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Studies on Metal Eco-toxicity of River Ravi Stretch from Shandera to Head Baloki

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Abstract
The effect of aquatic toxicity on the fate and dynamics of plankton including uptake and accumulation of heavy metals by the plankton and sediments has been studies with a view to assess its ill-effects on the river Ravi aquatic ecosystem. Eight heavy metals, viz. zinc, iron, magnesium, manganese, cadmium, lead, nickel and mercury in sediments and plankton have shown direct relationships with the intensity of water pollution. Both plankton and sediments appeared as good indicators of freshwater contamination by metals in fiver ecosystem. Tne uptake and accumulation of all heavy metals (except iron) in both plankton and sediments were positively and significantly dependent upon metal toxicity in water. The accumulation of iron by sediments was negatively but significantly ($P<0.01$) dependent on iron in water. Among phytoplankton, *Bumuleria*, *Cladophora*, *Chlorella*, *Fragilaria*, *Synedra*, *Scendesmus*, *Tabellaria* and *Zygnema* indicated direct relationships with the intensity of pollution at highly polluted sites. Among zooplankton, *Brachionus* and *Polyarthra* were almost absent at highly polluted sampling stations. However, the genera, viz. *Aphanizomenon*, *Bacillaria*, *Closterium*, *Cyclopedia*, *Cocconeis*, *Cosmarium*, *Chrococus*, *Denticulla*, *Euglena*, *Spirulina*, *Spirogyra* and *Volvox* showed considerable tolerance against heavy metals toxicity. *Keratella* and *Filinia* appeared to be the tolerant genera against heavy metals toxicity while *Cyclops* and *Philodena* were found as the sensitive forms.

Introduction
Rivers and lakes are a very important part of our natural heritage. They have been widely utilized by mankind over the centuries, to the extent that very few, if any, are now in a "natural" condition. One of the most significant manmade changes has been the addition of chemicals, containing a lot of heavy metals, to the waters. Such inputs to water can be derived from a variety of sources, some of them obvious, and others less so. They can be varied so that the concentrations of chemicals in water are rarely constant. Contaminated sediments are another significant source of pollution. These may be derived from inputs of suspended solids to which toxic substances are adsorbed, such as soil particles in surface water run-off from fields treated with pesticides. Alternatively, the natural suspended material in a watercourse as well as the river bed surface can adsorb chemicals and metals from water. When the suspended material settles out, the toxic material forms a sink or reservoir; the extent to which this can cause harm to aquatic life depends on the strength of the bond between chemical and the particles. Thus, a knowledge of the distribution of heavy metals in water, sediments and plankton play a key role in detecting sources of heavy metal pollution in aquatic ecosystem (Forstner and Wittmann, 1981). Braunbeck (1994) detected environmentally related concentrations of organic compounds using histological and cytological parameters in rainbow trout liver. From an ecological point of view, survival, growth, reproduction, spawning and hatching success, in fish under different levels of toxicity, provide end-points of undoubted significance. Since reaction and adaptation to environmental parameters, regardless of whether they are natural or manmade, are hierarchical process involving different levels of biological organization (Lloyd, 1992; Vogt, 1987), macroscopically overt signs of toxicity are almost always preceded by changes at the organ, tissue, cellular, and molecular levels (Segner and Braunbeck, 1990).

Materials and Methods
Data on metal-toxicity of water, plankton and sediments were collected from the following seventeen sampling stations selected throughout the stretch of river Ravi, i.e. from Shandera to head Baloki (Fig. 1), following proportionate sampling procedure (Steel and Torrie, (1986) at both right and left banks.

