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Investigating the levels of selected heavy metals in surface water of Shah Alam River (A tributary of River Kabul, Khyber Pakhtunkhwa)

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Abstract

Pakistan is one of the countries facing fresh water pollution mainly due to untreated discharge of industrial wastes into rivers. Here only 1% of industrial waste is treated before its discharge to the rivers. River Kabul is an important river in Khyber Pakhtunkhwa province; it receives 80000 m^3 industrial effluents every day. River Shah Alam, a tributary of River Kabul that receives most of the sewage from Peshawar, as well as from 30 surrounding villages. It also receives effluents from sugar mills, distilleries, paper mills, tanneries, ghee mills and textile mills in that area.

The purpose of this study was to investigate the levels of heavy metals cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), manganese (Mn), lead (Pb) and zinc (Zn) in the surface water of the Shah Alam River. The surface water samples were collected at 5 sampling sites. These sites were selected based on upstream and downstream industrial and domestic sewage discharge locations. Surface water samples were collected from each site in a 5 month period, from December to April (2004-05). Cd, Cr, Cu, Mn, Ni, Pb and Zn were assayed using an atomic absorption (AA) spectrophotometery and the results shown as mg of heavy metal/ L of fresh water sample (mg/L). The order of heavy metal concentration was Ni > Mn ≥ Zn > > Cu > Cd ≈ Pb > > Cr. The highest concentration of Ni determined was ≈ 30 times whereas Cd and Pb levels were ≈ 10 times higher than the permissible World Heatlh Organization (WHO) established safe drinking water quality standards. The levels of Cu, Cr, Mn and Zn were within the prescribed limits.

Although a weak correlation existed between metal concentration and temperature increase but since the temperature change was only within 2-3° C (degree Celsius) over the sampling period therefore we could not deduce concentration dependence on water temperature. Except for the Mn, no strong correlation existed between water pH and metal concentration. Although metals concentration has been reported to increase with decreasing pH but in our studies no such correlation existed (except for Mn).

A decline in most metal concentrations downstream could be due to; metal sorption to anaerobic sediments, uptake by algae and aquatic fauna or dilution. Metals can accumulate in sediments and can become bioavailable to aquatic fauna (bottom feeders). An investigation into the concentrations of heavy metals in river sediments is needed for better assessment of heavy metals bioaccumulation in fish.

Keywords: Heavy metals; surface water; Shah Alam River

1. Introduction

Over the last few decades fresh water contamination has become a matter of concern (Vutukuru, 2005; Dirilgen, 2001; Voegborlo et al., 1999; Canli et al., 1998). Among other organic and inorganic pollutants our aquatic systems may extensively be contaminated with heavy metals (Velez and Montoro, 1998; Conacher, et al., 1993). Heavy metal contamination of aquatic system has attracted the attention of several investigators both in the developed and developing countries. Industrial effluents and domestic waste/sewage constitute largest sources of heavy metal which contribute to the steadily increasing metallic contaminant in aquatic and terrestrial environment in most part of the world thereby causing adverse effects on aquatic biota and human health (Wang, 2002, Dautremepuits et al., 2004). The most common heavy metal pollutants are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), manganese (Mn) and zinc (Zn). Their source of entry into the aquatic system could either be single, identifiable or dispersed (often difficult to identify). The fact that heavy metals cannot be decomposed through biological degradation and have the ability to accumulate in the environment (Asaolu and Olaofe, 2005; Olowu et al., 2010) make these toxicants deleterious to the aquatic environment and humans who depend on aquatic products as sources of food. Heavy metals can accumulate in the tissues of aquatic animals and hence can be of public health concern to both animals and humans (Asaolu and Olaofe, 2005; Olowu et al., 2010; Kalay et al., 1999; Ashraf, 2005). Pakistan is one of the countries facing fresh water pollution mainly due to untreated discharge of industrial wastes into rivers. According to ministry of environment and urban affairs in six cities of Pakistan, including Peshawar, a number of industries discharge their effluents without any treatment. Establishment of industrial estates in Peshawar resulted in the discharge of heavy loads of untreated waste water in a number of streams and rivers. For example, River Kabul in the Khyber Pakhtunkhwa province alone receives 80000 m^3 industrial effluents every day causing a decrease in agricultural productivity as well as fish production (Government of Pakistan Position paper, 2010). Various pollution sources contribute in Kabul River surface water contamination; it receives untreated waste water from industrial estates in Peshawar through Bara canal and Budni Nalla. Moreover Sugar mills, distilleries, paper mills, tanneries, ghee mills and textile mills in the Charsadda and Peshawar area discharge their effluents into Kabul River (IUCN, 1994). The lack of waste water treatment plants has resulted in discharge of highly polluted wastes to the River Kabul, which is a very important source of fresh water for fisheries and agriculture. Little is known about the heavy metal loads that River Kabul receives.

