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Heavy metals concentration in the sediment load of river Kalpani at district Nowshera, Khyber Pakhtunkhwa Pakistan

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Abstract

The present study was conducted to assess the heavy metals concentration at Kalpani river at district Nowshera Khyber Pakhtunkhwa Pakistan. The heavy metals studied were lead (Pb), chromium (Cr), cadmium (Cd), Zinc (Zn) and Nickel (Ni). Sampling was carried out during the months of July to October, 2013. The heavy metals concentration was determined by using Perkin Elmer AS 3100 flame atomic absorption spectrophotometer. The concentration of the studied heavy metals was varying among sampling months and sites. Overall mean values recorded (wet weight) for Cr, Zn and Ni were $0.214 \pm 0.016 \mu\text{g g}^{-1}$, $0.552 \pm 0.099 \mu\text{g g}^{-1}$ and $0.509 \pm 0.069 \mu\text{g g}^{-1}$ respectively while Pb and Cd was not detected in any sediment sample across all the sampling sites. The results showed, heavy metals were present in the order of $\text{Zn} > \text{Ni} > \text{Cr}$ while Pb and Cd was not detectable at all. Results showed that all the studied heavy metals were falling in suggested permissible limits except Zinc, which was falling out of permissible limits for all sampling months and sampling sites.

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Introduction

Studies have shown that heavy metals are accumulated in water, sediments and also in the bodies' organs of aquatic organisms. Evaluating the concentrations of heavy metals accumulated in living organisms reflects the degree of environmental pollution across the water body. Among other aquatic species, fish are a suitable biomarker of environmental pollution, because of their prominent position in the aquatic food chain and trophic level (Fazio *et al.*, 2014; Sthanadar *et al.* 2013c).

Swift increase in population and industrialization has resulted in environmental pollution, being a major threat to life (Espinoza-Quiñones *et al.*, 2005; Ullah *et al.*, 2014; Sthanadar *et al.*, 2015a). It is a matter grave of concern for humans on one hand and also threatening other forms of life. Where, fish is being at the top front among aquatic organisms, (Praveena *et al.*, 2007). Aquatic pollutants like inorganic chemicals can readily lead to fish mortalities (Ullah and Zorriehzahra, 2014). Moreover, pollutants can be pesticides from agricultural fields, municipal wastes, effluents from industries, domestic wastes and sewage effluents (Aprile and Bouvy, 2008; Arimoro and Ikomi, 2008; Shanbehzadeh *et al.*, 2014; Sthanadar *et al.*, 2015b). All these ultimately flow into water bodies and incorporate into sediments (Issa *et al.*, 2010; Ullah, 2014). These chemicals are also having large amount of inorganic anions as well as heavy metals (ECDG, 2002), which are the result of sewage disposal, petroleum contamination and industrial effluents (Santos *et al.*, 2005). Previous studies have shown that heavy metals can readily incorporate into food chains and further bio-magnify across different trophic levels (Kishe and Machiwa, 2003). Evidently, in lethal concentrations, they can easily lead to mortalities while in sub lethal concentration, they accumulate in aquatic organisms and impair their normal physiology, anatomy and biochemistry etc. accompanied by stunted growth, reduced reproductive potentials and disturbed behaviour (Phillips and Rainbow, 1993; Olubunmi and Olorunsola, 2010; Sthanadar *et al.*, 2013a,

Sthanadar *et al.*, 2013b). Consumption of fish from such a pollutant water bodies has also toxic effects on human beings and can lead to serious complications as well (Sthanadar *et al.*, 2013c). Among these metals some are really necessary to be investigated, as they play a vital role in biochemical process of all aquatic organisms (Saeed and Shaker, 2008). These metals are also termed as trace metals. However their lethal concentration can be fatal for aquatic organisms such as fish (Rainbow, 1995; Prabu, 2009; Kane *et al.*, 2012). These metals can also result industrial wastes such as Copper and Lead, which are in turn Algaecides due to Copper or these may be due to phosphatic fertilizer such as Cadmium (Mason, 2002).

Fish use to be in direct contact with the sediments and water column of the aquatic environments. Therefore it is considered as the major factors controlling their health state and disease epidemics in both natural (wild) as well as culture (rearing) conditions (Saeed and Shaker, 2008). Aquatic environmental pollution because of both organic and inorganic chemicals poses a serious threat to the survival of aquatic organisms, fish being more noticeable of these (Bryan and Langston, 1992).

River beds or sediments are playing the role of final destination for human manufactured chemicals and compounds as well as naturally present or derived components from natural sources or natural events such as rock weathering, floods and earthquakes (Espinoza-Quiñones *et al.*, 2005; Nasr *et al.*, 2006).

