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Toxic Metals Analysis in Zabi Dam Fishes Collected from District Karak, Khyber Pakhtunkhwa, Pakistan

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Abstract

Heavy metals above their permissible limit are extremely threaten for animals and other microbes, so its acquire attention to study and to find solution. It was therefore of interest to conduct study to estimate accumulation of heavy metals in fishes of Zabi Dam Karak Pakistan. Zebi dam is located on North East of Karak city. Three samples of fishes namely *Labeo rohita* (rahu), *Cyprinus carpio* (Common Carp) and Goldfish collected randomly from different sides of Zabi dam. Samples were analyzed for these selected heavy metals cadmium, zinc, iron, copper, nickel and lead. The pattern of decreasing concentrations for fishes on average showed the following result $Fe > Pb > Zn > Cu > Ni > Cd$ in which Pb showed highest average result while Cd and Ni Showed lowest. In all the three parts of head, abdomen and tail *Labeo rohita* the highest concentration is shown by Fe (9.501mg/kg) in head while lowest concentration shown by Ni and Cd (0 mg/kg) in all parts. In case of *Cyprinus carpio* Pb has the highest level (26.28 mg/kg) among all metals in head while lowest (0 mg/kg) concentration showed by both Ni and Cd.

Keywords: Heavy metals, Zabi dam, Fishes

Introduction**Heavy metals**

The term "heavy metals" refers to any metallic element that has a relative density greater than $4g/cm^3$. Heavy metals exhibit metallic properties such as ductility, malleability, conductivity, cation stability, and legend specificity. Heavy metals include; Lead (Pb), Cadmium (Cd), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe) and the Platinum group elements. Some heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V, and Zn are required in minute quantities by organisms. However, excessive amounts of these elements can become harmful to organisms. Other heavy metals such as Pb, Cd, Hg, and as (a metalloid but generally referred to as a heavy metal) do not have any beneficial effect on organisms and are thus regarded as the "main threats" since they are very harmful to both plants and animals [1]. The fate of heavy metals introduced by human activities, chemical and geochemical processes into the aquatic ecosystem have recently become the subject of widespread concern; These metals may accumulate to a very high toxic levels and cause severe impact on the aquatic organisms without any visible sign [2]. The document is focused on the following heavy metals included Cadmium (Cd), Cupper (Cr), Iron (Fe), Nickel (Ni), Lead (Pb), Zing (Zn), in Fishes and water of Zebi dam (Sabir abad Karak). Karak is a district of the Khyber Pakhtunkhwa province of Pakistan. It is situated in the south of Kohat District and on the north sides of Bannu and Lakki marwat district. It is about 123 km away from the provincial capital Peshawar.

Zabi Dam Karak Sabir Abad:

Zebi Dam is a small dam located in KPK province of Pakistan. This dam was built in Karak district to store the rain water and used for various purposes such as, drinking, domestic usage as and in agriculture [3].

Sources of heavy metals

The most important sources of heavy metals in the environment are the anthropogenic activities such as mining, smelting procedures, steel and iron industry, chemical industry, traffic, draining of sewerage, dumping of Hospital wastes, recreational activities and agriculture as well as domestic activities. Chemical and metallurgical industries are the most important sources of heavy metals in soils. Conversely, metals also occur in small amounts

naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation. As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, thus causing heavy metal pollution in water bodies. The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity, plant growth etc. Increase in population, urbanization, industrialization and agriculture practices have further aggravated the situation [4].

Some important heavy metals

Zinc

Zinc is naturally found in water. Its compounds are present in insecticides and fungicides and as a result end up in water. The wide distribution of zinc in all body tissues and fluids reflects its essential role in metabolic activity as a component of key cell enzymes. The body's total zinc content ranges from about 1.5 g in women to 2.5 g in men. Plasma zinc has a rapid turnover rate and it represents only about 0.1 percent of total body zinc content. This level appears to be under close homeostatic control. High concentrations of zinc are found in the choroid of the eye 274µg/g and in prostatic fluids 300-500 mg/l.

The permissible limit of zinc in fishes according to WHO standards is 3.36 mg/kg [5].

Copper

Copper is present in earth crust commonly in the form of oxide and sulphides ores but rarely as metal in the mineral and enter the water by mineral dissolution. There are many factors responsible for the variation in both total and available copper concentration of soil and these are the anthropogenic inputs onto land, such as manures and pesticides and deposition from the atmosphere largely due to pollution.