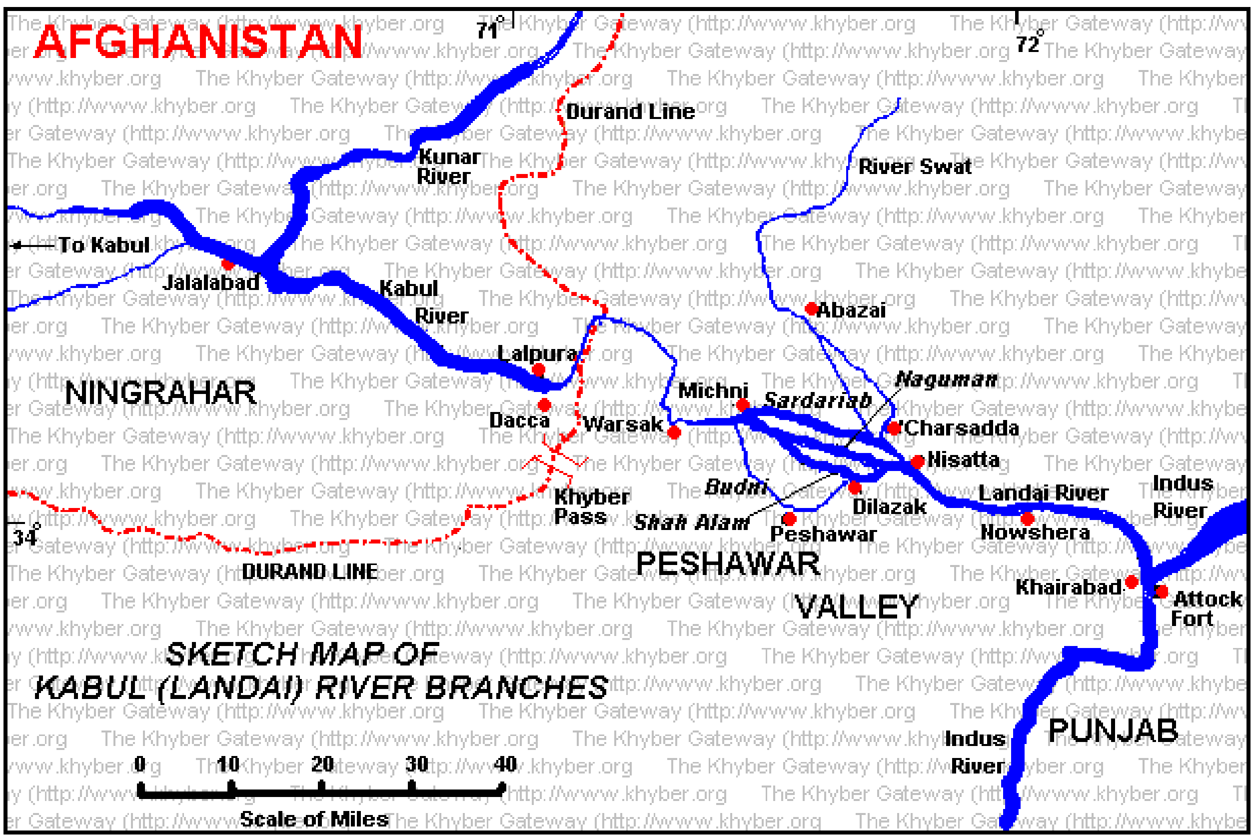


Fig. 1. Map of the study area.

2. Materials and methods

2.1. Study area

Our sampling location for this study was Shah Alam River a tributary of Kabul River. It receives all the sewage from Peshawar via the Ganda Erab and Budni Nalla, as well as sewages from 30 surrounding villages. Shah Alam River was selected for this study because it is in the way of various industrial and domestic effluent discharge sites. Hence one would expect it to be more polluted segment of River Kabul. Moreover River Naguman which also emerges from River Kabul, receives effluents from tanneries and sewages from 27 villages ultimately joins Shah Alam River.

