



## Assessment of heavy metals in surface water of River Panjkora Dir Lower, KPK Pakistan

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Article published on September 10, 2014

**Key words:** Heavy Metals, River Panjkora, Water Quality, WHO.

### Abstract

Heavy metals are known environmental toxins causing a number of deadly diseases worldwide. They accumulate in human and other animal tissues through food and water and causing mortality. In developing countries contamination of water with heavy metals is a major problem. It is very need of the day to assess and evaluate suitability of water bodies for drinking and agricultural purposes. Here we show heavy metals Lead (Pb), Copper (Cu), Manganese (Mn), Zinc, Iron (Fe) and Chromium (Cr) concentration in water samples of River Panjkora for six months starting from December to May in order to assess and evaluate its suitability for drinking and agricultural purposes. Atomic Absorption Spectrophotometry showed that Cu, Pb and Cr concentration were not detectable in the River water. Mn and Zinc remained within the permissible limits of WHO with a mean value of 0.0266 mg/l and 0.068 mg/l respectively. However iron was found exceptionally higher concentration in the water with a mean value of 4.733 mg/l during the study period. The high concentration of iron may be possibly due to soil erosion and floods resulting from heavy rains. The study reveal that if iron level could be controlled the water of River Panjkora is suitable for agricultural purposes in terms of the studied heavy metals.

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## Introduction

Metals are considered major environmental pollutants as they are non-biodegradable, cytotoxic, mutagenic and carcinogenic in nature (More *et al.*, 2003). Heavy metals coming from different sources contaminate fresh and marine water and affecting the aquatic life (Yousafzai and Shakoori, 2008; Farombi *et al.*, 2007). Heavy metals are present in natural water as they are dissolved by it while flowing, human activities such as use of chemicals in agriculture, disposal of industrial and domestic waste into water bodies add these metals into ground and surface water making it unsuitable for human and aquatic life (Midrarulhaq *et al.*, 2005; Ilyas and Sarwar, 2003).

Different heavy metals contaminating ground and surface water have various hazardous consequences for human health and aquatic life. Heavy metals may have profound effects in combination. A summary of the effects of heavy metals evaluated in the present study is given below.

Due to its corrosion resistant, dense, ductile and malleable properties lead was used in building materials, protective coatings, ammunition, paints and wine preservative for more than 5000 years (Florea and Busselberg, 2006). It may cause developmental delay, miscarriage of the fetus even in low concentration if exposed to it during pregnancy (Bellinger, 2005). It may have adverse effects on skeletal system, digestive system and kidneys in higher concentration (Gidlow, 2004).

Copper is plentiful soft heavy metal in the environment and essential trace element for plant and animal life; It plays fundamental role in biochemistry of all living organisms, it's a component many of metallo-enzyme and respiratory pigments (Eisler, 1998; Demayo and Taylor, 1981). Accumulation of copper in animal body in excess amount is toxic and in human may lead to hepatic cirrhosis and hemolytic anemia (Parsad *et al.*, 2006). Copper is highly toxic to fish and may affect growth, reproduction, enzyme activity etc. (Gharedaashi *et al.*,

2013). WHO set maximum permissible limit of copper in drinking water is 2 mg/l (WHO, 2008).

Cadmium is insoluble in water although its chloride and sulphate salts are freely soluble, from toxicological point of view it is of great concern (Windholz *et al.*, 1976). Little is known about its benefits to animals and plants (Hammons *et al.*, 1978). It's a toxic metal and can cause acute and chronic toxicity (Nordberg, 2004) long time exposure to cadmium may cause kidney damage (Barbier *et al.*, 2005), reproductive problems and cancer (Jhonson *et al.*, 2003; Waalkes *et al.*, 1988).

Manganese is one of the most abundant metals in earth crust, usually occurring with iron. Naturally it's occurring in soil and rocks, an important mineral of human diet and essential trace nutrient for all living beings (PCRWR, 2007; Emsley, 2003). It's required for the functioning of many cellular enzymes such as manganese super oxide dismutase, pyruvate carboxylase etc. (IPCS, 2002). Excessive introduction by human activities disturb its natural balance in ground and surface water (USEPA, 2004). Intake of manganese in higher amount in food and water lead to a number of health disorders including permanent neurological disorders similar in symptoms to idiopathic Parkinson disease (Cowan *et al.*, 2009; Crossgrove and Zhen, 2004; Olanow, 2004). WHO standard limit of manganese in drinking water is 0.5 mg/l.

