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# An assessment of heavy metals in sediments from two tributaries of lower stretch of Hugli estuary in West Bengal

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# ABSTRACT

Sediments from two tributaries (Haldi and Rupnarayan) of lower stretch of Hugli estuary were analysed for Lead, Cadmium, Copper, Nickel, Zinc, Iron, and Cobalt. Average concentration of Ni, Pb, Co, Zn, Cu, and Cd in sediments from Haldi river was 22.4, 13.9, 11.8, 48.7, 17.0, 1.3 mg/kg respectively and the concentration of Fe was 2.01 %. On the other hand average concentration of Ni, Pb, Co, Zn, Cu, Cd in Rupnarayan river sediments was 22.4, 14.3, 11.8, 49.5, 15.1, 1.6 mg/kg and the concentration of Fe was 1.72 %, respectively. A variable correlation coefficient was observed between the metals. The average Pollution Load Index (PLI) of heavy metals in the sediments of both the rivers was 0.50. The concentrations of heavy metals determined in this study were found to be lower than earth's background and sediment quality guideline values. The heavy metals in these tributaries do not reflect any severity of contamination.

Keywords: Heavy metal, River sediments, Pollution Load Index (PLI).

# **INTRODUCTION**

Trace metal pollution occurs in aquatic environments, especially in rivers and oceans, due to anthropogenic activities. Industrial effluent, urban run-off, atmospheric deposition as well as upstream run-off are absorbed into deposits and incorporated into the surface sediments.

Metals dissolved in soil solution, surface and interstitial waters and those adsorbed on the sediment by cation exchange processes are usually readily available to aquatic and benthic organisms as well as to plants. Metals strongly bound to the sediments and complexes with other chemical compounds are of less concern as they are most likely unavailable to the biota. Bottom

sediments accumulate metals and affect the near-bottom water layer due to mobilization / immobilization processes [1]. Metal contaminated sediment may act as a secondary pollution source for aquatic ecosystem, and study of metal concentration in sediment is useful for the estimation of pollution trends [2-3].

Estuaries function as the major routes of chemical contamination to the marine environment and increase the levels in water, sediment and biota [4]. Haldi and Rupnarayan rivers are two estuarine tributaries of lower stretch of Hugli estuary in West Bengal, India. The economics of both the rivers involve utilization of their water resources itself together with the use of water for navigation, irrigation, power generation and supply of water to the riverside towns. These two rivers carry waste discharges of Kolaghat thermal power station, Haldia industrial city and nearby Haldia port and their inputs to river Ganga is higher during low tides.

Studies on heavy metals have been reported around Kolkata (West Bengal) in different compartments of aquatic environment including Hugli estuary [5-11]. This study was carried out to check the pollution load index and distribution of heavy metals (Nickel, lead, cobalt, zinc, iron, copper and cadmium) in the surface sediments from Haldi and Rupnarayan tributaries of Hugli estuary in West Bengal.

# MATERIALS AND METHODS

# Sampling

Four locations on Haldi River and five locations on Rupnarayan River were selected on an average distance of 10 km (**Figure1**). Sampling locations on the rivers are summarized below.

Sampling Locations	Haldi River	Sampling Locations	Rupnarayan River
H 1	Moina	R1	Ghatal
H 2	Matangini Setu	R2	Kolaghat Town
Н 3	U/s Haldia Town	R3	D/s Kolaghat Town
H 4	Confluence with Hugli	R4	Tamluk
-	-	R5	Confluence with Hugli

 Table 1: Sampling stations on Haldi and Rupnarayan Rivers in West Bengal

Surface sediment samples were collected in triplicate from middle of the river using stainless steel Van-Veen sediment grab. All visible pebbles and wood sticks were removed manually. Samples were thoroughly mixed together and an aliquot was transferred using plastic spatula into pre-cleaned acid washed wide mouth polyethylene containers. All the samples were ice preserved and transported to the laboratory. The samples were stored at 4 °C in refrigerator until pre-treatment and analysis.