2.2. Sampling and analysis

Surface water samples were collected from five sampling locations on Shah Alam River for 5 months starting from December to April (2004-05). The sampling locations were selected based on various pollution sources that contribute to water pollution of Shah Alam River. Water samples (0.5 L) were collected in polyethylene bottles, pre-washed with acidic water. Samples were transported to the laboratory and stored at ± 4°C. Water temperature (T), pH and Electrical Conductivity (EC) values were measured on spot by using a portable pH meter (WTW Inolab pH level 1) and conductivity meter, respectively. Heavy metal (Cd, Cr, Cu, Mn, Ni, Pb and Zn) concentrations were determined directly in the filtrates by using Shimadzu AA-6601, Atomic Absorption Spectrometr. All water samples were treated in triplicate. Working standard for each of the metals ranged from 0.0 ppm to 1.5 ppm. The values were used to plot a standard curve. The standards and blank were treated in the same way as the real samples to minimize matrix interferences during analysis. The measured concentrations were expressed in mg/L units.

Following are the details of the selected five sampling locations;

a. Upstream Khazana sugar mill
b. Downstream Khazana sugar mill
c. Downstream Budni Nulla
d. Downstream Gand Erab
e. Downstream Naguman river

In our entire results and discussion section these sampling points will be referred as A, B, C, D and E.

3. Results and discussion

Variations of heavy metal concentrations in different sampling points are discussed. Among the selected metals measured, the levels of Ni, Mn and Zn were highest at almost all sampling locations followed by Cu, Cd and only small but environmentally significant levels of Pb and Cr were determined. High concentration of Ni was determined upstream as well as downstream the sugar mill and other effluent sources (Fig. 2). Zn and Mn concentrations are lower upstream but increases downstream, as effluents from various sources enter the river. The concentration of Cu remained almost unchanged at all points except at point A where it was not detectable, whereas Pb concentration was highest at point D and Cr could only be determined at point B (Fig. 2). A steady decline was observed in the concentrations of all determined metals (except for Cu) after they reached their maximum level. The order of heavy metal concentration was Ni > Mn ≥ Zn > > Cu > Cd ≈ Pb > > Cr. The maximum determined concentration of Ni was ≈ 30 times higher than the permissible World Health Organization (WHO) safe drinking water quality standards; Cd and Pb levels were ≈ 10 times, where as the levels of Cu, Cr and Zn were within those limits (Table 1).

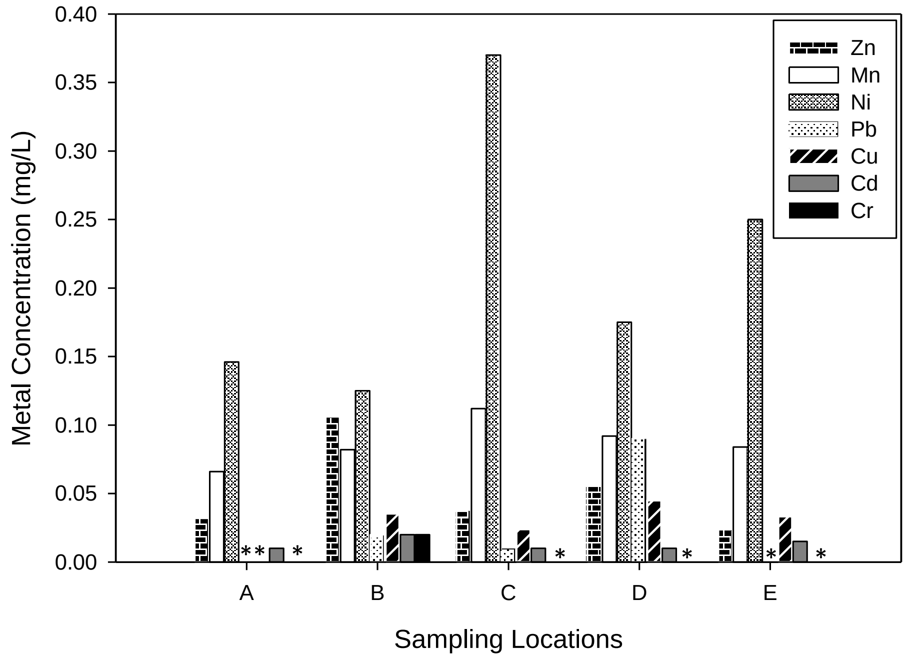


Fig. 2. Average metal concentrations across all five sampling months at all five sampling locations; (*: Indicates undetectable metal concentration at a given sampling location).

