International Journal of Ecology and Environmental Sciences 43 (4): 275-285, 2017
ISSN: 2320-5199 (Online)


# Assessment of Heavy Metals in Water, Sediment and Adjacent Soil of a Contaminated Channel in Durgapur Industrial Zone, West Bengal, India

KRISHNENDU KUMAR POBI[1], SUMANTA NAYEK[@2] AND RAJNARAYAN SAHA[3] *

*Department of Chemistry, National Institute of Technology, M.G. Avenue, Durgapur713209, West Bengal, India.*
*[@] Dept. of Environmental Science, Amity Institute of Applied Sciences, Amity University, Kolkata, West Bengal, India*
Emails: [1] krishnendupobi@gmail.com; [2]-sumanta.nayek@gmail.com, [3] rajusaharupa@yahoo.com
*Corresponding Author;

## ABSTRACT

The present study assessed heavy metals in water, sediments and adjacent soil of a contaminated channel in Durgapur industrial zone, India. Physicochemical characterization of water showed that pH (7.86-12.39), TSS (113-303 mg $L^{-1}$), COD (358.6-532.8 mg $L^{-1}$), Fe (6.11-26.37 mg $L^{-1}$), Pb (1.54-3.38 mg $L^{-1}$) and Hg (0.112-1.260 mg $L^{-1}$) in channel water exceed BIS standard. Mean contcentrations of Pb, Cd, Cr, Ni, and Hg in channel sediment are well above the TEC (threshold effect concentrations). The metal $C_f$ value in channel waters follow the order Hg >Pb> Fe > Cr > Cd > Cu >Mn> Ni. EF and $I_{geo}$ values of metals in channel sediment follows the order of Hg > Cd > Fe >Pb>Mn> Cr > Ni > Cu. The distribution of heavy metals in the soil profiles are in the order of Fe >Mn> Cr >Pb> Cu > Cd > Ni > Hg. The high EF and $I_{geo}$ value of Hg in soil even at 50-60cm depth, indicate high mobility and accumulation of Hg which may contaminate ground water. Multivariate statistical appraisals indicate that heavy metal contamination in channel water, sediments and soil are mainly due to the industrial discharges/contribution. The strong positive correlation are observed between EF of heavy metals in channel sediments and surface soil, and also between the EF and $I_{geo}$ of heavy metals in the deeper layers of soil adjacent to channel .

Key Words: Heavy Metal Distribution; Wastewater Channel; Pollution Indices; Multivariate Analysis.

## INTRODUCTION

Industrial growth and development are highly desirable; however rapid industrialization is associated with environmental degradation caused by the discharge of toxic chemicals along with the heavy metals that enter into air, water and soil (Harguinteguy et al. 2014, Guagliardi et al. 2013). Industrial effluents and wastes dumped into water bodies alter its physicochemical characteristics and elevate the heavy metal concentration according to the nature of effluent being discharged (Blinova et al. 2012, Rai 2009). Even if they are present in low, undetectable quantities, their recalcitrance and consequent persistence in the environment imply that through natural processes such as biomagnification, concentrations may increase to such an extent that they begin exhibiting toxic effects (Atkinson et al. 1998).

Water contaminated with industrial discharge contains appreciable amounts of toxic metals and in the long run, can affect the surrounding soils and elevate the concentration of toxic metals in soil (Ghosh et al. 2012, Gupta et al. 2008). Soil or sediment qualities also get changed; the existing pollutants can seep into the soil system and change its physicochemical properties (Gao et al. 2012, Barman et al. 2001). Sediments are ecologically important components of the aquatic habitat and are also a reservoir of contaminants, which play a significant role in maintaining the trophic status of any water body (Silva et al. 2013, Singh et al. 1997). Sediments, not only act as the carrier of contaminants, but also the potential secondary sources of contaminants (Calmano et al. 1990, Thornton et al. 1975). Therefore analysis of sediments is a powerful approach not only for studying the distribution and persistence of contaminants

in sediments but also for reconstructing historical inputs of these compounds, improving management strategies, and evaluating the effectiveness of recent pollution control measures (Lara-Martin et al. 2015). Earlier many research work investigated (Iwegbue et al.2006, Jaradat et al. 2005) on heavy metal concentration in vertical soil profiles. The results showed that very high concentrations of heavy metals in the surface soil and then the heavy metal concentration decrease with depth even they could still gradually move down to the deep soil layers, caused deep soil pollution with long-term leaching threats to ground water contamination.

The objectives of this study are (i) to monitor and assess the distributions of heavy metals in channel water-sediment system, (ii) to identify the sources of heavy metals using multivariate statistical techniques (iii) to explore the degree of heavy metal contamination in the contaminated area using pollution indices and iv) to determine the concentration of heavy metals and physicochemical characteristics of soil profiles along the channel with a view to providing information on risks to human environment and guidance for redevelopment.