Quality of sediments as well as its pollutant load evaluation is considered as a fine indicator of aquatic pollution itself and for assessing pollutants in water columns, because it is the final abode to organic pollutants as well as heavy metals (Mason, 2002; Adeyemo *et al.*, 2008). The present study was designed to assess the heavy metals load (Lead, Cadmium, Zinc, Chromium, Nickel) present in the sediments of river Kalpani at District Nowshera, Khyber Pakhtunkhwa Pakistan, which will pave the

way for further studies across the study.

Materials and methods

Sampling

Sediments sampling was carried out from July to October 2013, from river Kalpani, Khyber Pakhtunkhwa Pakistan.

Samples Analysis

Samples analysis was carried out by following standard procedure and protocol for heavy metals detection in sediments by using Perkin Elmer AS 3100 flame atomic absorption spectrophotometer (Sthanadar *et al.*, 2013c).

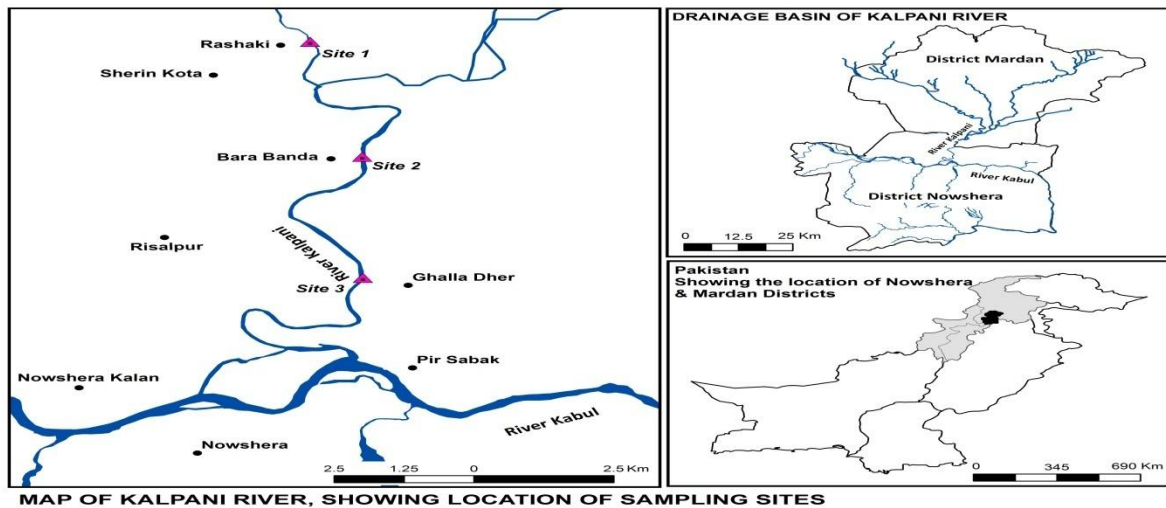


Fig. 1. Map of Kalpani River at district Nowshera & Mardan, Khyber Pakhtunkhwa Pakistan.

Statistical Analysis

All the statistical analysis (mean, standard deviation, standard error, ANOVA (one way) and Pearson correlation coefficient for the study metals) was carried out by using Statistical package SPS, Version 10.

Results and discussion

The bioaccumulation profile of the studied heavy metals, including lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn) and nickel (Ni) in the sediments of river Kalpani were analysed. The heavy metals profile was recorded in triplicate for each sample. The sediment samples were collected from three different sites in the river. The heavy metals accumulation took place in the order of Zn>Ni>Cr.

Table 1. Site wise heavy metals concentration in sediments of river Kalpani ($\mu\text{g g}^{-1}$).

Analytes	Months	Site 1	Site 2	Site 3	Mean	St. Dev.	St. Er.	DF	p>0.05*
Zn	July	0.17	0.62	0.47	0.42	0.187	0.1080	8	0.0000
	Aug	0.61	0.58	0.63	0.6	0.021	0.0120	8	0.6240*
	Sep	0.61	0.61	0.61	0.61	0.000	0.0000	8	0.9940*
	Oct	0.58	0.58	0.56	0.57	0.010	0.0055	8	0.6787*
Cr	July	0.27	0.22	0.25	0.24	0.021	0.0120	8	0.0623*
	Aug	0.19	0.19	0.19	0.191	0.001	0.0003	8	0.9771*
	Sep	0.22	0.19	0.19	0.12	0.042	0.0245	8	0.3574*
	Oct	0.21	0.19	0.27	0.22	0.034	0.0196	8	0.0066
Ni	July	0.8	0.65	0.72	0.73	0.061	0.0354	8	0.0695*
	Aug	0.52	0.54	0.51	0.52	0.013	0.0073	8	0.6647*
	Sep	0.81	0.52	0.21	0.21	0.288	0.1664	8	0.0000
	Oct	0.41	0.31	0.11	0.27	0.125	0.0720	8	0.0001

Table 2. Month wise heavy metals concentration in sediments of river Kalpani ($\mu\text{g g}^{-1}$).