Shandera Toll Tax bridge, right bank (Station 1); In front of Baradarri (S2); Farrukhabad nulla (S3); Shardpur (S4); Thatta Polian wale (S5); In between Q.B.link canal and Head Baloki (S6); Head Baloki, right bank (S7); Shandera Toll Tax bridge, left bank (S8); Munshi Hospital nulla (S9); Taj Company nulla (S10); Baker Mandi nulla (S11); Choohang (S12); Sundder (S13); Head Baloki,left bank (S14); Hudiara nulla (S15); Q.B. link canal (S16); Degh fall (S17). Samples were collected on fortnightly bases for three months, i.e. from November 1993 to January, 1994. Sampling was done in the morning hours between 9:00 a.m. to 12:00 noon. Water samples were collected from just below the surface and column (two meters below the surface), mixed to have a composite sample, for the heavy metals and physico-chemical variables. Each sampling station was divided into three sub-stations, at equal distances from the coming source (within the diameter of 100m). Water temperature, dissolved oxygen and pH were: determined through meters, viz. HANNA HI-8053, HI-9143 and HI-8520 respectively. However, total hardness was determined through the method described by APHA (1971). Zinc, iron, manganese, cadmium, lead, and nickel concentrations, in water, were determined through atomic. absorption spectrophotometer, by following method Nos. 3500-Zn B, 3500-Fe B, 3500-Mn B, 3500-Cd B, 3500-Pb