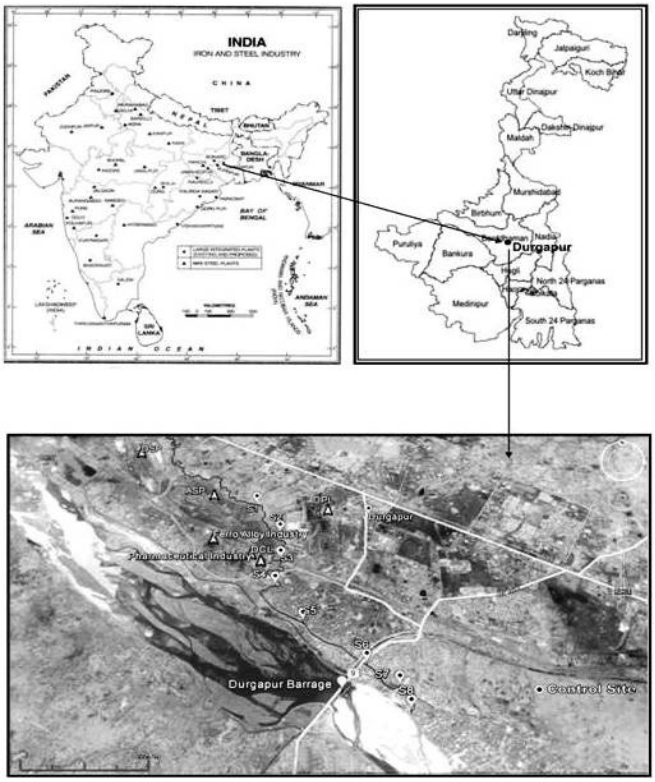


Figure 1. Location of the study area.

## STUDY AREA

Durgapur industrial zone consists of various industries like Chlor-alkali, Pharmaceutical, Ferro-alloy, sponge iron, integrated steel plant with coke oven, thermal power plant etc. Durgapur is geographically located at 23.48°N and 87.32°E. The climate of this area is tropical with two distinct seasons i.e. dry (summer and winter) and rainy (during monsoon). Industrial effluents are discharged through an unlined channel to the Tamla Nalha which serves as storm water drain for this region.

## METHODOLOGY

### Sample Collection and Analysis

Water samples were collected at regular intervals from the wastewater discharge channel (Figure 1). All samples were taken in wide mouth plastic bottles. Water pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured on site by using portable analyzer (Multi-Parameter PCS Testr$^{TM}$ 35, Oakton) were measured on sites and other physicochemical parameters were analyzed according to standard methods for the examination of water and wastewater (APHA 2000).

For heavy metal analysis, the samples were fixed with 0.5 mL of concentrated nitric acid in the field to prevent heavy metals precipitation and were taken in an ice box to the laboratory. The samples were digested with 3:1(v/v) mixture of concentrated $HNO_3$ and $HClO_4$ (APHA 2000). Digested water filtered with Whatman-42 filter paper and filtrate analyzed for Lead (Pb), Cadmium (Cd), Chromium (Cr), Iron (Fe), Copper (Cu), Nickel (Ni), and Manganese (Mn) in atomic absorption spectrophotometer (GBC, Avanta) and Mercury (Hg) was estimated by cold vapour atomic absorption.

Sediment grab samples were collected all along the channel. Surface samples were collected from 0-12 cm depth using a stainless steel hand digger and were immediately kept into air-tight plastic bags. Soil samples were also collected from depths of 0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm using a soil corer. In the laboratory, sediment/soil samples were air-dried, crushed and sieved through 2 mm mesh, analyzed for pH, and electrical conductivity (EC) as per standard methods (APHA 2000) and for organic carbon (OC in %) by Walkey and Black (1934) method.

For estimation of heavy metal concentrations, 0.5 g of composite sediment/soil sample was digested with a

mixture of concentrated $HNO_3$ and $HClO_4$ (3:1) (USEPA 2007, Method 3051A). The solution was filtered, diluted to 50 mL with ultrapure water and Pb, Cd, Cr, Fe, Cu, Ni, Mn were analyzed by atomic absorption spectrophotometer (GBC, Avanta) and Hg was estimated by cold vapour atomic absorption.

As there was no previously recorded background value for metal concentration before the industry set up, a set of control bed rock samples were collected from nearby uncontaminated site (Nadiha, Durgapur 4-5 km away from the contaminated zone) which is considered to be devoid of any type of industrial contamination and taken as background reference value.

**Quality Control and Assurance**

Special care was taken during sample collection, preservation, and during every experimental procedure. E-Merk (AR grade) standards were used for the preparation of standard curve during analysis of metals and physicochemical parameters. Ultrapure water (resistivity=18.2 Mωcm$^{-1}$) (Sartorius Stedim Biotech, arium® 61316) was used for the preparation of all solutions. All glassware used were cleaned by soaking in dilute acid for at least 24 hours and rinsed properly in ultrapure water before use. Every analysis was triplicated to ensure the accuracy of the experimental data/ results.