Zinc is essential for growth and survival of animals (Shankar and Parsad, 1998) but overexposure to zinc lead to adverse effects on health (Azizullah *et al.*, 2011). Association of zinc with dwarfism and hypogonadism in adolescent males has been confirmed (Casey and Hambidge, 1980).

Iron the second most abundant metal in the earth's crust and essential element for the physiology of living organisms, mostly found in oxides forms combine with oxygen and sulphur containing compounds (Elinder, 1986; Knepper, 1981).

Deficiency of iron is more common problem as compared to overexposure however concentration higher than the permissible limit can cause serious health and environmental problems such as cancer, neurological disorders, liver and heart diseases (Azizullah *et al.*, 2011; Beckman *et al.*, 1999; Milman *et al.*, 2001; Berg *et al.*, 2001). Desirable level of iron in drinking water is 0.3 mg/l recommended by WHO.

Water being the vital element for all living things and medium of aquatic life has acquired increasing concern from researchers worldwide. Approximately 3% of the total water on earth is freshwater and only 0.01% of which is available for human use (Hinrichsen and Tacio, 2002). Contamination of water from different sources is threatening aquatic life in particular. Over the last few decades contamination of water from heavy metals has gained greater focus (Waqar *et al.*, 2013), because it poses threat to public water supplies as well as damaging the aquatic life (Sthanadar *et al.*, 2013). Among 122 nations Pakistan stands at 80th number, regarding drinking water quality (Azizullah *et al.*, 2010). In Pakistan only 1% of industrial waste is treated before discharging into the rivers and streams (Khan *et al.*, 2011). About 2000 million gallons of waste water is added into the surface water on daily basis in the country (WB-SCEA, 2006). Poor quality of drinking water is responsible for 40% of the mortalities in the country. Comparing with the international standards of drinking water quality less than 26% of the population of the country has access to safe drinking water (Chhatwal, 1990; Azizullah *et al.*, 2010). Ullah *et al.* (2014b) has reviewed different works carried out in different areas of Khyber Pakhtunkhwa Pakistan dealing with water quality issues. However no scientific data is available on heavy metal concentrations in River Panjkora. The current study was undertaken with the objectives to assess the heavy metals concentration in River Panjkora and to evaluate its suitability for drinking purposes and for fish fauna comparing with WHO drinking water quality standards.

## Materials and methods

### Study Area

District Dir Lower is located within coordinates 34°, 37' to 35°, 07' North and 71°, 31' to 72°, 14' East. It's bounded by District Dir Upper from the North, District Malakand from the South, Tribal Area Bajur Agency and Afghanistan from the west, and Swat and Upper Dir Districts from the East. It covers a total area of 1583 sq. kilometers. River Panjkora originates from Kohistan and enter into the District from North-East and flows South-West along the boundary with Bajur agency up to its confluence with River Swat at District Malakand. Water samples were collected from River Panjkora near Timergara bypass.

### Water Sample Collection

Plastic bottles airtight, well washed with tap water followed by washing with sample water were used for the collection of samples from the surface water of River Panjkora. Six samples were collected, one in each month, starting from December 2011 to May 2012. All the samples were collected in 1 liter container and preserved in 5 ml  $\text{NHO}_3$ . The samples were brought to PCSIR (Pakistan Council of Scientific and Industrial Research) Laboratories Complex Peshawar, stored at 4 °C and analyzed within in a week.

### Procedure of Heavy Metal Analysis

To remove the turbidity water samples of 100 ml was taken in 250 volumetric flask followed by addition of 5 ml  $\text{NHO}_3$  (55%) to acidify the sample. The acidified samples were evaporated on a hot plate in fume hood to 20 ml. The samples were then removed from hotplate and cooled to room temperature. Additional 5 ml  $\text{NHO}_3$  was added to the cooled samples and evaporated to 20 ml again. After cooling at room temperature the samples were diluted to 100 ml with tap water after filtration. Atomic absorption spectrophotometry (Atomic Absorption Spectrophotometer (Spectra AA 2000) was done using air acetylene flame to detect heavy metals Zinc, Lead, Copper, Cadmium, Iron and Manganese in the samples. Characteristic standard solutions for each

heavy metal were prepared and aspirated into flame atomic absorption spectrophotometer (Spectra AA 2000) to prepare the standard curves. The concentration of selected heavy metal was read from the curve. The concentration of heavy metal was reported in mg/l. All the reagents used during the study were of analytical grade.