Drinking water is the primary source of excess copper. Populations living near sources of copper emissions, such as copper smelters and refineries and workers in these and other industries may also be exposed to high levels of copper induct by inhalation.

The permissible limit of Copper for fishes is 0.30 mg/kg as recommended by WHO [6].

Lead

Lead is a chemical element in the carbon group with symbol Pb and atomic number 82. Lead is a soft, bluish-gray and malleable metal, which is regarded as a heavy metal and another metal which occur in small quantity in the earth's crust. Lead is a highly poisonous metal (regardless if inhaled or swallowed), affecting almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and children.

The permissible limit of Pb in fishes is recommended by WHO is 0.30 mg/kg [7].

Iron

Iron is a chemical element with symbol Fe and atomic number 26. The boiling point of iron is 3134 k and its melting point is 1811 k, while its density is 7.874 g/cm³. By mass it's the most common element of earth, iron is fourth on most abundant after oxygen, silicon and aluminum in the earth's crust. It is fundamental for the development and growth of all plants and animals. Iron play important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin. The rich source of dietary iron include red meat, lentils, beans, poultry, fish, leaf vegetable, watercress, tofu,

chickpeas, blackstrap molasses and fortified bread etc. Maximum allowed concentration of iron in fishes is 1.74 mg/kg according to WHO report [8].

Nickel

Nickel is a light colored hard metal and found naturally in the earth's crust having +2 oxidation states in most organic and inorganic substances. Normal concentration in soil is about 50 mg/kg while its concentration is low in water.

Nickel is vital for all plants and plays role in plants metabolism. However, its concentration required for normal plant growth is very low "(0.05 – 10 mg/kg dry weight)" [9]. It's widely used in industry and is a common aquatic pollutant. In aquatic ecosystems nickel inter- acts with numerous inorganic and organic compounds and occurs as soluble salts adsorbed onto substances of different chemical origin. The WHO recommended level of Ni for fishes is 0.04mg/kg [10].

Cadmium

Cadmium, a naturally occurring element found in the earth's crust, was discovered in 1817, but was not used commercially until the end of the 19th century. This soft, silver-white metal was first used in paint pigments. Today, about three fourths of cadmium is used as an electrode component in alkaline batteries, with the remainder used in pigments, coatings, and plating and as a stabilizer for plastics. The primary and most serious adverse health effects of long- term exposure to cadmium include kidney dysfunction, lung cancer, and prostate cancer. Cadmium may cause local skin or eye irritation and can affect long-term health if inhaled or ingested. Cadmium make the part of food chain of fish and these fishes after using by human beings makes cause of some dangerous diseases.

The permissible limit of Cadmium in fishes recommended by WHO, is 0.05 mg/kg [11].

Effect of heavy metals on fishes

In the recent years, world consumption of fish has increased simultaneously with the growing concern of their nutritional and therapeutic benefits. In addition to its important source of protein, fish typically have rich contents of essential minerals, vitamins and unsaturated fatty acids. The American Heart Association recommended eating fish at least twice per week in order to reach the daily intake of omega-3 fatty acids.

However, fish are relatively situated at the top of the aquatic food chain; therefore, they normally can accumulate heavy metals from food, water and sediments and. The content of toxic heavy metals in fish can counteract their beneficial effects; several adverse effects of heavy metals to human health have been known for long time. This may include serious threats like renal failure, liver damage, cardiovascular diseases and even death and. Therefore, many international monitoring programs have been established in order to assess the quality of fish for human consumption and to monitor the health of the aquatic ecosystem. In the last few decades, the concentrations of heavy metals in fish have been extensively studied in different parts of the world. Most of these studies concentrated mainly on the heavy metals in the edible part (fish muscles). However, other studies reported the distribution of metals in different organs like the liver, kidneys, heart, gonads, bone, digestive tract and brain.

According to the literatures, metal bioaccumulation by fish and subsequent distribution in organs is greatly inter-specific. In addition, many factors can influence metal uptake like sex, age, size, reproductive cycle, swimming patterns, feeding

behavior and living environment (i.e., geographical location) [12].