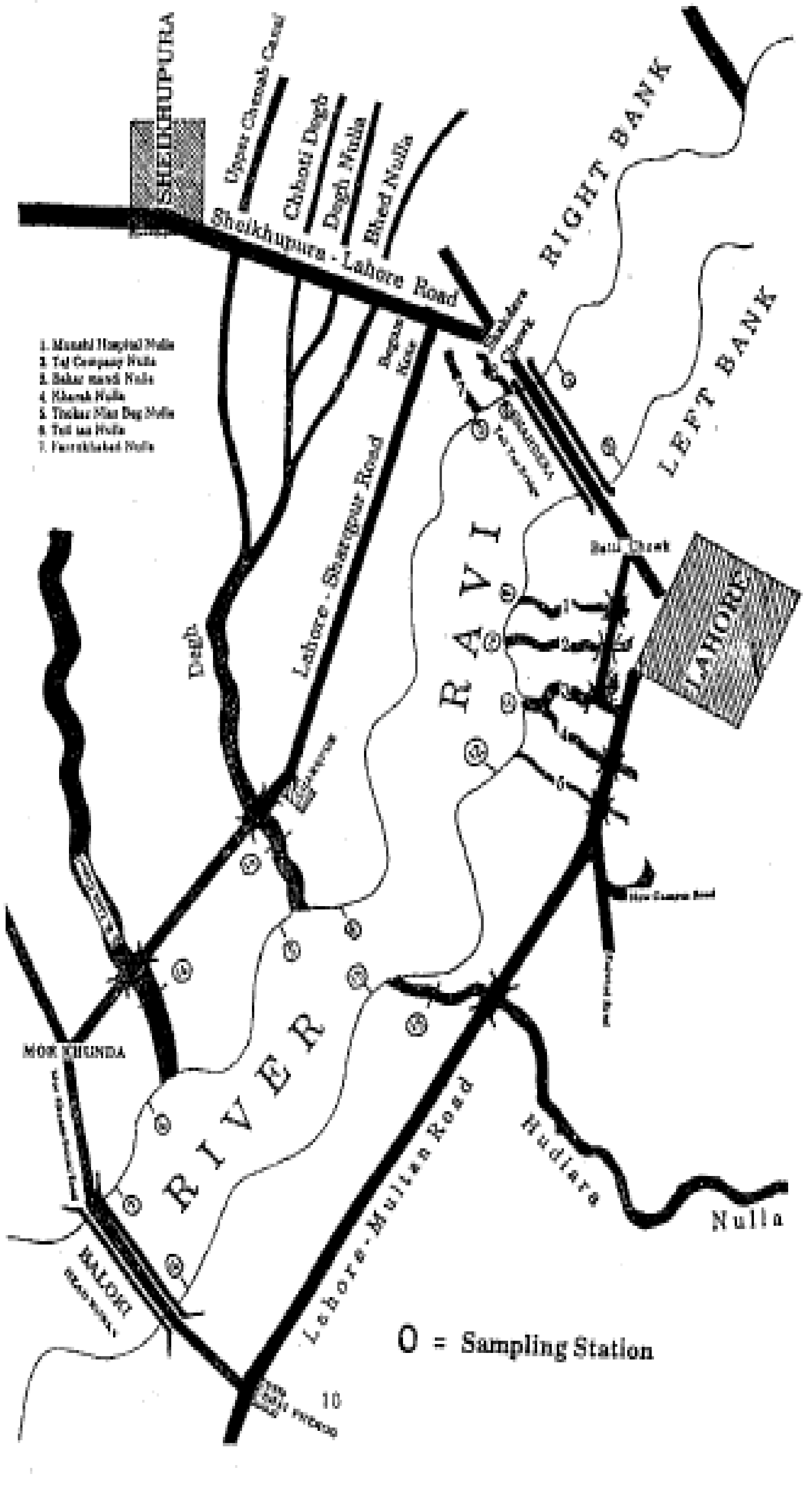

Fig. 1: Map of study area showing the locations of 17 sampling stations

B and 3500-Ni B respectively. The metal concentrations in plankton samples were also determined on dry weight basis. Dry samples of planktonic biomass were digested in Perchloric and Nitric acids and metals ion concentrations were determined by the Atomic Absorption Spectrophotometer through the methods of SMEWW (1989) as mentioned above. The samples of sediments for heavy metals determination by Atomic Absorption Spectrophotometer were prepared according to Parker (1972), Harding and Whitton (1981) and SMEWW (1989) methods. Correlations and regression analyses were performed through computer packages (MSTATC AND MICROSTAT) to find-out relationships/trends among various parameters under study.

Results

Relationships Among Water, Plankton and Sediments for the Uptake and Accumulation of Heavy Metals: Table 1 shows six monthly means for metals ion concentrations and physico-chemical variables of water, plankton and sediments at 17 sampling stations. The uptake and accumulations of all heavy metals (except iron) in plankton were positively and significantly dependent upon metals in water (Table 2). However, the adsorption of all heavy metals (except iron) by sediments were dependent positively on the metals toxicity in water. The adsorption of iron by sediments was negatively but significant ($P < 0.01$) dependent on iron in water. Accumulation of all heavy metals (except iron) in plankton showed positively significant dependence on the adsorption of metals by sediments.

Plankton as an index of freshwater contamination by metals: Myxophyceae, Bascillariophyceae and chlorophyceae were the important dominating groups distributed in the river throughout the period of study. Among phytoplankton, *Burnilleria, Cladophora, Chlorella, Fragilaria, Synedra, Scendesmus, Taipeiferia* and *Zygnema* indicated direct relationship with the intensity of pollution at highly polluted sites because these genera were almost absent or were with significantly low densities at Farrukhabad nulla (S3), Munshi Hospital nulla (S9), Taj Company nulla (S10), Bakar Mandi nulla (S11), Hudiara nulla (S15) and Degh fall (S17). Among zooplankton populations, *Brachionus* and *Polyarthra* were almost absent at highly polluted sampling sites. However, the genera, viz. *Aphanizomenon, Bacillaria, Closterium, Cyclotella, Cocconeis, Cosmarium, Chrococus, Denticulla, Euglena, Spirulina, Spirogyra* and *Volvox* showed considerable tolerance against heavy metals toxicity at different sampling stations. *Keratella* and *Filinia* appeared to be the tolerant genera against heavy metals toxicity while *Cyclops* and *Philodena* were found as the sensitive forms.

Uptake and Accumulation of Heavy Metals by Sediments and Plankton Dependent Upon Physico-chemical Variables: Table 3 shows final step equations computed for the regression of heavy metals accumulation by sediments and plankton on physico-chemical variables.

Adsorption of heavy metals by sediments: Zinc in sediments showed positively significant regression on total hardness, water temperature and zinc in water. This regression model explains 99.43 percent variations of zinc in sediments due to these variables. High value of R^2 for the relationship depicts high reliability of this regression model. The pH of water appeared as a single water quality variable that was responsible for 82.45 percent variations in iron adsorption by river sediments. The regression coefficient between manganese in sediments and water was positively significant at $p<0.01$. Cadmium in sediments was 70.50 percent dependent upon water temperature and metal ions in water. The partial regression coefficient for water temperature was negative and non-significant while for cadmium in water was positive and highly significant. Adsorbed lead in sediments was 82.01 percent dependent on lead concentration in water. The regression coefficient for this model was positive and highly significant. Nickel in water along with total hardness caused 88.75 percent variations towards adsorption of nickel by the sediments. The regression coefficients for both the variables were positive and highly significant (Table 3).

