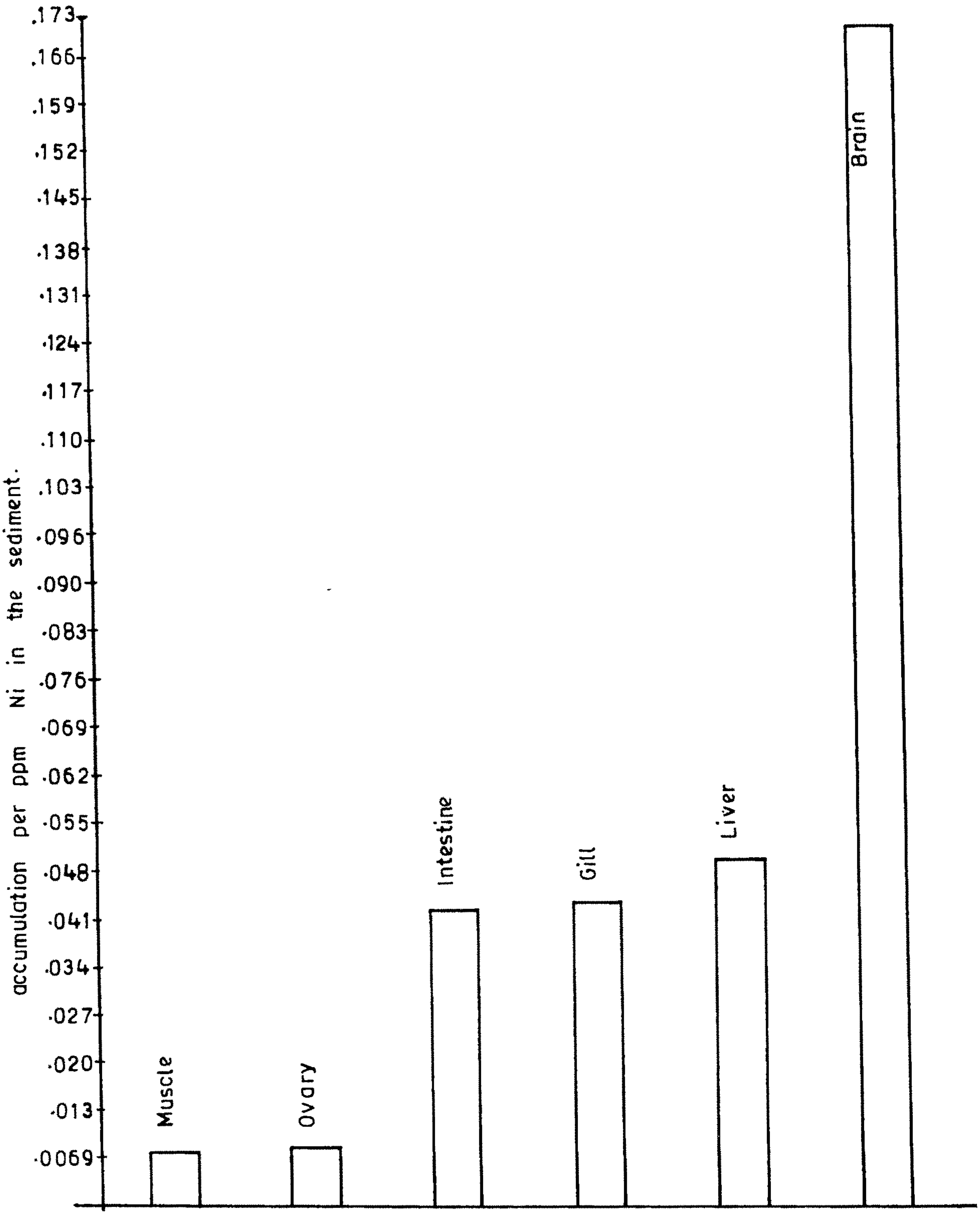

Fig 10 Absolute content of Nickel in various tissues in relation to unit content (1 ppm; mg/kg) in the sediment.