Fishes of Zabi dam

Labeo rohita (rahu)

Kingdom: Animalia
Phylum: Chordata
Class: Ctinopterygii
Order: Cypriniformes
Family: Cyprinidae
Scientific Name: Labeo Rohita
Common name: Rahu

It occurs widely in northern and central India, Bangladesh, Nepal, Myanmar and Pakistan. *Labeo rohita* (rohu) is the natural inhabitant of freshwater sections of the rivers. *Labeo rohita* (rohu) thrives well in all fresh waters below an altitude of approximately 549 m. *Labeo rohita* (rohu) is a bottom feeder and prefers to feed on plant matter including decaying vegetation. *Labeo rohita* (rohu) is a bottom feeder and prefers to feed on plant matter including decaying vegetation. *Labeo rohita* (rohu) attains maturity towards the end of the second year in ponds. The spawning season of *Labeo rohita* (rohu) generally coincides with the southwest monsoon. Spawning takes place in flooded rivers. The fecundity of *Labeo rohita* (rohu) varies from 226,000 to 2,794,000, depending upon the length and weight of the fish and weight of the ovary. The spawn of this fish is collected from rivers during monsoon and reared in tanks and lakes [13].

Carassius auratus (Goldfish)

Kingdom: Animalia
Phylum: Chordata
Class: Actinopterygii
Order: Cyprinidae
Genus: Carassius
Species: C. auratus

The Cyprinidae family is the largest family of freshwater fishes in the world, and may be the largest family of vertebrates (with the possible exception of Gobiidae). Common names associated with various members of this family include minnow, carp, chub, and shine.

Goldfish is the common name for a freshwater fish, *Carassius auratus*, of the carp or minnow family, Cyprinidae, that is native to East Asia and has been domesticated and developed into many ornamental breeds for aquariums and water gardens. Over the centuries, through human creativity acting on the foundation of an original carp species, many color variations have been produced, some far different from the original "golden" color of the first domesticated fish. Goldfish, *Carassius Auratus*, may grow to a maximum length of 23 inches (59 cm) and a maximum weight of 9.9 pounds (4.5 kg), although this is rare; few goldfish reach even half this size. The longest goldfish was measured at 47.4 cm. In optimal conditions, goldfish may live more than 20 years, but most household goldfish generally live only six to eight years, due to being kept in bowls.

If left in the dark for a period of time, a goldfish will turn lighter in color. Goldfish have pigment production in response to light. Cells called chromatophores produce pigments that reflect light, and give coloration. If a goldfish is kept in the dark it will appear lighter in the morning, and over a long period of time will lose its color [14].

Cyprinus carpio (Common Carp)

Kingdom: Animalia
Phylum: Chordata

Class: Actinopterygii
Order: Cyprinidae
Genus: Cyprinus
Species: C. carpio
Binomial name: Cyprinus Carpio
Common name: Common Carp

Synonyms and Other Names: German carp, European carp, mirror carp, leather carp, koi

The common carp (*Cyprinus carpio*) is a widespread freshwater fish of eutrophic waters in lakes and large rivers in Europe and Asia. The wild populations are considered vulnerable to extinction, but the species has also been domesticated and introduced into environments worldwide, and is often considered a very destructive invasive species, being included in the List of the world's 100 worst invasive species. It gives its name to the carp family: Cyprinidae.

The common carp is native to Asia, and has been introduced to every part of the world with the exception of the Middle East and the poles. They are the third most frequently introduced species worldwide, and their history as a farmed fish dates back to Roman times. Carp are used as food in many areas, but are now also regarded as a pest in some regions due to their ability to out-compete native fish stocks. Wild common carp are typically slimmer than domesticated forms, with body length about four times body height, red flesh, and a forward-protruding mouth. Their average growth rate by weight is about half the growth rate of domesticated carp. They do not reach the lengths and weights of domesticated carp, which (range, 3.2–4.8 times) can grow to a maximum length of 120 centimetres (47 in), a maximum weight of over 40 kilograms (88 lb) [15].

Material and Methods

Area of sample collection

Fishes from Zabi dam Karak were collected roughly from four "4" sides during the months of February and March 2015 in order to analyze them for heavy metals contamination.

Sample collection

Fishes were collected from Zabi dam with the help of non-local special fisherman using different types of nets and hooks. Fishes were preserved in 5% formalin solution in separate bottles. The samples were collected in sterile polythene bags and kept in the laboratory deep freezer (-20°C) to prevent deterioration till further analysis. We worked on Dry method and a clean washed high quality corrosion resistant stainless knife was used to cut the fish into head, tail, scales and abdomen and was placed in china dishes.