Accumulation of metals in plankton: The uptake and accumulation of zinc in plankton was 87.27 percent dependent on zinc in both sediments and water. However, the regression coefficient for zinc in sediments was positively significant ($p<0.01$) while for zinc in water was negative but highly significant (Table 3). Accumulation of manganese in plankton was 80.59 percent dependent on manganese in sediments and the regression coefficient for this variable was positive and highly significant. Cadmium accumulation in plankton was also positively dependent upon concentration of cadmium in sediments. The regression model computed for the uptake and accumulation of lead in plankton reveals negative but significant regression on pH of water while the partial regression coefficient for lead in sediments was positively significant at $p<0.05$. This model explains 74.37 percent contribution of pH and lead in sediments towards accumulation of this metal in plankton. Nickel in water appeared as a single variable that caused 94.98 percent contribution towards uptake of this metal by the plankton High value of R^2 for this regression depicts high precision of the model.

Relationships Among Heavy Metals Toxicities in Sedimen: The establishment of metal levels in sediments is necessary for detecting the sources and extent of metal pollution in the aquatic eco-systems. The suspended particles carried by various industrial effluents and domestic sewage are ultimately deposited as the sediments containing measurable quantities of heavy metals like lead, zinc, cadmium, nickel, manganese, iron, etc.

Table 1: Mean values for heavy metals in water, sediments and plankton, and physico-chemical variables.

Variable		Mean	S.D.	S.E.	Minimum	Maximum
Zinc						
Water	(mg l^{-1})	1.24	1.051	0.25	0.3	5.02
Sediments	(µm l^{-1})	158.42	120.763	29.28	38.5	562.47
Plankton	(µg l^{-1})	83.52	14.223	3.45	52.3	114.66
Iron						
Water	(mg l^{-1})	4.13	1.479	0.35	1.2	7.78
Sediments	(µg l^{-1})	11037.75	910.110	220.73	9627.8	12711.83
Plankton	(µg l^{-1})	4831.05	757.525	183.72	2310.6	6210.10
Manganese						
Water	(mg l^{-1})	1.33	0.594	0.14	0.3	3.15
Sediments	(µg l^{-1})	2505.50	586.590	142.26	1694.0	3961.44
Plankton	(µg l^{-1})	428.33	127.982	31.04	260.6	759.52
Lead						
Water	(mg l^{-1})	0.65	0.224	0.05	0.2	1.28
Sediments	(µg l^{-1})	182.85	46.128	11.18	123.5	321.12
Plankton	(µg l^{-1})	5.21	2.037	0.49	2.9	9.85
Nickel						
Water	(mg l^{-1})	0.81	0.441	0.10	0.3	2.43
Sediments	(µg l^{-1})	501.23	161.461	39.16	227.8	963.30
Plankton	(µg l^{-1})	8.37	3.667	0.88	3.9	21.40
Cadmium						
Water	(mg l^{-1})	0.33	0.083	0.02	0.2	0.51
Sediments	(µg l^{-1})	75.15	7.947	1.92	61.5	87.17
Plankton	(µg l^{-1})	9.39	2.654	0.64	6.3	14.53
Water Temperature (°C)		19.53	3.118	0.75	16.2	25.78
Water pH		8.06	0.273	0.06	7.4	8.36
Dissolved Oxygen	(mg l^{-1})	5.05	2.633	0.63	1.3	8.77
Water Hardness	(mg l^{-1})	248.51	71.820	17.41	156.0	444.00

Iron adsorption by the sediments was negatively but significantly affected by nickel, lead and zinc (Table 4), However, zinc adsorption showed direct (positively significant) relationship with nickel, lead, cadmium and manganese. Manganese was positively and significantly correlated with nickel, lead and cadmium also. Cadmium had positive and highly significant regression on nickel and lead. The correlation between lead and nickel was positive and highly significant also.