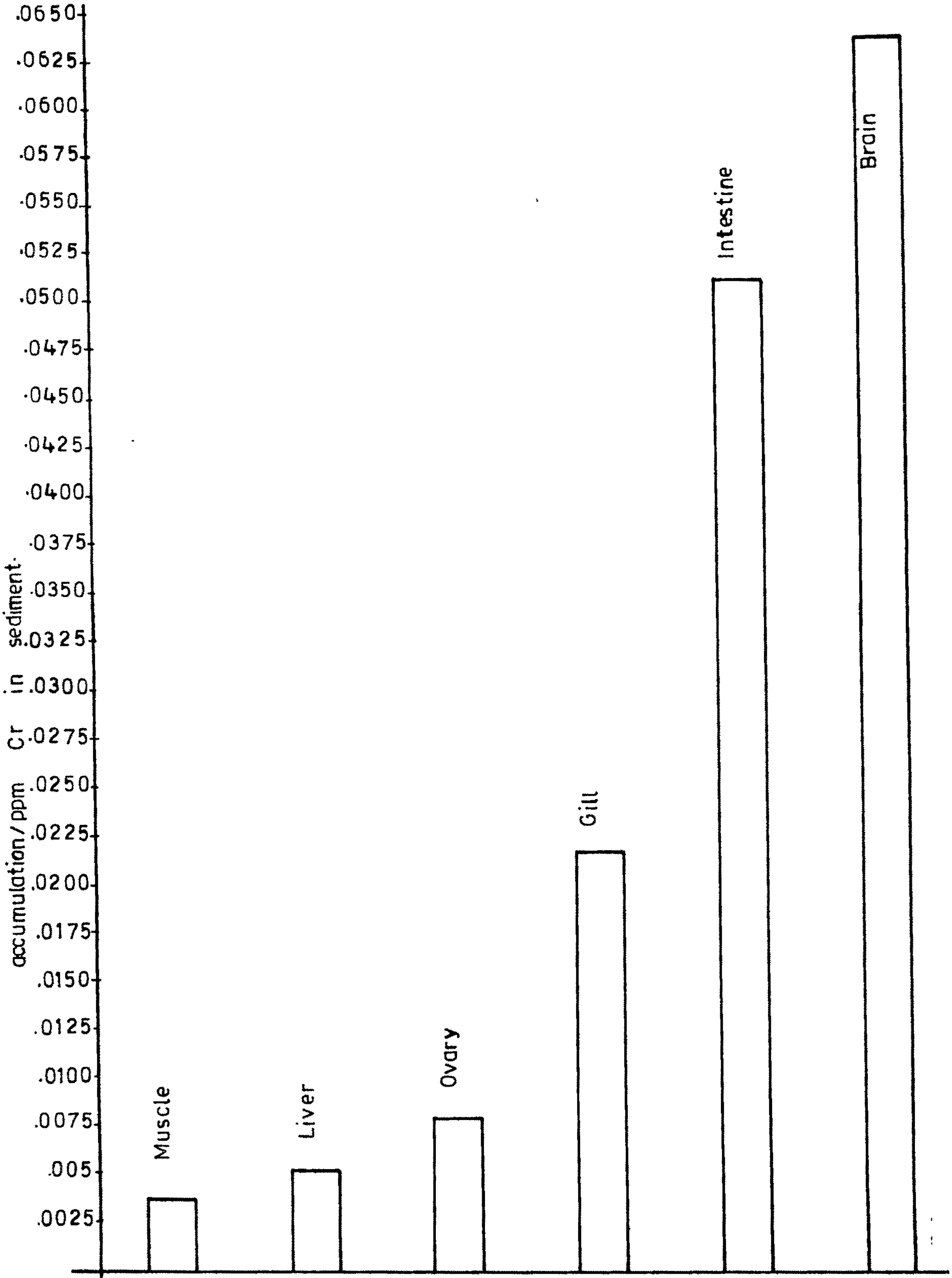

Fig 11 Absolute content of chromium in various tissues in relation to unit (1 ppm; mg/kg) content in the sediment.