Preparation of samples

All these samples were oven dried at 110C for next 24 hour and then these dried samples of fishes were grinded by using pistol and mortar. One "1" gram of each sample was taken by using Analytical balance.

Digestion of samples

Each sample was acid digested using nitric acid and hydrogen per oxide and was kept for next 24 hour. Samples in China dish were heated on a hot plate to evaporate excess amount of HNO₃ continuing until sample was completely digested and become colorless. The fluid was cooled to room temperature.

Filtration of samples

The digested sample was filtered through Whatman filter paper no. 42 in 100 ml graduated cylinder up to 25 ml so that

25 ml of each sample was prepared. 25 ml of each filtered samples was taken in special plastic bottles along with all samples. These samples of fishes were subjected to atomic absorption spectrometer (Perkin Elmer) for being analyzed for metals like Cd, Cr, Zn, Ni, Fe, Cu and Pb. The instrument setting and operational conditions were done in accordance with the manufacturers' specifications.

Result and Discussion

The concentration of heavy metals in different parts of fishes, (head, tail, abdomen and scales) of Zabi dam is shown by the graphical representation of the following tables.

Table 1: Heavy metals concentration (mg/kg) in three body parts (head, abdomen and tail) of *Labea rohita* collected from the water of Zabi dam (mean value ± standard)

Heavy metal	Head	Abdomen	Tail
Cu	0.073±0.008	0.104±0.016	0.026±0.010
Fe	9.501±0.081	3.604±0.103	4.126±0.019
Ni	ND	ND	ND
Zn	3.069±0.242	4.102±0.009	3.068±0.124
Pb	5.878±0.330	5.292±0.129	4.746±0.736
Cd	ND	ND	ND

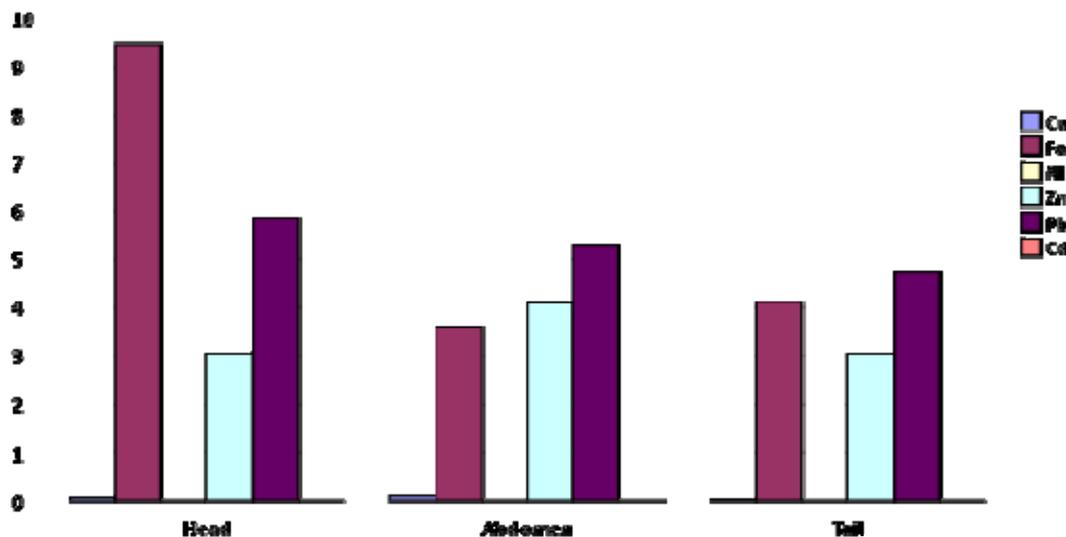


Fig 1: Concentration of heavy metals in fish sample selected from Zabi dam Karak

Figure 1 represents the level of six selected heavy metals (Ni, Cu, Zn, Pb, Fe and Cd) in the fish species of Zabi dam, in which the Fe have the highest level in all metals in the head of (*Labea rohita*). The recorded level of the values of all heavy metals in head, abdomen and tail of (*Labea rohita*) are: In head region Fe>Pb>Zn>Cu>Cd=Ni, in Abdomen Pb>Fe>Zn>Cu>Cd=Ni, and in Tail region Pb>Fe>Zn>Cu>Cd=Ni respectively.