**Pollution Indices**

The $C_f$ (Backman et al. 1997) is the ratio between the concentration of a metal in the water/sediment/soil and the upper permissible value or its background value (concentration in uncontaminated water/sediment/soil). $C_f$ values were interpreted as suggested by Hakanson (1980),

$$C_f = \frac{\text{Analytical Value for ith Component}}{\text{Permissible Value for ith Component}}$$

where, $C_f$ <1 indicates low contamination; 1> $C_f$ <3 is moderate contamination; 3>$C_f$ <6 is considerable contamination; and $C_f$ >6 is very high contamination.

Heavy metal evaluation index (HEI) (Edet and Offong. 2002) gives an overall quality of the water-sediments with respect to heavy metals. HEI is estimated as

$$\text{HEI} = \sum_{i=1}^{n} \frac{H_c}{H_{max}}$$

where $H_c$ is the experimental value of the i$^{th}$ parameter and $H_{max}$ is its background reference value. Heavy metal evaluation index (HEI) computed as <400= low, 400-800 = medium and >800= high metal contamination.

Enrichment factor (EF; Barman et al. 2000) has been calculated to evaluate natural or anthropogenic sources of heavy metals and determine the degree of soil pollution with respect to the soil at the uncontaminated (control) site. It is the ratio between the concentration of the heavy metal in the contaminated soil and that in the uncontaminated soil.

$$\text{EF} = \frac{[M]/[Fe]_{soil}}{[M]/[Fe]_{baseline}}$$

where [M] = total heavy metals concentrations measured in soil samples (mg kg$^{-1}$) and [Fe] = total concentration of iron as the reference element (mg kg$^{-1}$; Lee et al. 1998, Abrahim and Parker 2008). Five categories are recognized on the basis of enrichment factor (Loska and Wiechuya 2003). EF value <1- 2 = deficiency to minimal enrichment, 2> EF < 5 = moderate enrichment, 5 > EF < 20 = significant enrichment, 20 > EF <40 = very high enrichment, and EF >40 = extremely high enrichment.

Muller (1981) introduced the Index of Geo-accumulation ($I_{geo}$) which enables the assessment of metal accumulation in bottom sediments by comparing present and pre-industrial concentration.

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

where $C_n$ is the measured metal concentrations in soil/sediment fraction (<2µm) and $B_n$ is the geochemical background value of metals. The factor 1.5 is introduced to include possible variations of background value due to natural fluctuations. Geoaccumulation Index is classified as: $I_{geo}$ value <1 = uncontaminated or no pollution, 1 >$I_{geo}$< 2 = slightly polluted, 2>$I_{geo}$< 3 = moderately polluted, 3>$I_{geo}$< 4 = strongly or highly polluted, and $I_{geo}$ > 4 = extremely polluted (Muller 1981).

**Statistical Analysis**

Pearson's Correlation was computed for the water, sediment and soil parameters for analyzing the inter-relations between them. Factor analysis was used as a numerical method of discussing variables and identifying geochemical processes by extracting minimum acceptable Eigenvalue greater than 1. Principle Component Analysis (PCA) along with varimax rotation was performed for physicochemical parameters of channel water samples and sediments to analyze the interrelated variations and also identify their possible source. Pearson's correlations (r) were performed between $C_f$ value of metals (both water and sediments) with metal $I_{geo}$ value for the better interpretation/understanding of metal accumulation, distribution and their interrelations in water and sediment system. Statistical calculations were carried out at significance level 0.05 by XLSTAT (version 15.1).

RESULTS AND DISCUSSION

**Physicochemical Characteristics of Channel Water**

The effluents from different industries are discharged through commonly open channel namely Tamla Nalha without any proper treatments. The physicochemical characteristics and heavy metal concentrations of channel waters are furnished in Table 1, and compare with the industrial effluent discharge standards for inland surface waters (IS 2490 Part I: 1981) set by the Bureau of Indian Standards (BIS). The pH of water plays an important role to maintain geochemical equilibrium. The pH of channel waters varies between 7.86 and 12.39, indicating alkaline nature of channel water well above than BIS standards. Electrical conductivity reflects the capacity of water to conduct the electric current by the presence of ions. The EC value for water sample varies from 1.88 to 5.82 mS $cm^{-1}$. High suspended solid (TSS), Total dissolved solid (TDS) and chemical oxygen demand (COD) gives better idea about the solid and chemical load transported by the channel water into the water body and exceeded the BIS industrial effluents discharge standards for surface water (Wakawa et al. 2010). The values of biological oxygen demand (BOD), oxidation-reduction potential (ORP), and total hardness (TH) in channel waters are within the range as per the Indian standards (IS 2490 Part I: 1981).