Discussion

The levels of heavy metals in sediments play a key role in determining the sources and the extent of metallic ion pollution in aquatic environment (Edgren, 1978; Ajmal and Razi-ud-Din, 1988). The suspended particles carried by various industrial effluents and domestic sewage are ultimately deposited as the sediments containing measurable concentrations of lead, zinc cadmium, chromium, copper, nickel, cobalt, manganese, iron, etc. (Forstner and Wittmann, 1981). The presence of heavy metals in sediments was due to the precipitation of their hydroxides, carbonates and sulfides which settle down and form the part of sediments. However, the composition of these precipitation is greatly influenced by various hydro chemical conditions of the water body. Significantly higher concentrations of all the heavy metals in the sediments were detected at Farrukhabad nulla, Munshi Hospital nulla, Taj Company nulla, Baker Mandl nulla and Hudiara nulla. These higher values for different heavy metals were attributed to industrial waste waters and sewage effluents being dumped into the river through these tributaries. These discharges increased the metals ion concentrations in water which enhanced the adsorption of all metals, except iron, by the sediments significantly. However, iron accumulation in sediments showed inverse relationship with the metal ions in water (Table 2). Since water at all the sampling stations was found to be alkaline in nature so, under alkaline pH conditions iron gets hydrolyzed (Stumm and Lee, 1960)

Table 2: Uptake and accumulation of heavy metals in plankton and sediments dependent on metals ions concentrations in water.

Regression Equation (Y = a + bx)						r
(I) Accumulation of metals from water to plankton:						
Zn in plk. Biomass	=	70.10	+	10.80 (2.11)	(Zn in water)	0.798**
Fe in plk. Biomass	=	4232.90	+	144.63 (126.90)	(Fe in water)	0.282NS
Mn in plk. Biomass	=	206.56	+	166.38 (35.37)	(Mn in water)	0.772**
Cd in plk. Biomass	=	5.05	+	13.07 (7.59)	(Cd in water)	0.406*
Pb in plk. Biomass	=	0.41	+	7.32 (1.38)	(Pb in water)	0.807
Ni in plk. Biomass	=	1.79	+	8.10 (0.48)	(Ni in water)	0.975**
(ii) Accumulation of metals from water sediments:						
Zn in sediments	=	17.70	+	113.33 (4.96)	(Zn in water)	0.986* *
Fe in sediments	=	12810.75	+	428.69 (114.04)	(Fe in water)	-0.696**
Mn in sediments	=	1443.26	+	796.92 (150.71)	(Mn in water)	0.807**
Cd in sediments	=	49.95	+	75.83 (15.71)	(Cd in water)	0.787**
Pb in sediments	=	60.64	+	186.17 (22.51)	(Pb in water)	0.906**
Ni in sediments	=	235.30	+	327.13 (42.38)	(Ni in water)	0.894**
(ii) Accumulation of metals from sediments to plankton:						
Zn in plk. Biomass	=	67.32	+	0.10 (0.01)	(Zn in sediments)	0.868**
Fe in plk. Biomass	=	5646.66	+	0.07 (0.21)	(Fe in sediments)	-0.089NS
Mn in plk. Biomass	=	-62.41	+	0.20 (0.02)	(Mn in sediments)	0.898**
Cd in plk. Biomass	=	-1.66	+	0.15 (0.08)	(Cd in water)	0.441*
Pb in plk. Biomass	=	-1.37	+	0.04 (0.01)	(Pb in water)	0.816**
Ni in plk. Biomass	=	-1.83	+	0.02 (0.003)	(Ni in water)	0.897**

(Values within brackets are standard errors). NS = Non significant; * = Significant at $P<0.05$; ** = Significant at $P<0.01$

and forms insoluble hydroxides which settle down into the sediments of the river. The hydroxides and oxides of iron and manganese constitute significant sink of heavy metals in the aquatic ecosystem. These hydroxides and oxides readily sorbed or co-precipitated the cations and anions and even a low percentage of $Fe(OH)_3$ and MnO_3 has a controlling influence on the heavy metals distribution in an aquatic ecosystem (Jenne, 1976). The high concentrations of different metals in sediments of the river Ravi may also be attributed to the fact that metals might have precipitated along with hydroxides and oxides of iron and manganese. Since inverse relationship was found between the water pH and all heavy metals in water so, the mobility of these metal ions in sediments have been influenced by pH of water (Boqomazov *et al.*, 1991). Temperature of water played an important role in the metallic toxicity of water also, because the occurrence of heavy metals in water showed significantly positive relationship with water

Table 3: Uptake and accumulation of metals in sediments and plankton dependent on different physico-chemical variables.