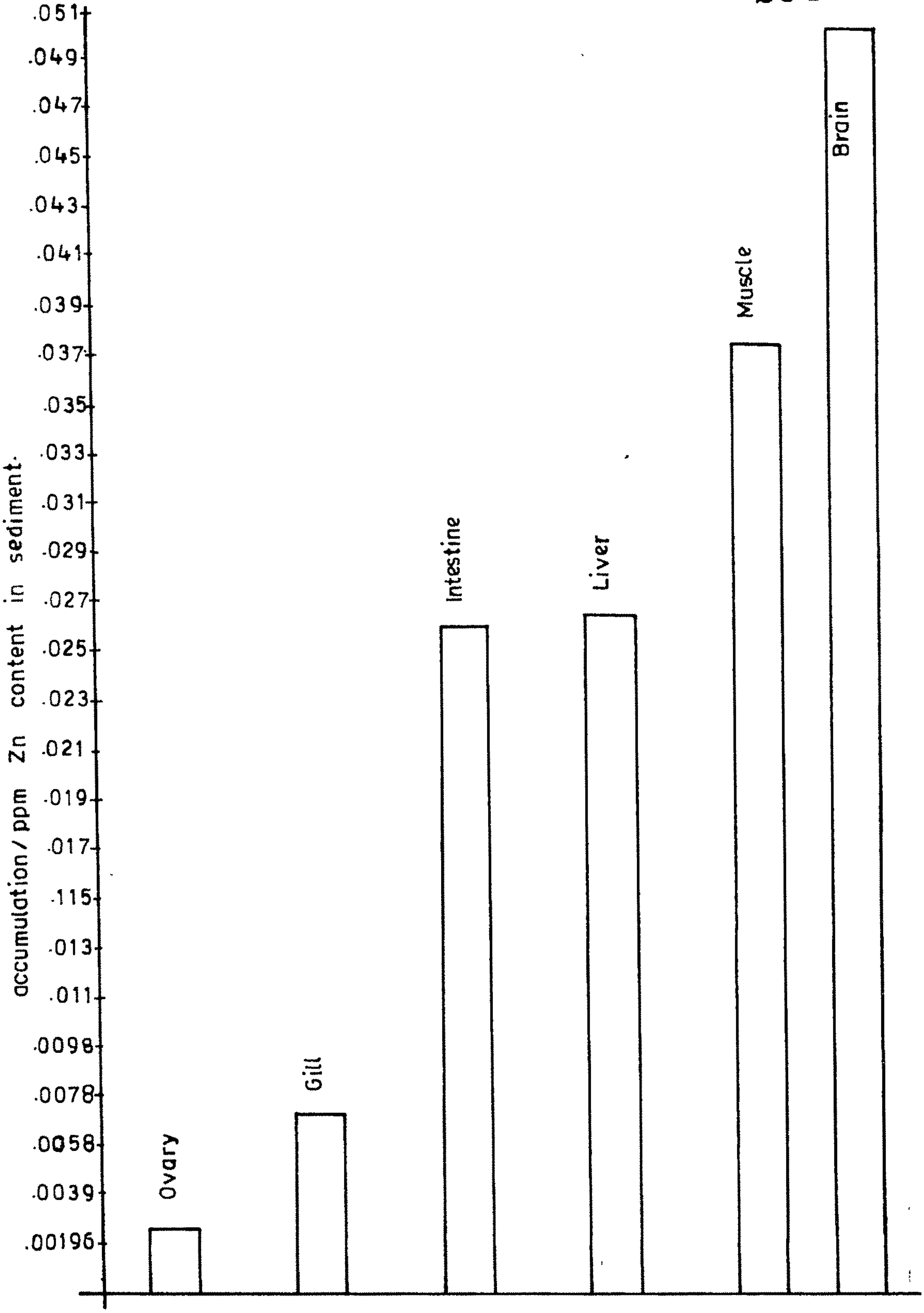

Fig 12 Absolute content of Zinc in various tissues in relation unit (1ppm; mg/kg) content in the sediment.