Table 1.Physicochemical characterization and heavy metal concentration of channel water.

| Parameters | Min | Max | SD | IS standards |
|---|---|---|---|---|
| pH | 7.86 | 12.39 | 1.14 | 5.5-9.0 |
| EC | 1.88 | 5.82 | 0.91 | - |
| ORP | 102.00 | 378.00 | 71.05 | - |
| TSS | 113.00 | 303.00 | 52.94 | 100 |
| TDS | 939.00 | 1580.00 | 159.94 | 2100 |
| TH | 35.79 | 82.34 | 14.39 | 250 |
| BOD | 21.36 | 29.56 | 2.33 | 30 |
| COD | 358.64 | 532.80 | 47.48 | 250 |
| Pb | 1.54 | 3.38 | 0.52 | 0.1 |
| Cd | 0.028 | 0.396 | 0.09 | 2 |
| Cr | 0.102 | 0.673 | 0.15 | 2 |
| Fe | 6.11 | 26.37 | 5.02 | 3 |
| Cu | 0.032 | 0.317 | 0.09 | 3 |
| Ni | 0.027 | 0.232 | 0.06 | 3 |
| Mn | 0.036 | 0.242 | 0.05 | 2 |
| Hg | 0.112 | 1.260 | 0.36 | 0.01 |

All parameters are expressed in $L^{-1}$ except pH & EC($mS.Cm^{-1}$); - standard not mentioned
IS Standard: IS 2490 Part I: 1981

Heavy metals are found in noticeable amounts in the channel water samples as it contains industrial effluents from chemical processes where large amounts of the metals are used as raw materials or as process catalysts. Total metal concentration in channel water samples follow in the order of Fe >Pb> Hg > Cr > Cd > Cu > Ni >Mn. Among the studied metals Fe, Pb and Hg in water samples exceeded the IS standard, while concentrations of other heavy metals are well under the recommended standards. Pb and Hg are examples of heavy metals that have been classified as priority pollutants by the USEPA (Keith et al. 1979).

**Heavy Metal Concentration in Surface Sediments**

Physicochemical study of sediment characteristics shows that pH of channel sediment is highly alkaline (7.98-9.8), with high electrical conductivity (EC) values of (1259-2208 μS $cm^{-1}$). Organic carbon (OC) of sediment samples are in the low range (1.06-1.36%). Metal concentration in the channel surface sediments (Table 2) follows the order of Fe >Mn> Cr >Pb> Cd > Cu > Ni > Hg. Iron is the most abundant metal in water and in channel soil-sediment, which can be attributed to its high content in ferroalloy industrial wastewater, and also

because of laterite soil type in this area. Among the studied metals, only Cu and Ni are lower in lower concentration than the sediment quality guidelines (SQGs) (MacDonald et al. 2000).

Table 2.Physicochemical characteristics and heavy metal concentration in channel sediments.

| Parameter | Min | Max | SD error | Background | TEC[a] | PEC[b] |
|---|---|---|---|---|---|---|
| pH | 7.98 | 9.8 | 0.23 | 7.17 | - | - |
| EC | 1259 | 2208 | 113.74 | 167.67 | - | - |
| OC | 1.02 | 1.36 | 0.04 | 2.91 | - | - |
| Pb | 111.64 | 167.80 | 6.99 | 28.11 | 35.80 | 128.00 |
| Cd | 41.40 | 88.74 | 5.62 | 8.04 | 0.99 | 4.98 |
| Cr | 214.73 | 246.10 | 3.42 | 64.8 | 43.40 | 111.00 |
| Fe | 406.85 | 491.23 | 11.38 | 85.78 | - | - |
| Cu | 61.98 | 66.23 | 0.58 | 32.3 | 31.60 | 149.00 |
| Ni | 27.88 | 32.58 | 0.66 | 14.74 | 22.70 | 48.60 |
| Mn | 231.11 | 312.88 | 10.05 | 69.6 | - | - |
| Hg | 2.12 | 4.9 | 0.35 | 0.02 | 0.18 | 1.06 |

All other parameters express in mg $kg^{-1}$ except EC in µS $cm^{-1}$, OC in % of channel sediment.
a TEC, Threshold Effect Concentrations (MacDonald et al. 2000).
b PEC, Probable Effect Concentrations (MacDonald et al. 2000).