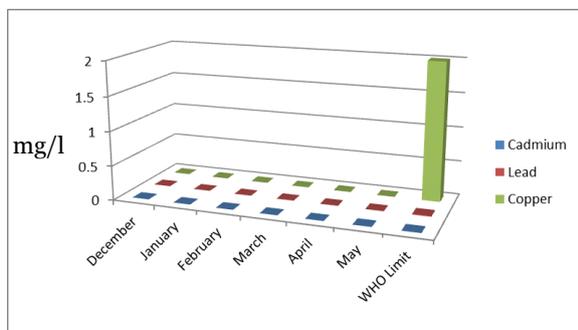
**Results and discussion**

The water samples of River Panjkora were studied from December to May in order to assess selected heavy metals concentration. The results are shown in Fig 1 and table 1. It reveals that Copper (Cu), Lead (Pb) and Cadmium (Cd) were not detected in the samples see Table 1. Concentration of Zinc ranged from its lowest value 0.028 mg/l to 0.091mg/l highest during the sampling months. The highest

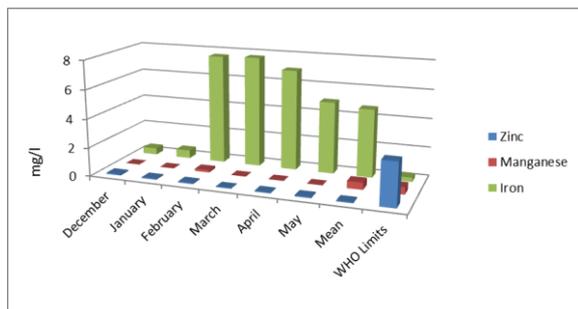
concentration of Zinc was detected during December and Lowest during March. All values of Zinc are not significantly varying during the study with a mean value of 0.0686 mg/l see table 1 and table 2 and Fig 2. WHO permissible limit for Zinc in drinking water is 3 mg/l. The concentration of Zinc in the current study remained well below the WHO set safety limit. Khan *et al.* 2014 found Zinc concentration in River Indus between 0.18-0.28 mg/l with a mean value of 0.22 mg/l. Zinc concentration in Bara River was found between 0.02-0.06 µg/l (Nazif *et al.*, 2006). Highest concentration detected in surface water samples of Shah Alam River was 0.2 mg/l (Khan *et al.*, 2011). Usually Zinc concentration in ground and surface water in Pakistan remain below WHO standard limits (Azizullah *et al.*, 2011).

**Table 1.** Showing Cu, Pb and Cd values in surface water samples of River Panjkora. mg/l.

Months	December	January	February	March	April	May	WHO Limits
Copper	0	0	0	0	0	0	2
Lead	0	0	0	0	0	0	0.01
Cadmium	0	0	0	0	0	0	0.003



**Fig. 1.** Showing Cu,Pb and Cd concentration in surface water samples of River Panjkora.



**Fig. 2.** Showing concentration of Zinc, Mn and Fe in surface water samples of River Panjkora.

Manganese was detected only once during February which is 0.16 mg/l. WHO standard limit for Mn in drinking water is 0.5 mg/l. Manganese concentrations were detected between 0.071-0.2 µg/l in tube wells near Palosai drain Peshawar (Ilyas and Sarwar, 2003). Nazif *et al.* (2006) showed Mn concentration in River Bara to be 0.77 µg/l to 0.85 µg/l. Khan *et al.* (2014) revealed that Mn concentration in river Indus at Beka Swabi ranged from 0.6- 0.65 mg/l with a mean value of 0.62 mg/l. Khan *et al.* (2011) studied heavy metals in surface water of Shah Alam river where they found highest Mn concentration was 0.18 mg/l. According to Azizullah *et al.* (2011) in majority of cases Mn concentrations in surface water exceed WHO safety limits for drinking water in Pakistan. Manganese concentration in water samples of River Panjkora were well below the standard limits of WHO during the study period.