# **Pre-Treatment of Samples**

Sediment samples were air dried in a dust free environment for 24 hrs and ground to fine powder using pestle and mortar. The powdered sediments were passed through plastic sieve (100 mesh size) and stored in sealed plastic bags for metal analysis. Samples were digested as per USEPA Method 3050B [12]. Briefly, one gram of each sediment sample were placed in Teflon beakers in duplicate, 20-mL of HNO<sub>3</sub> (1:1 v/v) was added and refluxed without boiling at 95  $^{0}$ C for 5 minutes. The samples were allowed to cool for 5 minutes, and 5 ml of concentrated acid was

added and refluxed at 95  $^{0}$ C until no brown fumes were given off. The samples were cooled, 2 ml of water and 3 ml of 30% H<sub>2</sub>O<sub>2</sub> were added and heated at 95  $^{0}$ C for 10 minutes. The samples were cooled and centrifuged at 2000-3000 rpm for 10 minutes till clear supernatant appeared which was stored in pre-cleaned plastic bottles till further analysis by instrument.



Figure 1: Sampling locations on Haldi and Rupnarayan River in West Bengal

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### Instrumental Analysis

Heavy metals determination was carried out using Flame Atomic Absorption Spectrometer (FAAS, GBC Avanta Australia). Instrument was calibrated using appropriate dilutions (five levels) of standard reference material solutions (Merck NJ, USA). Performance of the instrument was concurrently checked by observing the precision of the standard reference concentration. Samples were analyzed in triplicate at instrument conditions optimized during calibration. The final results were calculated by incorporating the final digestion volume and sample weight digested. The results were reported on dry weight basis. The method detection limits for Ni, Pb, Co, Zn, Fe, Cu and Cd were determined as 0.06, 0.10, 0.05, 0.01, 0.06, 0.05 and 0.01,  $\mu$ g.ml<sup>-1</sup> respectively. Accuracy of the measurement was assessed by processing a certified reference material (SW 8022) along with the samples. The recovery of the metals was ranged between 98±3 to 112±7 percent as shown in **Table 2**. Method blanks were processed in duplicate along with the samples analyzed to check any loss or cross contamination.

## Contamination Factor (CF) and Pollution Load Index (PLI) of metals

The pollution load index (PLI) is used for pollution assessment by uniform sampling of intertidal sediments within an estuary, measuring their metal contents and deriving contamination factors with reference to the baseline metal levels (World Shale Value) [13]. The back ground shale values are as follows: 47200, 19, 68, 45, 95, 0.3 and 20 mg kg<sup>-1</sup> for Fe, Co, Ni, Cu, Zn, Cd and Pb, respectively. Contamination Factor (CF) for each metal was calculated by dividing the observed concentration in sediment by baseline value for that metal.

Contamination Factor (CF) = ---

Observed Concentration of the metal

Background value of the metal\*

\* Turkian and Wedepohl (1961)

Subsequently the pollution load index (PLI) for the site =  $n\sqrt{CF_1xCF_2xCF_3...,CF_n}$ , where n is equals the number of contamination factors.

Table 2:	Comparison	of measured	values with	true values o	of certified	reference materia	I (SW 8022)
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Element	True value	Measured value*	Recovery (±%)
Nickel	160	174	109±9
Lead	124	121	98±3
Cobalt	100	100	100
Zinc	289	312	$108\pm\!8$
Iron	13771	15431	112±7
Copper	71	73	103±2
Cadmium	173	173	100

\*Average of three replicates

# **RESULTS AND DISCUSSION**

The average concentration of Ni, Pb, Co, Zn, Cu, and Cd in sediments from Haldi river was 22.4, 13.9, 11.8, 48.7, 17.0, 1.3 mg/kg respectively and of Fe was 2.01 %. The average concentration of Ni, Pb, Co, Zn, Cu, Cd and Fe in Rupnarayan river sediments was 22.4, 14.3, 11.8, 49.5, 15.1, 1.6 mg/kg respectively and of Fe was 1.72 %.