Table 2: Heavy metals concentration (mg/kg) in three body parts (head, abdomen and tail) of *Cyprinus carpio* fish collected from the water of Zabi dam (mean value ± standard)

Heavy metal	Head	Abdomen	Tail
Cu	0.035±0.007	ND	0.001±0.013
Fe	1.912±0.023	20.82±0.052	1.630±0.002
Ni	ND	ND	1.026±0.031
Zn	3.273±0.343	2.425±0.103	2.673±0.031
Pb	26.28±0.493	13.18±0.073	19.66±0.552
Cd	ND	ND	ND

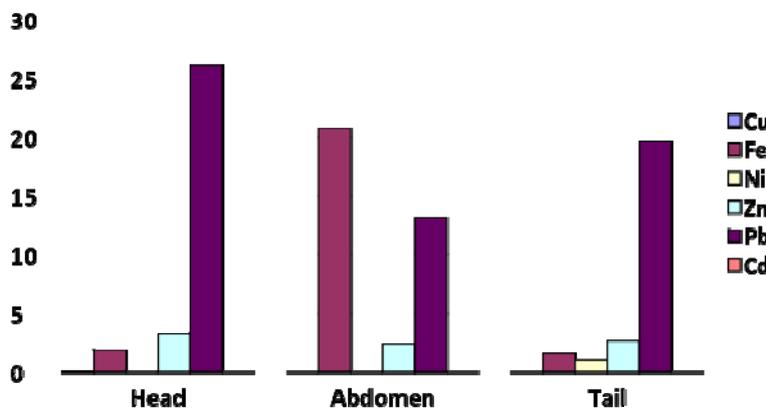


Fig 2: Concentration of heavy metals in fish sample selected from Zabi dam Karak

Figure 2 represents the level of six selected heavy metals (Ni, Cu, Zn, Pb, Fe and Cd) in the fish species of Zabi dam, in which the Pb has the highest level in all metals in the head of (*Cyprinus carpio*). The recorded level of the values of all heavy metals in head, abdomen and tail of (*Cyprinus carpio*) are: In head Pb>Zn>Fe>Cu>Cd=Ni, in Abdomen Fe>Pb>Zn>Cu=Cd=Ni, and in Tail region Pb>Zn>Fe>Ni>Cu>Cd respectively.

Table 3: Heavy metals concentration (mg/kg) in three body parts (head, abdomen and tail) of Golden fish collected from the water of Zabi dam (mean value \pm standard)

Heavy metal	Head	Abdomen	Tail
Cu	0.051 \pm 0.014	0.092 \pm 0.024	ND
Fe	3.246 \pm 0.110	5.748 \pm 0.047	3.701 \pm 0.026
Ni	ND	0.122 \pm 0.017	ND
Zn	4.965 \pm 0.004	3.243 \pm 0.009	3.186 \pm 0.010
Pb	5.205 \pm 0.306	6.642 \pm 0.087	7.415 \pm 0.131
Cd	ND	ND	ND

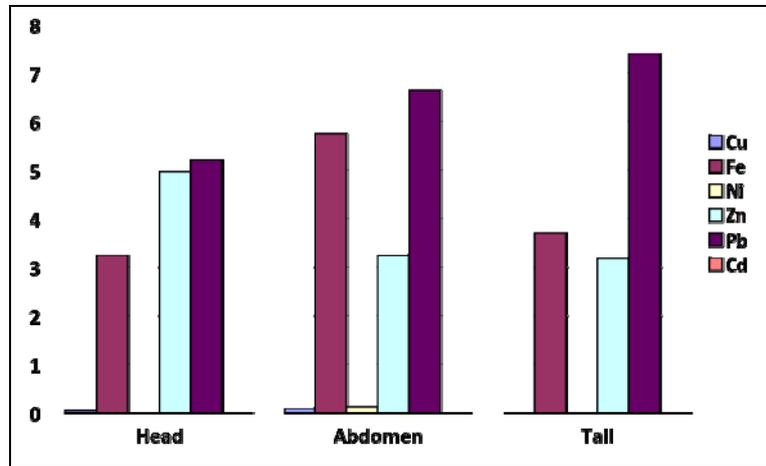
**Fig 3:** Concentration of heavy metals in fish sample selected from Zabi dam Karak

Figure 3 represents the level of six selected heavy metals (Ni, Cu, Zn, Pb, Fe and Cd) in the fish species of Zabi dam, in which the Fe have the highest level in all metals in the head of (golden fish). The recorded level of the values of all heavy metals in head, abdomen and tail of (golden fish) are: In head region $Pb > Zn > Fe > Cu > Cd = Ni$, in Abdomen $Pb > Fe > Zn > Ni > Cu > Cd$, and in Tail region $Pb > Fe > Zn > Cu = Cd = Ni$ respectively.