Table 1. Comparison of the max. Metal concentrations determined in surface water of Shah Alam River with WHO water quality standards.

Metal	**WHO Standard (mg/L)**	**Highest concentration in study (mg/L)**
Cd	0.003	0.03
Cr	0.050	0.02
Cu	2.000	0.08
Pb	0.010	0.09
Mn	0.500	0.18
Ni	0.020	0.65
Zn	3.000	0.2

Source for WHO standards: PCRWR, http://www.pcrwr.gov.pk/wq_standards.htm

Table 2. Maximum (Max) and Minimum (Min) determined levels of the selected heavy metals in surface water of Shah Alam River at various sampling locations.

Location	**Metal concentration (mg/L)**													
	Zn		**Mn**		**Ni**		**Pb**		**Cu**		**Cd**		**Cr**	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
A	0.02	0.05	0.02	0.15	0.02	0.4	ND	ND	ND	ND	0.01	0.01	ND	ND
B	0.04	0.2	0.01	0.13	0.12	0.13	0.02	0.02	0.01	0.06	0.01	0.03	0.02	0.02
C	0.03	0.06	0.02	0.16	0.09	0.65	0.01	0.01	0.02	0.08	0.01	0.01	ND	ND
D	0.0	0.1	0.0	0.18	0.0	0.26	0.0	0.09	0.0	0.07	0.0	0.01	ND	ND

	2		1		9		9		2		1			
E	0.02	0.08	0.02	0.13	0.25	0.25	ND	ND	0.02	0.04	0.01	0.02	ND	ND

ND: not determined/ below detection limit.

3.1. *Metal concentration trends at various sampling locations*

Table 2 represents a summary of the range of heavy metals concentration determined at each sampling location. Concentration trends for each metal are discussed below;

Nickel which was determined in highest concentrations of all metals has elevated levels at point A and C i.e. 0.4 and 0.65 mg/L respectively was the maximum determined at those points. Concentration at all other locations was close to half of the highest levels determined. Although highest Mn levels were determined at point D (0.18 mg/L), the levels determined at all other points were not significantly different from each other and the maximum levels at all locations were slightly lower than the highest determined level (within SD ± 0.021). Point B represents the highest Zn levels (0.2 mg/L max determined). This point is immediately downstream Khazana sugar mill and the elevated Zn concentration could be due to the sugar mill contribution of Zn to the surface water (Baskaran et al., 2009). Although Pb concentration is small compared to Ni, Mn and Zn, yet the levels are very significant from environmental health perspective. Pb levels were higher than WHO established standards (Table 1). The highest Pb (0.09 mg/L max.) concentration was determined at point D. This point is downstream the domestic effluents and effluents from tanneries. Pb concentrations were not detectable at point A and E. Cu was below the limit of detection at point A. The highest level was determined at point C (0.08 mg/L), among other sources; sugar mill has been reported to contribute in Cu contamination in the environment (Baskaran et al., 2009). The concentrations at all other points were only slightly lower than this highest determined level. Cd concentration ranged from 0.01-0.03 mg/L at all points and Cr could be determined only at point B.

3.2. *Metal concentration across sampling months (variation in temperature and pH)*

Temperature and pH affect the contaminants fate in the river; control their speciation and thus their distribution within the dissolved or particulate fractions (Nicolau et al., 2006). The concentrations of Mn sharply increased at all sampling locations in the month of February and remained almost stable till the end of sampling period (Fig. 3c). An increase in Zn, Cu and Ni concentrations was observed in the month of January at some sampling locations (Figs. 3A, 3B and 3D).