Analytes	Sampling	July	Aug	Sep	Oct	Mean	St. Dev.	Std. Er.	DF	p>0.05*
Zn	Site 1	0.17	0.61	0.61	0.58	0.493	0.215	0.1077	11	0.0000
	Site 2	0.62	0.58	0.62	0.57	0.598	0.026	0.0131	11	0.0162
	Site 3	0.47	0.63	0.6	0.56	0.565	0.070	0.0348	11	0.0001
Cr	Site 1	0.27	0.2	0.22	0.21	0.225	0.031	0.0155	11	0.0689*
	Site 2	0.22	0.19	0.19	0.19	0.198	0.015	0.0075	11	0.6477*
	Site 3	0.25	0.18	0.18	0.27	0.220	0.047	0.0235	11	0.0323
Ni	Site 1	0.8	0.52	0.81	0.41	0.635	0.201	0.1007	11	0.0000
	Site 2	0.65	0.54	0.52	0.31	0.505	0.142	0.0710	11	0.0000
	Site 3	0.72	0.51	0.21	0.11	0.388	0.279	0.1397	11	0.0000

Table 3. Pearson correlation coefficient matrix for Zinc across all sampling sites.

Zinc	Site 1	Site 2	Site 3
Site 1	1.0000		
Site 2	0.9350	1.0000	
Site 3	-0.7035	-0.5948	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 4. Pearson correlation coefficient matrix for Chromium across all sampling sites.

Chromium	Site 1	Site 2	Site 3
Site 1	1.0000		
Site 2	0.4394	1.0000	
Site 3	0.9304	0.4042	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 5. Pearson correlation coefficient matrix for Nickel across all sampling sites

Nickel	Site 1	Site 2	Site 3
Site 1	1.0000		
Site 2	0.4275	1.0000	
Site 3	0.7738	0.8735	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 6. Pearson correlation coefficient matrix for Zinc across all sampling months.

Zinc	July	August	September	October
July	1.0000			
August	-0.4336	1.0000		
September	0.3273	-0.9934	1.0000	
October	-0.6547	-0.3974	0.5000	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 7. Pearson correlation coefficient matrix for Chromium across all sampling months.

Chromium	July	August	September	October
July	1.0000			
August	0.3974	1.0000		
September	0.6363	0.9608	1.0000	
October	0.3500	-0.7206	-0.5000	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Lead and Cadmium were not detected in any of the months during the study period. The mean values recorded for chromium were $0.24 \mu\text{g g}^{-1}$, $0.191 \mu\text{g g}^{-1}$, $0.12 \mu\text{g g}^{-1}$ and $0.22 \mu\text{g g}^{-1}$ for the month of July, August, September and October respectively with a mean value of $0.193 \pm 0.018 \mu\text{g g}^{-1}$. The mean values recorded for zinc were $0.42 \mu\text{g g}^{-1}$, $0.6 \mu\text{g g}^{-1}$, $0.61 \mu\text{g g}^{-1}$ and $0.57 \mu\text{g g}^{-1}$ for the month of July, August, September and October respectively with a mean value of $0.55 \pm 0.089 \mu\text{g g}^{-1}$. The mean values recorded

for nickel were $0.73 \mu\text{g g}^{-1}$, $0.5 \mu\text{g g}^{-1}$, $0.21 \mu\text{g g}^{-1}$ and $0.27 \mu\text{g g}^{-1}$ for the month of July, August, September and October respectively with a mean value of $0.433 \pm 0.120 \mu\text{g g}^{-1}$. Table 1 and Figure 2 are showing month wise concentration of the observed heavy metals across all sampling months in the sediments of river Kalpani. Figure 4 is showing the month wise mean heavy metals concentration during all sampling months.

Table 8. Pearson correlation coefficient matrix for Nickel in all sampling months.

Nickel	July	August	September	October
July	1.0000			
August	-0.6251	1.0000		
September	0.5166	0.3454	1.0000	
October	0.3634	0.5000	0.9854	1.0000

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 9. Pearson correlation coefficient matrix for studied heavy metals in the month of July.