## Heavy Metals in Channel Adjacent Soil

The result of the physicochemical characterization and heavy metal concentrations of the studied soil profiles are represented in Table 3. The analysis shows that the pH of the soil samples is slightly alkaline. The soil pH acts as a useful index of availability of nutrients and metal concentration in the soil samples. The pH value of soil samples varies from 7.12 to 7.88, with an average pH value of 7.50. The electrical conductivity(EC) of the water-extract of the soils indicates the relative ions and organic matter contents of the soil samples. The EC value of the channel soils varies from 648µS $cm^{-1}$ at 50-60cm to 856 µS $cm^{-1}$ at 0-10cm, with an average EC value of 745.17 µS $cm^{-1}$. The concentration of OC of soil samples ranges from 2.64% at 50-60 cm to 6.62% at 10-20 cm. The vertical distribution of the heavy metals in soil layers adjacent to the effluent channel soil shows that there is a prominent decreasing trend with the depth of soil. Heavy metal concentrations in the surface soils are significantly higher than the heavy metal concentration in control soils. The mean concentration of heavy metals in vertical soil layers follow the order of Fe >Mn>Cr >Pb>Cu>Cd > Ni >Hg (Table 3). Correlation analysis reveals that soil pH is significantly and positively correlated with all metal concentrations but soil OC is highly correlated with Hg (r=0.735), Cd (r=0.587), Cr (r=0.658), Mn (r=0.556) and Fe (r=0.735) suggesting their higher movability and accumulation at channel adjacent soil layers.

## Statistical Analysis

The correlation between two variables reflects the degree to which the variables are related. The Pearson's correlation matrix of the various water parameters and heavy metals concentrations, presented in Table 4, shows that high positive correlation exists between pH-ORP,

Table 3.Vertical distribution of heavy metals in stream adjacent soil at different depths.

| Parameters | 0-10 cm | 10-20 cm | 20-30 cm | 30-40 cm | 40-50 cm | 50-60 cm | Mean ± SD | Background value |
|---|---|---|---|---|---|---|---|---|
| pH | 7.88 | 7.74 | 7.65 | 7.32 | 7.26 | 7.12 | 7.50±0.30 | 7.17 |
| EC | 856 | 834 | 765 | 714 | 654 | 648 | 745.17±88.65 | 167.67 |
| OC | 2.83 | 3.62 | 3.41 | 3.3 | 2.78 | 2.64 | 3.10±0.40 | 2.91 |
| Pb | 124.52 | 114.8 | 94.72 | 75.24 | 68.12 | 59.4 | 89.47±26.31 | 28.11 |
| Cd | 54.25 | 50.51 | 44.12 | 32.65 | 20.62 | 16.34 | 36.42±15.77 | 8.04 |
| Cr | 178.64 | 182.24 | 174.65 | 154.28 | 143.32 | 140.52 | 162.28±18.53 | 64.8 |
| Fe | 368.45 | 376.14 | 362.26 | 324.18 | 286.64 | 248.51 | 327.70±51.32 | 85.78 |
| Cu | 58.62 | 56.85 | 55.12 | 52.08 | 49.53 | 48.64 | 53.47±4.04 | 32.3 |
| Ni | 27.86 | 26.46 | 25.14 | 24.64 | 23.84 | 22.28 | 25.04±1.96 | 14.74 |
| Mn | 248.65 | 246.26 | 228.15 | 198.82 | 186.21 | 178.56 | 214.44±30.66 | 69.6 |
| Hg | 3.58 | 3.64 | 3.62 | 3.15 | 2.68 | 2.14 | 3.14±0.61 | 0.02 |

EC in µS $cm^{-1}$, OC in %, metal concentration in mg $kg^{-1}$ of soil.

Table 4.Correlation matrix of physicochemical parameter and heavy metals of the channel water.

| Variables | pH | EC | ORP | TSS | TDS | TH | BOD | COD | Pb | Cd | Cr | Fe | Cu | Ni | Mn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | **1** | | | | | | | | | | | | | | | |
| EC | -0.228 | 1 | | | | | | | | | | | | | | |
| ORP | **0.750** | -0.475 | 1 | | | | | | | | | | | | | |
| TSS | -0.412 | 0.856 | -0.650 | 1 | | | | | | | | | | | | |
| TDS | 0.586 | -0.180 | 0.626 | -0.243 | **1** | | | | | | | | | | | |
| TH | **0.844** | -0.466 | 0.944 | -0.674 | 0.627 | **1** | | | | | | | | | | |
| BOD | **-0.707** | 0.375 | -0.770 | 0.512 | -0.386 | -0.825 | 1 | | | | | | | | | |
| COD | **0.746** | -0.495 | 0.870 | -0.696 | 0.561 | 0.908 | -0.735 | 1 | | | | | | | | |
| Pb | **0.712** | 0.152 | 0.651 | 0.013 | 0.567 | 0.643 | -0.559 | 0.560 | **1** | | | | | | | |
| Cd | **0.747** | -0.431 | 0.907 | -0.595 | 0.748 | 0.904 | -0.639 | 0.869 | 0.635 | 1 | | | | | | |
| Cr | **0.721** | -0.057 | 0.814 | -0.203 | 0.556 | 0.774 | **-0.710** | 0.731 | **0.895** | 0.760 | 1 | | | | | |
| Fe | 0.690 | -0.303 | 0.873 | -0.483 | 0.662 | 0.868 | **-0.705** | 0.803 | 0.712 | 0.886 | 0.839 | 1 | | | | |
| Cu | **0.873** | -0.334 | 0.903 | -0.542 | 0.612 | 0.960 | **-0.799** | 0.881 | 0.734 | 0.880 | 0.836 | 0.859 | 1 | | | |
| Ni | **0.742** | -0.190 | 0.860 | -0.338 | 0.632 | 0.860 | **-0.756** | 0.784 | 0.823 | 0.848 | 0.951 | 0.889 | 0.879 | 1 | | |
| Mn | 0.691 | -0.135 | 0.836 | -0.325 | 0.564 | 0.806 | **-0.654** | 0.786 | 0.806 | 0.839 | **0.914** | 0.859 | 0.881 | 0.897 | **1** | |
| Hg | **0.723** | -0.384 | 0.844 | -0.615 | 0.538 | 0.845 | -0.482 | 0.819 | **0.547** | 0.877 | 0.669 | 0.773 | 0.827 | 0.717 | 0.785 | **1** |