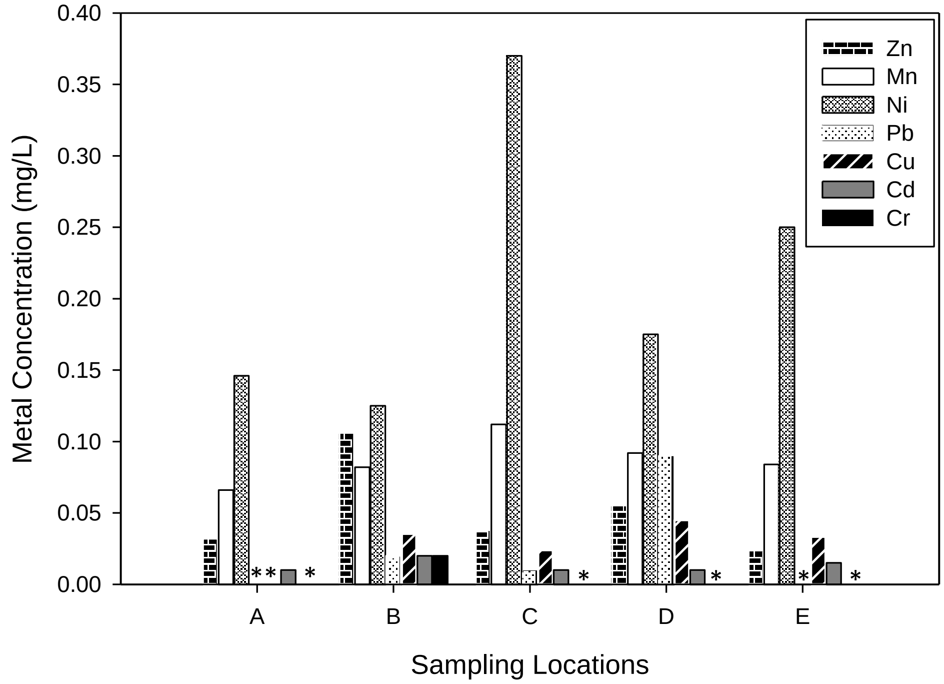


Fig. 3. Selected heavy metal concentrations over sampling months in the surface water of Shah Alam River water.

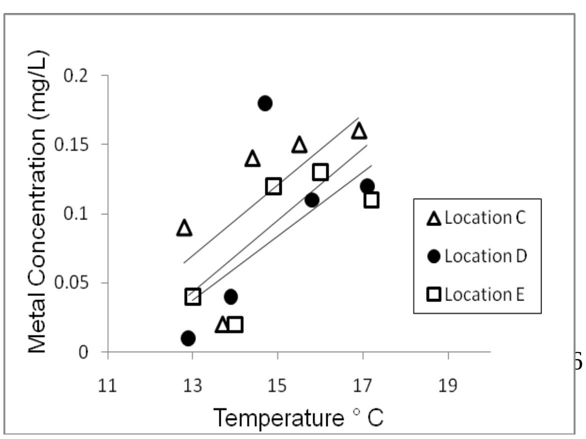
Table 3 lists the average physiochemical parameters (Temperature and pH) of the river water studied at all five sampling locations. We tried to investigate the relationships between these physicochemical parameters and the dissolved metals of the sampling site of the Shah Alam River water. Except for the Mn, a very weak correlation was found to exist between concentration and these two parameters. The estimation of the linear relationships for Mn is given (Fig. 4) and Table 4 gives the linear regression correlation coefficients (R^2) for Mn and the physicochemical parameters (temperature and pH). The correlations between other studied metals and the temperature or pH was not remarkable. A strong correlation also existed between water temperature and pH (Fig. 5).

Table 3. Physiochemical parameters of the Surface water of Shah Alam River.

Parameter	Min	Max	Average
Temperature ° C	12.3	17.2	14.6
pH	6.94	8.95	7.5

Table 4. The goodness of fit (R^2) obtained from linear regression of Mn concentration vs. physicochemical parameters (Temperature and pH) in the selected sampling locations of Shah Alam River.

Parameter/ Location	**R^2**				
	A	B	C	D	E
Temperature	0.23	0.26	0.5	0.4	0.57
pH	0.2	0.3	0.53	0.5	0.62



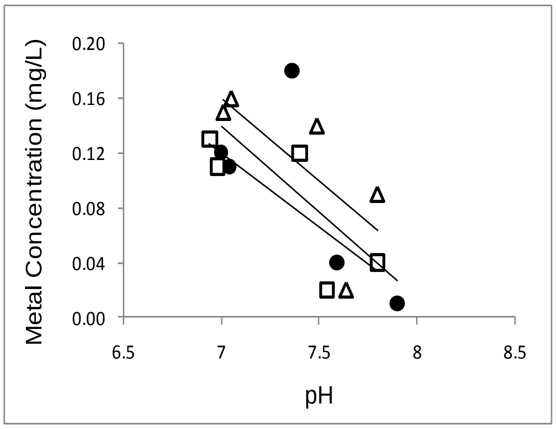


Fig. 4. Linear regression of Mn concentration vs. water physicochemical parameters (Temperature and pH) in three selected sampling locations of Shah Alam River.