Regression equation (Y = a + bx)											R^2
(I) Adsorption of metals by sediments:											
Zn	-82.21	+	0.21**	(T.H.)	+	3.37	(W.T.)	+	97.86	(W.Zn)	0.9943
			(0.05)			(1.62)			(3.78)		
Fe =	-13391.38	+	3030.91**	(pH)							0.8245
			(361.11)								
Mn =	1443.26	+	796.92**	(W.Mn)							0.6508
			(150.71)								
Cd =	61.89	-	1.28NS	(W.T.)	+	115.25**	(W.Cd)				0.7050
			(0.64)			(24.06)					
Pb =	60.64	+	186.17**	(W.Pb)							0.8201
			(22.51)								
Ni =	94.33	+	0.77	(T.H.)	+	265.26**	(W.Ni)				0.8875
			(0.23)			(37.73)					
(ii) Accumulation of metals in plankton:											
Zn=	64.05	+	0.34**	(S.Zn)	-	27.93**	(W.Zn)				0.8727
			(0.07)			(7.72)					
Fe - No variable met the criteria of step of step-wise regression analysis.											
Mn =	62.41	+	0.19**	(S.Mn)							0.8059
			(0.025)								
Cd	-1.66	+	0.15*	(S.Cd)							0.4942
			(0.08)								
Pb	25.56	-	3.04	(pH)	+	0.02*	(S.Pb)				0.7437
			(1.48)								
Ni=	1.79	+	8.10**	(W.Ni)							0.9498
			(0.48)								

Values within brackets are standard errors. NS = Non significant; *Significant ($P < 0.05$); ** = Highly significant ($P < 0.01$); T.H. = Total hardness; W.T. = Water temperature; W = Water; S = Sediments.

Table 4: Correlation coefficients among metals ion concentration sin sediments.

Variable	Correlation coefficients				
	Nickel	Lead	Cadmium	Manganese	Zinc
Iron	-0.369**	-0.304**	0.157NS	-0.021 NS	-0.265
Zinc	0.821**	0.786**	0.460**	0.588**	
Manganese	0.627**	0.593**	0.593**		
Cadmium	0.422**	0.377**			
Lead	0.870* *				

** = Significant at $p < 0.01$; NS = Non-significant

temperature. The uptake and accumulation of all the heavy metals by the plankton were also positively (significantly) dependent on water temperature. Davies (1992) reported negative correlation between pH and exchangeable zinc from water into sediments. During present investigation, the increase of iron in sediments resulted in significant decrease of nickel, lead and zinc adsorption because, zinc and manganese may interfere. with iron adsorption because of similar physico-chemical properties and shared adsorption pathways (Rossander-Hulton *et al.*, 1991). However, most zinc and lead entering the soil from industrial wastes is adsorbed by the soil through a mechanism which appeared to be stronger than normal exchange reactions which make these metals very immobile and difficult to leach (El-Falaky, 1990). Both zinc and manganese adsorption by the sediments showed significantly direct correlation with the cadmium and lead (Table 4). The organic matter was also found in high concentrations at highly polluted sampling sites due to the disposal of sewage and industrial wastes. Curtis (1966) and Ajmal and Razi-ud-Din (1988) reported that metals like chromium, manganese, molybdenum and nickel in river ecosystem showed a positive association with organic carbon present in the sediments. A positive correlation occurs when metal ions interact in solution with dissolved organic matter that get in turn concentrated by adsorption. In present case it seems quite possible that metals might have interacted with the organic matter in the aqueous phase and then settled down resulting in high concentration of metals in the sediments. All this would have resulted in a positive and highly significant regression of all the metallic ions (except iron) concentrations in sediments on metal concentrations in water (Table 2). This, however, does not necessarily involve preferential metal bonding of organic substances since a number of mechanisms e.g. sorption by clay minerals and precipitation of iron or manganese oxides produce simultaneous accumulation of organic materials as well as typical metals, particularly by in the fine grained sediment fractions (Ajmal and Razi-ud-Din, 1988).

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