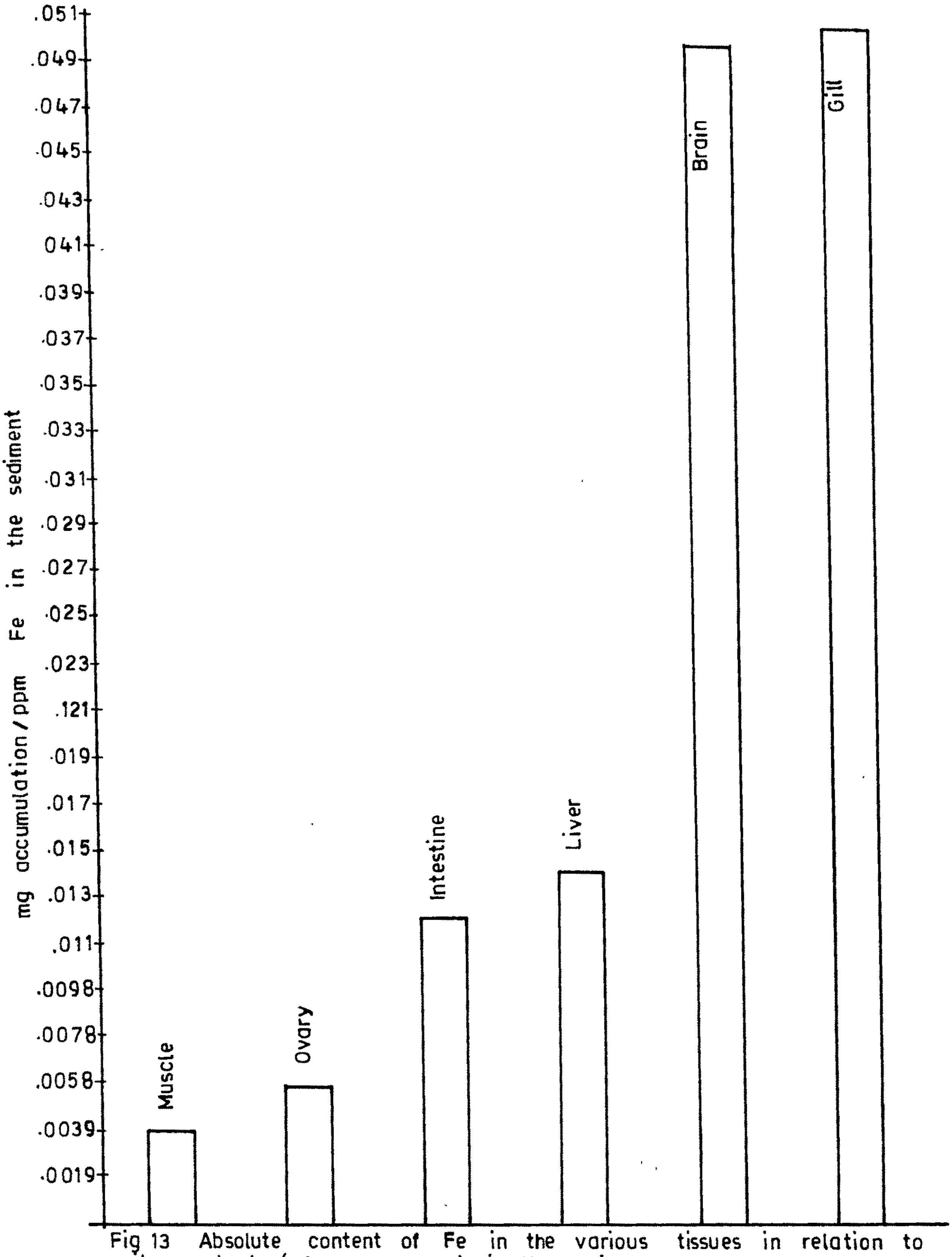

Fig 13 Absolute content of Fe in the various tissues in relation to unit content (1ppm; mg/kg) in the sediment.