Note: Values in bold are significantly different from 0 with a significance level $\alpha = 0.05$

pH-TH, pH-COD, pH and heavy metals (Pb, Cd, Cr, Cu, Ni, and Hg). Though in most natural systems pH and heavy metals tend to be negatively correlated but here the heavy pollution load from the plant offsets any natural system (Gupta et al. 2013). Among the metals, Pb-Cd, Pb-Cr, Cu-Ni, Cr-Mn, Pb-Hg and Cr-Fe have the strong positive correlation between themselves showing that their primary sources are the same (industrial discharge).

High negative correlations are observed (Table 4) for BOD-pH, BOD-COD, and BOD–heavy metals (Cr, Fe, Cu, Ni, and Mn). BOD is negligible in the chemical factory wastewater and hence, the strong negative correlation with pollutants that are present in large amounts in the water samples. Moreover, the heavy metal loading and high pH of the water reduces the biodegradability of the effluent thereby reducing BOD.

To gain further insight into the source and nature of the pollutants, factor analysis was performed to identify a small number of factors that explain most of the indices observed in water quality monitoring and to assess water quality with combined factors (Gupta et al. 2013). Only factors with Eigen values greater than 1 are retained. The results of the factor analysis are presented in Table 5. Two factors are extracted, which account for 82.66% of the total variance. The first factor (F1) explains 70.35% of the total variance, and contains a high positive loading of pH, ORP, TDS, TH, COD, Pb,

Table 5. Factor analysis (after Varimax rotation) for channel water.

| Variables | F1 | F2 |
|---|---|---|
| pH | **0.777** | 0.295 |
| EC | -0.005 | **-0.855** |
| ORP | **0.806** | 0.530 |
| TSS | -0.161 | **-0.987** |
| TDS | **0.635** | 0.190 |
| TH | **0.810** | 0.559 |
| BOD | **-0.669** | -0.393 |
| COD | **0.728** | 0.582 |
| Pb | **0.925** | -0.180 |
| Cd | **0.806** | 0.489 |
| Cr | **0.959** | 0.041 |
| Fe | **0.851** | 0.345 |
| Cu | **0.877** | 0.409 |
| Ni | **0.938** | 0.192 |
| Mn | **0.914** | 0.174 |
| Hg | **0.702** | 0.489 |
| Eigenvalue | 11.26 | 1.97 |
| Variability (%) | 70.35 | 12.31 |
| Cumulative % | 70.35 | 82.66 |

Values in bold correspond for each variable to the factor for which the squared cosine is the largest

Table 6.Correlation matrix of Channel surface sediment.

| Variables | pH | EC | OC | Pb | Cd | Cr | Fe | Cu | Ni | Mn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | **1** | | | | | | | | | | |
| EC | 0.043 | **1** | | | | | | | | | |
| OC | 0.653 | 0.388 | **1** | | | | | | | | |
| Pb | **-0.812** | 0.053 | **-0.727** | **1** | | | | | | | |
| Cd | -0.097 | -0.483 | -0.523 | 0.490 | **1** | | | | | | |
| Cr | -0.229 | 0.654 | 0.200 | 0.058 | **-0.712** | **1** | | | | | |
| Fe | -0.321 | -0.071 | -0.242 | 0.587 | 0.292 | 0.153 | **1** | | | | |
| Cu | -0.519 | 0.629 | 0.216 | 0.228 | -0.652 | **0.733** | 0.085 | **1** | | | |
| Ni | -0.543 | 0.329 | -0.039 | 0.278 | -0.494 | 0.582 | 0.182 | **0.807** | **1** | | |
| Mn | -0.510 | 0.300 | 0.060 | 0.328 | -0.413 | 0.561 | 0.444 | **0.795** | **0.941** | **1** | |
| Hg | **-0.665** | 0.223 | -0.162 | 0.520 | -0.251 | 0.462 | 0.497 | **0.744** | **0.927** | **0.971** | **1** |

Note: Values in bold are significantly different from 0 with a significance level $\alpha = 0.05$

Cd, Cr, Fe, Cu, Ni, Mn and Hg, showing that they may be contributed primarily from the industrial processes and are little influenced by natural systems. The second factor (F2) accounts for 12.31% of the total variance, it contains high negative loading for EC and TSS showing that their origins may not be from industrial effluents, may be sourced from surface runoffs.