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Stn No.	Ni	Pb	Co	Zn	Fe	Cu	Cd	PLI	
Haldi River									
H1	$22.6\pm 5.6$	$15.7 \pm 2.3$	$11.3 \pm 2.6$	$46.4 \pm 8.9$	2.2±0.9	12.2±2.3	$0.9\pm0.4$	0.41	
H2	21.6±3.4	$11.6 \pm 3.6$	$11.3\pm2.2$	$60.8 \pm 12.2$	$2.1{\pm}1.1$	$15.8 \pm 3.1$	$1.4\pm0.5$	0.53	
H3	$21.9 \pm 2.5$	$13.6{\pm}1.5$	$10.7{\pm}1.9$	42.1±11.3	$1.4\pm0.8$	$16.6 \pm 4.2$	$1.5\pm0.6$	0.50	
H4	$23.5 \pm 5.6$	$14.8 \pm 3.3$	$14.0 \pm 3.5$	$45.5 \pm 8.9$	$2.4{\pm}1.2$	$23.6 \pm 3.6$	$1.4\pm0.5$	0.70	
Mean	22.4±4.3	13.9±2.7	$11.8\pm4.0$	48.7±8.1	$2.01{\pm}1.0$	17.0±3.3	1.3±0.5	0.54	
Rupnara	ayan River								
R1	$25.2 \pm 4.1$	$19.5 \pm 5.4$	$13.8 \pm 5.4$	$50.3\pm6.5$	$0.8\pm0.6$	17.9±6.3	1.9±0.9	0.50	
R2	22.2±2.3	$14.5 \pm 6.2$	$12.2 \pm 3.1$	51.1±7.8	$2.0{\pm}1.0$	$14.2\pm4.4$	$1.4\pm0.5$	0.56	
R3 R4	21.2±3.6 23.5±6.8	16.2±5.1 11.7±2.1	10.9±4.1 11.8±3.2	56.5±9.9 51.5±8.1	1.7±0.9 2.1±1.2	10.3±2.3 18.9±5.2	2.2±0.8 1.2±0.5	$\begin{array}{c} 0.54 \\ 0.42 \end{array}$	
R5	$19.9 \pm 8.1$	9.7±2.3	10.2±6.2	38.2±6.6	2.1±1.3	14.3±4.1	$1.4\pm0.4$	0.25	
Mean	22.4±3.4	14.3±4.2	$11.8 \pm 4.4$	$49.5 \pm 7.8$	$1.72{\pm}1.0$	15.1±4.5	$1.6\pm0.6$	0.45	

 Table 3: Mean values (heavy metals in mg/Kg except Fe in %) and Pollution Load Index (PLI) in sediments from two tributaries of Hugli estuary.



Figure 2: Contamination factors of heavy metal in sediments from two tributaries of lower stretch of Hugli estuary

The decreasing order of abundance of heavy metals in Haldi and Rupnarayan river sediments was observed as Fe > Zn > Ni > Cu > Pb > Co > Cd, which was in agreement with the natural progression concentration of elements in sediments and also similar to the order reported by other researchers [14-15]. The result shows that there is no much variation in the concentrations of the metals which may be due to the fact that the entire stretch of the study area is under influence of highly tidal influx. The tidal waves wash away the surface sediments of the rivers.

There is convention of using the pollution load index (PLI) for assessment of metal pollution [16]. The pollution load index (PLI) was computed (**Table 3**) from contamination factors (**Figure 2**). The PLI for Haldi and Rupnarayan river was observed as 0.54 (0.41-0.70) and 0.45 (0.25-0.56), respectively. The observed levels of studied metals suggest that although environmental or human health impact involving these metals is occurring in these rivers but at minimal level. Additionally, a PLI of 0.56 is considered to produce minimum hazard to sediment dwelling organisms.

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The observed concentrations of studied metals were in agreement with levels reported by other workers [17-20] in different aquatic ecosystems of India. The pattern of metal distribution in sediments of Haldi and Rupnarayan rivers did not show significant variation (**Figure 3**), which may be due to the movement of surface sediments by tidal currents.