concentrations but, which can be toxic in large concentrations are, As, Cu, Cr, Ni, Se, Ag and Zn. Other metals such as Pb, Cr and Hg, which are not essential to life are also toxic to organisms in concentrations commonly found in soils and natural waters. Heavy metals are known pollutants which affect the quality of life in aquatic ecosystem (Kaviraj and Konar, 1982), and concentrations of polluting heavy metals are significantly higher. In the aquatic biosphere, which has signficantly higher metal concentration (Waldichuk, 1974), uptake of heavy metals by aquatic organisms has been reported by many workers (Part and Svanberg, 1981; Norey *et al.*, 1990), and according to them, bioaccumulation of metals depends on the availability and persistence of metals in water and food, physical and chemical properties of metals, quality of holding water, uptake and transport of xenobiotics, biotransformation and, depuration. It is difficult to generalise about uptake and accumulation of metals in aquatic organism, not only because of specie difference but, also due to the fact that even in some species, different metals are accumulated differentialy in different tissues. This has been clearly shown by the differential concentration of trace metals in the tissues of fishes (Weiner and Giesy, 1979). Heavy metals being non-biodegradable, necessitates an understanding of their uptake, distribution and, persistence in tissues of organisms.

The present study on the Mahi estuary which receives effluents continuously, has shown that the only fish that can be found in the area, the mudskippers, have increased content of various metals studied, in their tissues. However, looking at the data on the metal content in the tissues of mudskippers which are obtained from other estuarine areas not receiving industrial effluents, it can be concluded that Pb, Fe and Zn are the major metal contaminants in the estuarine and coastal areas of central and south Gujarat. The metal content in the effluent water as well as the Mahi estuarine water receiving the effluent, shows higher incidence of Pb, Fe, and Zn, followed by Cd, Cu, Ni and Cr (Chapter- I). This is a reflection of the type of industries and industrial activities concentrated in the Nandesari area. In terms of total metal content in different tissues of the mud skipper, Pb is the most highly accumulated metal with maximum accumulation in liver and intestine followed by gill, brain muscle and ovary in the order of their accumulation and, Cd the least accumulated. The other metals accumulated in concentrations ranging between these two are, Zn, Fe, Cu, Ni and Cr in the order of their accumulation. In terms of the capacitiy of various tissues to concentrate metals, liver showed the maximal accumulation of Cu and minimal accumulation of Cd with, Pb, Zn, Ni, Fe and Cr in ranges between the two. Intestine also showed more or less similar pattern of accumulation with the heirarchial order being Cu, Pb, Zn, Cr, Ni, Fe and Cd. The order of accumulation of various metals by muscle is Zn, Pb, Cd, Cu, Fe, Ni and Cr. Brain also showed a similar higher accumulation of Zn and lower accumulation of Cr. However, the order of accumulation of other metals lying in ranges between the two is, Cd, Fe, Pb, Ni and Cu. Gills showed maximum accumulation of Fe, and minimal accumulation of Pb with Ni, Cu, Zn, and Cr in concentration ranging in between. The ovary also showed differential capacities of accumulation, with accumulation of metals in the order Pb, Fe, Zn, Cr, Ni, Cd and Cu.

Though the total metal contents of the tissues of mud skippers was in the order Pb>Zn>Fe>Cu>Ni>Cr>Cd>, actual metal accumulation in terms of per unit metal contamintion (1ppm) of the estuarine water and the sediment, shows greater accumulation with respect to Cu, Cd and Ni (see tables 2 and 3 and Figs- 8-14). A perusal of the tables and figures shows that among the seven metals, Cd and Cu maximally accumulated in majority of the tissues. Brain has the maximal accumulation of majority of metals followed by gills, intestine and liver. To be more precise, of the metals accumulated in the various tissues, Cd had the greatest accumulation in muscle, brain, gills and gonads while copper had the greatest accumulation in liver and intestine. Of the tissues showing various metal content, brain had the maximum accumulation of Cr, Zn, Ni and Cd while, gill had maximum accumulation of Fe, intestine of Cu and, liver of Pb. Though metal content of tissues in terms of ppm metal content in the water and the sediment has been calculated, in the present case, the actual accumulation in terms of ppm content in the sediment would be more relevant and valid as the mud skipper is sediment burrower. Cadmium sequestering organs of fish have been identified as liver, kidney and gills (Norey *et al.*, 1990). The above study showed that while gill was the major organ for Cd accumulation in the rainbow trout, the liver and kidney were the major organs of accumulation in the stone loach. Similarly, an uptake study of Cd in tissues of the Indian major carp, *Catla catla* (Vincent and Ambrose, 1994) showed the gill, kidney and liver to be the major organs of Cd accumulation in that order. However, the present study on mud skipper shows brain and muscle to be the major tissues of Cd accumulation followed by gills and gonads. This may suggest a species difference and even the modifying influence by co-contaminated metals. In this respect, Leland and Kuvabara (1985) have suggested that, mechanisms of accumulation and storage of free metals in aquatic animals are diverse, varying with chemical form, mode of uptake, and animal species. The degree of accumulation in aquatic organisms depends on the type of food chain, on the availability and persistence of the contaminant in water, and especially, on the nature and amount of the contaminant. The presence of other contaminant, especially other metals can also influence accumulation (Gearheart *et al.*, 1992).