July	Cr	Zn	Ni
Cr	1		
Zn	-0.954	1	
Ni	0.988	-0.989	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 10. Pearson correlation coefficient matrix for studied heavy metals in the month of August.

August	Cr	Zn	Ni
Cr	1		
Zn	-0.397	1	
Ni	0.327	-0.997	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 11. Pearson correlation coefficient matrix for studied heavy metals in the month of September.

September	Cr	Zn	Ni
Cr	1		
Zn	0.240	1	
Ni	0.955	0.517	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 12. Pearson correlation coefficient matrix for studied heavy metals in the month of October.

October	Cr	Zn	Ni
Cr	1		
Zn	-0.721	1	
Ni	-0.839	0.982	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Lead and Cadmium were not detected in any of the sampling sites during study period. The mean values recorded for chromium were $0.225 \mu\text{g g}^{-1}$, $0.198 \mu\text{g g}^{-1}$ and $0.220 \mu\text{g g}^{-1}$ for site 1, site 2 and site 3 respectively with a mean value of $0.214 \pm 0.016 \mu\text{g g}^{-1}$. The mean values recorded for zinc were $0.493 \mu\text{g g}^{-1}$, $0.598 \mu\text{g g}^{-1}$ and $0.565 \mu\text{g g}^{-1}$ for site 1, site 2 and site 3 respectively with a mean value of $0.552 \pm 0.099 \mu\text{g g}^{-1}$. The mean values recorded for nickel were $0.635 \mu\text{g g}^{-1}$, $0.505 \mu\text{g g}^{-1}$ and $0.388 \mu\text{g g}^{-1}$ for site 1, site 2 and site 3 respectively with a mean value of $0.509 \pm 0.069 \mu\text{g g}^{-1}$. The heavy metals accumulation took place in an order of $\text{Zn} > \text{Cr} > \text{Ni} > \text{Cd}$. Table 2 and Figure 3 are showing sampling sites wise concentration of the observed heavy metals across all sampling sites in sediments samples collected of river Kalpani. Figure 5 is showing the site wise mean heavy metals concentration across all sampling sites.

$0.505 \mu\text{g g}^{-1}$ and $0.388 \mu\text{g g}^{-1}$ for site 1, site 2 and site 3 respectively with a mean value of $0.509 \pm 0.069 \mu\text{g g}^{-1}$. The heavy metals accumulation took place in an order of $\text{Zn} > \text{Cr} > \text{Ni} > \text{Cd}$. Table 2 and Figure 3 are showing sampling sites wise concentration of the observed heavy metals across all sampling sites in sediments samples collected of river Kalpani. Figure 5 is showing the site wise mean heavy metals concentration across all sampling sites.

Table 13. Pearson correlation coefficient matrix for studied heavy metals in all sampling months.

Site 3	Cr	Zn	Ni
Cr	1		
Zn	-0.674	1	
Ni	0.229	-0.396	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 14. Pearson correlation coefficient matrix for studied heavy metals across Site 1.

Site 1	Cr	Zn	Ni
Cr	1		
Zn	-0.963	1	
Ni	0.681	-0.506	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 15. Pearson correlation coefficient matrix for studied heavy metals across Site 2.

Site 2	Cr	Zn	Ni
Cr	1		
Zn	0.570	1	
Ni	0.681	0.745	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 16. Pearson correlation coefficient matrix for studied heavy metals across Site 3.

Site 3	Cr	Zn	Ni
Cr	1		
Zn	-0.726	1	
Ni	-0.043	-0.488	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Table 17. Pearson correlation coefficient matrix for studied heavy metals across all selected sampling Sites.

Site 3	Cr	Zn	Ni
Cr	1		
Zn	-0.674	1	
Ni	-0.396	0.229	1

Bold r-Values >0.500 are significant at $p < 0.05$.

Tables 3 to 5 are showing Pearson correlation coefficient across all sampling sites for Zinc, Chromium and Nickel respectively while Tables 6 to 8 are showing Pearson correlation coefficient across all sampling months for Zinc, Chromium and Nickel respectively.

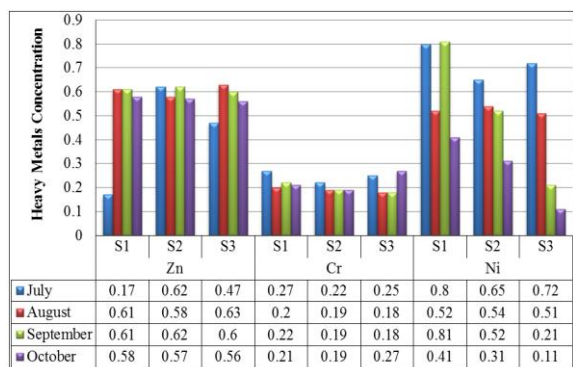


Fig. 2. Month wise heavy metals concentration in sediments of river Kalpani.