Figure 3: Comparison of heavy metal concentrations in sediments from two tributaries of lower stretch of Hugli estuary
Note: Fe in percent

Inter-metal correlations of sediment were investigated and results are presented in **Table 4**. The calculated correlations are based on Pearson product moment coefficients [21].

Pearson's moment correlation coefficient (at the significance level of 0.01) of the heavy metals calculated and presented in tables-3, and it was observed that Ni is significantly correlated to Pb, Co and Cu in sediments of both the rivers but Co was correlated with Fe and Cu in Haldi river. A strong correlation between Pb to Co, Zn and Cd was observed in Rupnarayan River. Cd was correlated with Cu in Haldi River.

Table 4: Pearson's moment correlation coefficients of heavy metals in sediments from Haldi and Rupnaryan River

	Lead	Cobalt	Zinc	Iron	Copper	Cadmium		
Haldi River								
Nickel	$0.7436^{*}$	$0.8736^{*}$	-0.4940	0.6160	0.6175	-0.2186		
Lead		0.3255	-0.7468	0.2553	0.0069	-0.6388		
Cobalt			-0.1276	$0.7171^{*}$	$0.8497^{*}$	0.1250		
Zinc				0.3466	-0.1855	0.0729		
Iron					0.2939	-0.4035		
Copper						$0.6245^{*}$		
Rupnar	ayan Rive	r						
Nickel	$0.6658^{*}$	$0.9431^{*}$	0.4315	-0.6979	$0.7125^{*}$	0.0647		
Lead		$0.7680^{*}$	$0.6219^{*}$	-0.8888	-0.0180	$0.7272^{*}$		
Cobalt			0.3769	-0.7682	0.5778	0.1327		
Zinc				-0.2625	-0.1743	0.4959		
Iron					-0.2158	-0.6250		
Copper						-0.5680		

marked with \* at the significant level of 0.01

	Ni	Pb	Co	Zn	Fe	Cu	Cd	Reference	
Earth's background values									
$WS^{a}$	68	20	19	95	4.72	45	0.3	[13]	
$\rm US^b$	-	19	-	95	4.10	33	0.11	[23]	
Guideline Va	Guideline Value								
ISQG <sup>c</sup>	-	35	-	123	-	35	0.6	[22]	
$\operatorname{PEL}^{d}$	-	91.3	-	315	-	197	3.5	[22]	
LEL <sup>e</sup>	-	31.0	-	120	-	16	0.6	[24]	
SEL <sup>f</sup>	-	250	-	820	-	110	10	[24]	
Present Study									
Haldi	22.4	13.9	11.8	48.7	2.01	17	1.3	-	
Rupnarayan	22.4	14.3	11.8	49.5	1.72	15.1	1.6	-	

 Table 5: Heavy metal concentrations in River sediments: A comparison with world shale value and sediment quality guideline values (mg/kg, except Fe in %)

<sup>a</sup> World Shale value, <sup>b</sup>Unpolluted Sediments, <sup>c</sup>Interim Sediment Quality Guideline, <sup>d</sup>Probable Effect Level, <sup>e</sup>Lowest effect level, <sup>f</sup>Severe effect level

The observed results of both the rivers were compared with guideline values and shown in Table-5. The results reveal that measured mean values of Ni, Pb, Co, Zn, Fe and Cu in sediments of both the rivers were lower than earth's background and guideline values [22-23] (**Table 5**). However Cadmium value was higher than guideline value but lower than PEL and SEL values [24].

There were no remarkable changes observed due to anthropogenic activities. Although discharge of metals into these rivers is occurring but PLI does not reflect severe heavy metal pollution, therefore it may be mentioned that sediment enriched with metals may be continuously disposed off the river during tidal water fluxes.

# CONCLUSION

The study of concentration of heavy metals in sediments in both the rivers does not reflect any severe hazards. No significant variation was observed among the sampling stations. It may be due to proper mixing of surface sediment during tidal flux.

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