Pearson's correlation (Table 6) for the surface sediment parameters shows a strong negative correlation between pH-Pb and pH-Hg. Though Pb and Hg being heavier are expected to deposit more in sediments with increasing pH but it may undergo chelation with organic material or other lithogenic influences, which either prevents its deposition and removes it with the water or helps in leaching down to deeper layers. Strong positive correlation is seen for Cu-Ni, Cu-Cr, Cu-Mn, Mn-Ni, Hg-Ni and Hg-Mn showing that they have similar precipitation and mobility patterns in sediments.

Factor analysis of the surface sediments is presented in Table 7. The three factors F1, F2 and F3 account for 85.32% of the cumulative variance. pH shows strong negative loading in F1 while the heavy metals Cr, Cu, Ni, Mn, and Hg show strong positive loading in F1 which 43.03% of the total variance. Therefore it can be concluded that these parameters are strongly influenced by industrial discharges. The second factor (F2) account 33.52% of the total variance and in F2, organic C has strong negative values while Pb and Cd show strong positive loadings. It indicates that even though these parameters have a different source in surface sediments, they may be influenced to some extent by industrial discharges. Fe has positive loading in F3 which contribute 8.76% of the total variance and it can be attributed to its high abundance in the background levels due to the lateritic soil.

Table 7.Factor loadings for channel surface sediment.

| Variables | F1 | F2 | F3 |
|---|---|---|---|
| pH | **-0.661** | -0.602 | 0.196 |
| EC | 0.414 | **-0.448** | -0.159 |
| OC | -0.087 | **-0.934** | 0.298 |
| Pb | 0.467 | **0.767** | 0.038 |
| Cd | -0.446 | **0.748** | 0.341 |
| Cr | **0.671** | -0.374 | -0.236 |
| Fe | 0.349 | 0.376 | **0.418** |
| Cu | **0.898** | -0.318 | -0.175 |
| Ni | **0.904** | -0.078 | 0.002 |
| Mn | **0.944** | -0.075 | 0.312 |
| Hg | **0.948** | 0.155 | 0.269 |
| Eigenvalue | 5.16 | 4.02 | 1.05 |
| Variability (%) | 43.03 | 33.52 | 8.76 |
| Cumulative % | 43.03 | 76.55 | 85.32 |

Values in bold correspond for each variable to the factor for which the squared cosine is the largest

Statistical analysis reveals that strong positive correlations between metal content in channel water with metal concentrations in channel sediments: such as water Pb with sedNi (r=0.957), Mn (r=0.951) and Hg (r=0.932); water Ni with sedMn (r=0.920) and Hg (r=0.956); water Mn with sedMn (r=0.925) and Hg (r=0.950) and water Hg with sedNi (r=0.938), Mn (r=0.970) and Hg (r=0.979), which suggests that these

metals are from a common source i.e., industrial waste disposal and effluents discharge into the channel, and subsequent precipitation/adsorption of heavy metals in channel sediments due to alkaline condition. Correlation analysis between sediment metal content and surface soils metal concentrations also execute strong positive correlation for Pb (0.98), Hg (0.94), Mn (0.91) and Ni (0.82); while for other metals correlation was found to be insignificant.

**Heavy Metal Contamination in Channel Water, Sediment and Adjacent Soil**

Several studies (Zahra et al. 2014, Gao et al. 2013, Gupta et al. 2010, Amin et al. 2009) have demonstrated that the metals concentration in water and soil-sediment system can be the sensitive indicator of contaminants in the hydrological system. Different pollution indices like Contamination factor ($C_f$), heavy metal evaluation index (HEI), enrichment factors (EF) and Geo-accumulation index ($I_{geo}$) were successfully used by earlier workers singly or in combination for assessing heavy metal enrichment/contamination in water and soil-sediment system.

In our investigation, metal $C_f$ values (Table 8) in the channel water samples followsare in the order of Hg > Pb>Fe>Cr>Cd>Cu>Mn>Ni. The heavy metal evaluation index (HEI=96.53) of channel waters was not much significant.

The EF and $I_{geo}$ values of heavy metals in surface sediment (Table 8) follow the sequence of: Hg > Cd > Fe >Pb>Mn> Cr > Ni > Cu. Heavy metal evaluation index (HEI=211.07) of channel sediments can be explain by the accumulation of metals due to the alkaline nature of the industrial discharge (Salati et al. 2010).