Discussions

Samples of fishes collection from Zabi Dam was carried out during February to March 2015 for the Heavy metals detection. For this research from Zabi Dam we collected 3 samples of fishes namely *Labeo rohita* (rahu), *Cyprinus carpio* (common carp) and Goldfish. Knowledge of heavy metal concentrations in fish is important with respect to nature of management and human consumption of fish use for medicinal purposes. Heavy metal in soil and water also effect growth and quality of these fishes and plant. Tallat *et al.* 2016 [16] conducted a study on heavy metals analysis in fishes and water of Changhoz dam district Karak, KPK, Pakistan. He selected the following three sample of fishes namely *Hypophthalmichthys molitrix* (silver fish), *Crossocheilus latius* (Dogra) and *Hypophthalmichthys nobilis* (Bighead). During his study he concluded that in *Hypophthalmichthys nobilis* (bighead) highest concentration is showed by Iron in region of Scales while Cd and Ni were not detected in any part, other element detected with concentration comparably less to Permissible limit. In *Hypophthalmichthys molitrix* (Silver fish) highest concentration showed by Ni in Abdomen while in other parts Ni along with Cd were not detected, Fe and Pb showed normal range while Zn and Cu showed less concentration than permissible rang.

In *Crossocheilus latius* (Dogra) highest concentration showed by Pb in scales, Cd not detected in any part while Fe and Zn showed concentration in rang of permissible limit.

In year 2015 Asim Ullah *et al* [17] made similar study Heavy Metal Detection in a Cyprinid Species, *Labeo rohita* Collected

from Shnebaye Stream of District Karak, Khyber Pakhtunkhwa Province, Pakistan. The obtained results on the level of selected metals in the three body regions of fish were found in decreasing order as follows, $Ni > Cd > Cu$, while zinc and lead were not detected in studies parts. Variations were also observed among the different size groups as well as among the different body regions of fish. Thus, the results of the present study revealed that all selected metals were in permissible limit.

In year 2014 Zobia Masood *et al.* [18] studied Heavy Metals Detection of a Carp Species, *Barilius bendelisis* (family cyprinidae) collected from the Shnebaye Stream of District Karak, Khyber Pakhtunkhwa Province, Pakistan. They founded the recorded level of the values of these heavy metals in plant (spirogyra) and soil were $Cd > Ni > Cu > Zn$ and $Cd > Ni > Cu > Zn$ respectively, while the values of selected heavy metals in surface, middle and startup water of stream were as follows; $Ni > Cu > Cd > Zn$ (surface water), $Ni > Cu > Cd > Zn$ (mid water) and $Ni > Cu > Cd > Zn$ (startup water), respectively.

In the present study Zabi Dam fish species *Cyprinus carpio* showed higher accumulation of Pb in head, *Labeo rohita* showed higher accumulation of Fe in head and Golden fish showed higher accumulation of Pb in their tail.

Conclusion

The main goal of this research work was to assess the concentration of some heavy metals in fishes, plants water, soil and spirogyra collected from Chonghoz and Zabi dam Karak.

Three plants of Changhoz dam and two plants of Zabi dam, three fish species from Changhoz dam and three from Zabi dam were analyzed for six heavy metal contamination. A total of 4 water samples and some samples of soil and spirogyra were collected and were analyzed for six heavy metals (Zn, Fe, Cd, Pb, Cu and Ni) using standard procedures. The results shows that water sample have heavy metals contamination nearly within permissible limit. In case of plant samples Cd slightly showed less concentration than permissible limit, Fe

showed normal range but in some parts was with higher concentration, Pb showed concentration less than permissible limit, Ni also showed less concentration than permissible limit and so on. In case of fishes Fe, Pb and Zn mostly showed normal limit but other heavy metals were less than permissible limit. In most samples of Zabi dam fishes showed the following decreasing order Pb>Zn>Fe but in Changhoz dam the order was Fe>Pb>Zn.

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