Our results reveal that concentration of iron in the water samples of River Panjkora remained above the

WHO safety limit which is 0.3 mg/l during all sampling months. Concentration of iron ranged from minimum 0.46 mg/l to 7.72 mg/l with a mean value of 4.73 mg/l. The result show changes in iron concentration during the sampling months but all the changes are irregular from December to May showing no single trend table 2. Sarwar and Ilyas (2003) reported iron concentration ranging between 0.46-0.99 µg/l from wells in Palosai Peshawar. Khan *et al.*

(2014) found iron concentration in water samples of River Indus from Beka Swabi between 0.18-0.72 mg/l. Nazif *et al.* (2006) reported Fe concentration in River Bara at Nowshehra ranging from 1.29 µg/l to 1.75 µg/l. In comparison with Punjab and Sindh Provinces, ground water of Khyber-Pakhtunkhwa show lower concentration of iron but still higher than the WHO permissible limits (Azizullah *et al.*, 2011)

**Table 2.** Showing Zinc, Mn and Fe values in surface water samples of River Panjkora mg/l .

Months	December	January	February	March	April	May	Mean	WHO Limits
Zinc	0.091	0.075	0.075	0.028	0.058	0.085	0.0686	3
Manganese	0	0	0.16	0	0	0	0.0266	0.5
Iron	0.46	0.57	7.65	7.72	7	5	4.733	0.3

Iron in high concentration can affect aquatic life through increased turbidity, reduced primary production, plants and fish eggs. Iron may physically clog into gills of fishes impairing their respiratory system. Trout and other fish species usually don not inhabit water bodies with higher iron concentration more than 1 mg/l (Vuori 1995; Linton *et al.*, 2007; Dalzell and McFarlane, 1999). Some studies have been documented on iron tolerance of different fishes such as mountain white fish can tolerate iron upto 0.935 mg/l (Brinkman and Vieira, 2011). Iron tolerance was estimated to be 2 mg/l in fathead minnows (Birge *et al.*, 1985; Smith *et al.*, 1973), 1.952 mg/l for coho salmon, 10.224 mg/l brook trout, brown trout 5.149 mg/l (Smith and Sykora 1976; Brinkman and Vieira, 2011), 1.48 mg/l for rainbow trout (Goettl and Davies, 1977).

Heavy metal contamination of surface water is attributed to a number of factors such as mining, industries and other anthropogenic activities and it is a more serious problem where industrial and anthropogenic influence is high. Heavy metals may show strong correlation with each other in their source of origination and distribution (Azizullah *et al.*, 2011; Giri *et al.*, 2013). Higher concentration of iron in the current study may be due to erosion of rocks and floods resulting from heavy rains the sampling months.

River Panjkora is a small clear river as compared to other rivers in the region. The river may receive least industrial effluents and anthropogenic waste because it's located in a rural area and no such industrial activities are going there. Some of the heavy metal pollution sources may be related to vehicle bargains and garages where effluents are directed towards the River. Ullah *et al.* (2014a) found most of the physical and chemical water quality parameters in ground water samples of District Dir Lower within permissible limits of WHO although sample taken from near River Panjkora were a bit higher than the rest of the samples and some parameters like sulphate, total hardness and calcium hardness exceeded the limits.

**Conclusion**

The present study reveal that heavy metals like Pb, Cu and Cd were not detected in the water samples of River Panjkora during the study period. Manganese and Zinc were found well below WHO standard limit for drinking water. The mean values of Mn and Zinc was 0.0266 mg/l and 0.0686 mg/l respectively. Iron was detected exceptionally higher than the standards of WHO with a mean value of 4.73 mg/l during the study period. Possible reason for higher concentration of iron may be due to erosion of rocks and floods caused from heavy rains during the

sampling periods. Although other parameters of water quality need to be assessed, current study show that the water of River Panjkora appear quite suitable for agricultural purposes if iron concentration could be controlled.

#### Acknowledgements

We are thankful to the entire staff of PCSIR laboratories Complex Peshawar, for their cooperation. Special thanks to Mr. Inayat ur Rahman Scientific officer and Mr. Mushtaq Ahmad Technician PCSIR Environmental section for their guidance and help during the experimental work.

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