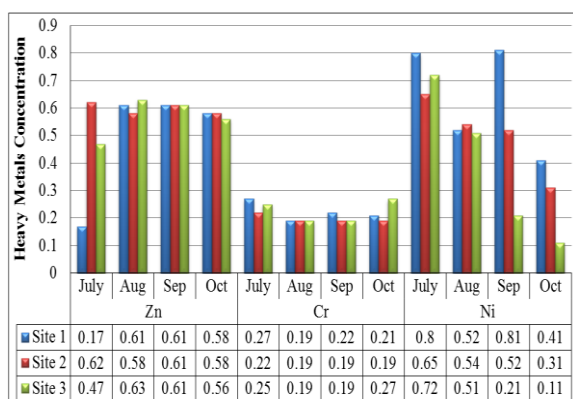


Fig. 3. Site wise heavy metals concentration in sediments of river Kalpani.

Tables 9 to 12 are showing Pearson correlation coefficient across all sampling months for the studied heavy metals (Zinc, Chromium and Nickel) across all sampling sites for the month of July, August, September and October respectively while Table 13 is showing Pearson correlation coefficient across all sampling months for the studied heavy metals (Zinc, Chromium and Nickel).

Tables 14 to 16 are showing Pearson correlation coefficient across all sampling sites for the studied heavy metals (Zinc, Chromium and Nickel) across all sampling months for Site 1, Site 2 and Site 3 respectively while Table 17 is showing Pearson

correlation coefficient across all sampling sites for the studied heavy metals (Zinc, Chromium and Nickel).

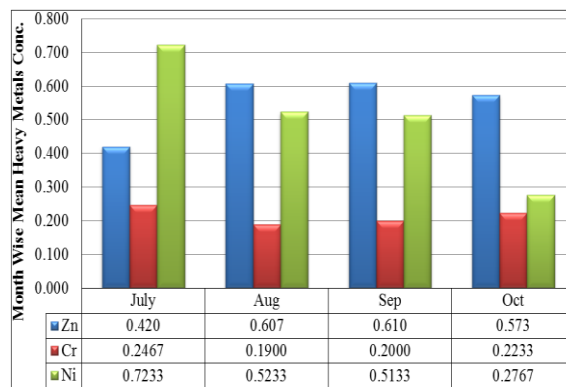


Fig. 4. Month wise mean heavy metals concentration in sediments of river Kalpani.

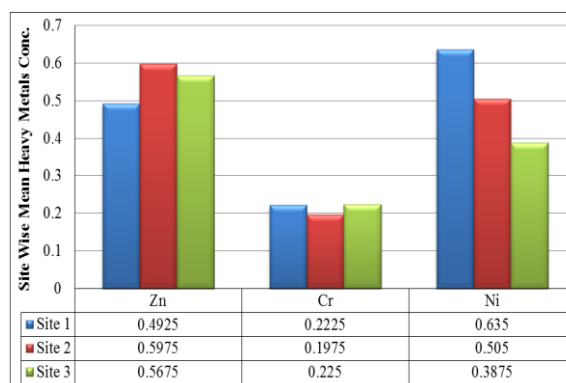


Fig. 5. Site wise mean heavy metals concentration in sediments of river Kalpani.

The studied heavy metals were falling in the permissible limits as suggested by McDonald *et al.* (2000) except Zinc, which was not lying within the proposed limit as normal permissible range suggested for Zinc is 0.015-0.107 $\mu\text{g g}^{-1}$ in sediments (dry weight). While comparing to this suggested permissible limit, Zinc was not in this range while others were in the recommended ranges.

Conclusion

The study confirms the presence of three heavy metals (Cd, Zn and Ni), with the entire absence of Pb and Cr in the samples collected from the sediments of Kalpani river at District Nowshera, Khyber Pakhtunkhwa. In the present investigation the detected heavy metals were in permissible limits except Zn across all sampling sites and months (McDonald *et al.*, 2000). The metals accumulation in

the skin tissue was in order of Zn>Ni>Cr. For conserving and maintaining the water quality and fish biodiversity from sediment prospective, it is recommended to assess heavy metals load of the river regularly. Environmental Protection Agency (EPA) should observe strict rules against polluting and contamination of the river. If managed properly, the river can play a very economical role from fishermen standpoint.

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