A cursory glance of table 4a-4f reveals that, the levels of various metals in liver or, whole body of fishes, either considered safe for human consumption or, recommended for protection of biotic species, are much lesser than what are recorded for in the mud skipper in the present study. Apparently, the mud skippers in the Mahi estuary, at and around the "J" point, have accumulated very high concentration of metals which are not only detrimental to the species concerned but also to human health, as the mud skippers form the cheaply available staple fish food for the economically weaker section of the society, and is the only species found in the Mahi estuary at or around the "J" point. It poses potentially great health hazard in the long run to the populace residing in the close-by villages.

COMMONLY OBSERVED CADMIUM LEVELS

HYDROSPHERE	
Coastal sea waters[1]	<0.05 ppb
Sediment[8]	3.300 ppb
LITHOSPHERE	
Marine sediments[1]	30-1000 ppb
Soil[1]	10-4500 ppb
BIOSPHERE	
Vegetables, Grains[2]	0 05-1 2 ppm
Crops, Plants[1]	<1.0ppm FW
Leaf tissue,Normal levels[8]	50-200 ppb DW

1 Eisler 1982, 2. Adriano 1986, 8. Kabata-Pendias

CADMIUM TOXICOLOGY

TOTAL CADMIUM LEVELS LIKEY TO CAUSE PRONOOUNED OR PROBABLE ADVERSE EFFECTS

Fresh water[1]		<10 ppb
Salt water[1]		4.5 ppb
Aquatic plants[5]		0.02 to 1.0 pppm
Estuary Fish[1] LC50		8.0 to 85 ppm
Apparent effects Threshold, sediment levels indicating detrimental effects on		
Leaf tissue, excessive or toxic level[7]		5 to 30 ppm DW
Vertibrate tissue residues[1]		
Contaminted	Kidney/liver	10 ppm FW
	Whole body	2 ppb FW
Life threatening	Kidney/liver	200ppm FW
	Whole body	5ppm FW
Drinking water Standards[6]		
Federal MCL*		5.0ppb
California MCL*		10.0 ppb

1:Eisler 1985, 5:Moore 1984, 6:Maykbeck 1989, 7: Dabis 1989

* Maximum Concentration Level

RECOMMENDED CADMIUM LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Freshwater, at 100ppm hardness[4]	1.1 ppb total Cd
Salt water[4]	9.3 ppbtotal Cd
Freshwater Sediment[7]	<1.0ppm DW
Fish tissue concentration, safe for human Consumption	0.5 ppm FW
Fish Liver EDL85[3])	0.40 ppm FW
Fish Liver EDL95[3]	1.65 ppm FW
Vertebrate tissues	
Kidney/Liver[1]	<10 0 mg/kg FW
Whole body[1]	<2.0 mg/kg FW
Vertebrate diet[1]	<100 mg/kg FW

1:Eisler 1985, 3·CWRCB 1990 4:EPA 1986 7· Davis 1989

TABLE 4b - CHROMIUM

CHROMIUM BACKGROUND LEVELS

BIOSPHERE[1]	
Fish	<8.0 mg/kg DW
Fresh Water fish	<0.25 ppm FW

1. Eisler 1986, 4: Moore 1984.

CHROMIUM TOXICOLOGY

LEVELS CAUSING DEATH OF SENSITIVE SPECIES [1]	
Levels producing sublethal effects[1]	
Rainbow trout[3]	51 ppb
fathead minnow[3]	1000 ppb

1:Eisler 1986 3: MATC,Eilser 1986.