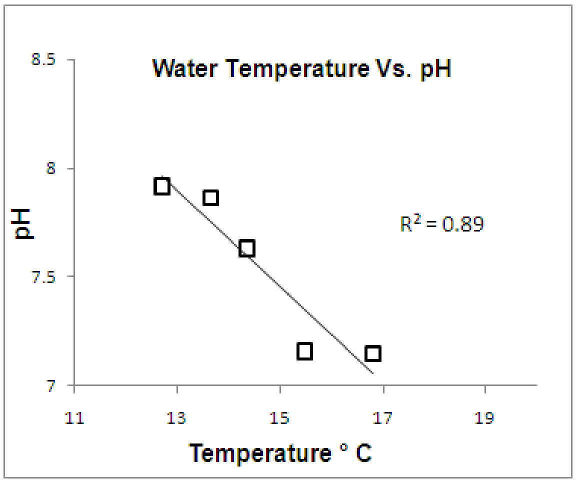


Fig. 5. Linear regression and the resulting regression coefficient (R^2) of average water Temperature against pH during the selected sampling months at selected sampling locations of Shah Alam River.

The solubility of heavy metals in surface water is predominately controlled by the water pH (Osmond et al., 1995) and water temperature (Iwashita and Shimamura, 2003). A Lower pH increases the competition between metal and hydrogen ions for binding sites and may also dissolve metal-carbonate complexes, releasing free metal ions into the surface water (Osmond et al., 1995). Although we did not observe a strong correlation between water pH and metal concentration, it may play a significant role in the dissolved metal increase in the much warmer periods of the year (Papafilippaki et al., 2008). Temperature impacts the rates of metabolism and growth of aquatic organisms, rate of plants' photosynthesis and solubility of oxygen in river water. At a higher temperature, plants grow and die faster, leaving behind matter that requires oxygen for decomposition. Trace elements which are accumulated to phytoplankton may become soluble during the decay of plants (Kabata–Pendias and Pendias, 1992). The seasonal variation of the water temperature in the Shah Alam River may influence the distribution of the studied metals via biological activity. The reason for weak/non existent correlation between metal concentration and water pH or temperature could be dilution or changes in industrial activities during various months of the year. It is also imperative that there was only 2-3° C change in water temperature during the entire sampling period. A more significant change could have been observed, should the study be extended to much hotter months of the year.

Some metals determined are known to be hazardous to human and ecological health. In our study Ni was determined in highest concentration. Ni exposure has been reported to produce hematological effects in both animals and humans. In humans, a transient increase in blood reticulocytes was reported among workers following consumption of water containing nickel sulfate and nickel chloride (Sunderman et al., 1988). In an in vitro study, Ni was found to increase lipid peroxidation in rat erythrocytes and human platelets (Chen et al., 1999, Chen and Lin 2001). Ni enhance oxidative stress in plasma (Chen et al., 2002) and has been reported to have significantly decreased the viability of lymphocytes in humans after acute treatment $NiCl_2$ (0–10 mM) (Chen et al., 2003). Cd and Pb were determined in small yet significant concentrations. The levels are higher than the WHO established water quality standards. The presence of Pb and Cd in water could potentially pose health threats to humans either via bioaccumulation process or through direct consumption of surface water. Cd exposures are associated with kidney and bone damage. Cd has also been identified as a potential human carcinogen, causing lung cancer and kidney damage (Jarup et al., 1998; IARC, 1993). Pb exposures have developmental and neurobehavioral effects on fetuses, infants and children, and elevate blood pressure in adults (Cresta et al., 1989; Huel et al., 1981). Although Cr levels are within the WHO limits but it is also a known carcinogen (WHO Europe, 2010)

A slight declining trend in most metal concentrations (Fig. 2) downstream could be due to number of reasons, they include, metal sorption to anaerobic sediments, uptake by algae and aquatic fauna. Metals can become ‘locked up’ in bottom sediments, where they remain for many years. Sediments have been reported to form the major repository of heavy metal in aquatic system (Asaolu and Olaofe, 2005 Olowu et al., 2010) which through various processes could make a concentration of heavy metals in the water high enough to be of ecological significance. Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish (Asaolu and Olaofe, 2005; Olowu et al., 2010). Unlike some organic pesticides, metals cannot be broken down into less harmful components in the environment hence both localized and dispersed metal pollution cause environmental damage.

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