RECOMMENDED CHROMIUM LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Freshwater to protect aquatic life[2]	
MATC* rainbow trout[3]	51 -105 ppb
MATC* fathead minnow[3]	1,000 - 3,950 ppb

2:EPA 1986 3:MATC, Eisler 1986.

* MATC - Maximum Acceptable toxicant concentration

TABLE 4c - COPPER

COPPER BACKGROUND LEVELS

BIOSPHERE

Plants require 5.20 ppm, in tissues[3]

Muscle	0.2-0.5ppm
Liver	1.0-110.0 ppm

3: Rand 1985.

COPPER TOXICOLOGY

Acutely toxic to marine & freshwater organisms[12]	5-4004ppm
LC-50 levels[1]	
Fresh water fish LC-50	10.0-100.0ppb.
Marine Fish LC-50	10.0 to 10.0009(xx) ppb
Levels producing sub lethal effects	
Fish[9]	20-200ppm

1:Eisler 1981 9:Moore 1984

RECOMMENDED COPPER LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Non trout fish liver[7]		
	EDL*85	13 ppm FW
	EDL*95	36.6 ppm FW
Trout liver[7]		
	EDL*85	171 ppm FW
	EDL*95	232 ppm FW

7:CWRCB 1990.

* EDL - Elevated Data level

LEAD BACKGROUND LEVELS

BIOSPHERE

Worldwide average[1]

Fish, whole	0.2ppm

1:Eisler 1988

LEAD TOXICITY

Levels causing death of sensitive species

Fish, 96 LC50[4]	0.5 to 10ppm

4: Moore 1984.

RECOMMENDED LEAD LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Fresh water to protect aquatic life,

100 ppm hardness[2]	3.2 ppb
Fish live EDL*85	0.10ppm FW
Fish live EDL*95	0.20ppm FW

2:EPA 1985

* EDL - Elevated Data Level

TABLE 4e - NICKEL

NICKEL BACKGROUND LEVELS

BIOSPHERE

Marine and freshwater fish	<1.0 ppm FW
Marine teleosts, edible tissues[2]	<0.3 ppm FW

2. Eisler 1981 EPA 1980 9: Kabata-Penduas 1984

NICKEL TOXICOLOGY

CONCENTRATION IN WATER CAUSING DEATH OF SENSITIVE SPECIES

LC-50 values	
Fish[3]	6.0 to 38
Fish[7]	5.0 to 100 ppm
Levels producing sub lethal effects	
Marine fish[9]	350 ppm

3: Kelly 1988 7: EPA 1980 9: Kabata Pendias 1984

RECOMMENDED NICKEL LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Fresh water to protect aquatic life[6]	160 ppb (at 100ppm CaCO3 hardness)
Salt water to protect aquatic life[6]	8.3 ppb

6: EPA 1986

ZINC BACKGROUND LEVELS

BIOSPHERE	
Marine biota[1]	
Teleosts	6.0-400 ppm DW

1:Eisler 1981.

ZINC TOXICOLOGY

Acutely toxic to fish water & marine-organesms[12]	0.2-500 ppm
Levels causing death, LC-50	
Fish[8]	0.09-100 ppm[8]
Marine organisms[2] Fish	60 mg/l
Levels producing sub lethal effects	
Marine organisms[2]	
Yearling Salmon	0.15-0.95 mg/l
Insects & fish absent at water level	0.4 mg/l

2:Connel 19984 12:Kabata - Pendias

RECOMMENDED ZINC LEVELS FOR PROTECTION OF BIOTIC RESOURCES

Freshwater to protect aquatic life,- 100 ppm handness[4]	100 ppb
Salt water to protect aquaticc life[4]	86 ppb

4:EPA 1986.