To study the pattern of heavy metal contamination and accumulation in the vertical soil profile, EF and $I_{geo}$ values are calculated (Table 9). Generally, the EF value of about 1 suggests that a given metal may be entirely from crustal materials or natural weathering processes (Zhang et al. 2002). Nevertheless, a slight positive deviation of EF value from unity may not arise from anthropogenic activities, for the natural difference in elemental composition between a pristine soil and the reference Earth's crust used in $C_f$ calculation could also cause it. EF value of >1.5 suggests that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes, so anthropogenic

Table 8. Heavy metal contamination in channel water and sediments with contamination factor($C_f$), enrichment factor(EF), geoaccumulation index ($I_{geo}$) and heavy metal evaluation index (HEI).

| Metals | Pb | Cd | Cr | Fe | Cu | Ni | Mn | Hg |
|---|---|---|---|---|---|---|---|---|
| Channel water : $C_f$ | 22.32 | 0.097 | 0.14 | 5.20 | 0.062 | 0.037 | 0.055 | 68.61 |
| Heavy metal evaluation index (HEI) = 96.53 | | | | | | | | |
| Channel sediment : | | | | | | | | |
| **EF** | 4.92 | 8.86 | 3.54 | 5.23 | 1.98 | 2.08 | 4.01 | 180.44 |
| **$I_{geo}$** | 1.72 | 2.56 | 1.24 | 1.80 | 0.40 | 0.47 | 1.42 | 6.91 |
| Heavy metal evaluation index (HEI) = 211.07 | | | | | | | | |

Table 9. Geoaccumulation index ($I_{geo}$) and enrichment factors (EF) of heavy metals at vertical depth of channel adjacent soil.

| Depth of soil (cm) | Pb | | Cd | | Cr | | Fe | | Cu | | Ni | | Mn | | Hg | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ | EF | $I_{geo}$ |
| 0 to 10 | 4.43 | 1.56 | 6.75 | 2.17 | 2.76 | 0.88 | 4.30 | 1.52 | 1.81 | 0.27 | 1.89 | 0.33 | 3.57 | 1.25 | 179.00 | 6.90 |
| 10 to 20 | 4.08 | 1.45 | 6.28 | 2.07 | 2.81 | 0.91 | 4.38 | 1.55 | 1.76 | 0.23 | 1.80 | 0.26 | 3.54 | 1.24 | 182.00 | 6.92 |
| 20 to 30 | 3.37 | 1.17 | 5.49 | 1.87 | 2.70 | 0.85 | 4.22 | 1.49 | 1.71 | 0.19 | 1.71 | 0.19 | 3.28 | 1.13 | 181.00 | 6.91 |
| 30 to 40 | 2.68 | 0.84 | 4.06 | 1.44 | 2.38 | 0.67 | 3.78 | 1.33 | 1.61 | 0.10 | 1.67 | 0.16 | 2.86 | 0.93 | 157.50 | 6.71 |
| 40 to 50 | 2.42 | 0.69 | 2.56 | 0.77 | 2.21 | 0.56 | 3.34 | 1.16 | 1.53 | 0.03 | 1.62 | 0.11 | 2.68 | 0.83 | 134.00 | 6.48 |
| 50 to 60 | 2.11 | 0.49 | 2.03 | 0.44 | 2.17 | 0.53 | 2.90 | 0.95 | 1.51 | 0.01 | 1.51 | 0.01 | 2.57 | 0.77 | 107.00 | 6.16 |
| Mean | 3.18 | 1.03 | 4.53 | 1.46 | 2.50 | 0.73 | 3.82 | 1.33 | 1.66 | 0.14 | 1.70 | 0.18 | 3.08 | 1.03 | 156.75 | 6.68 |

sources may become an important contributor (Gao et al. 2012). The EF values of Cu and Ni at all soil profiles shows deficiency to minimal enrichment. The EF values of Pb, Cr, Fe and Mn at in all depth and Cd at 30-40, 40-50 and 50-60cm are moderately enrichment in the soil system (Table 9). Significant enrichment is observed for Cd at 0-10, 10-20 and 20-30cm in vertical soils. Whereas the EF values for Hg at in all depths indicates extremely high enrichment. The high EF values for of most metals along the vertical depth of soil may pose potential ground water pollution and chronic health hazard (Gibb H. et al. 2014). Table 9 shows that the $I_{geo}$ values of Cu, Ni, and Cr in all vertical soil layers are <1, indicating no pollution due to these metals at these soil profiles. The $I_{geo}$ values of Fe at most soil profiles and Pb and Mn at 0-10, 10-20 and 20-30cm and Cd at 20-30 and 30-40cm indicates slight pollution due to anthropogenic contribution. Among the studied metals; Hg shows the highest $I_{geo}$ values along vertical depth of soils, falls under the "extremely polluted class" for all the examined layers.

The high correlation is observed between metal $C_f$ of channel water and metal $I_{geo}$ of sediments suggesting metal precipitation and accumulation in channel sediments. Similarly strong positive correlation observed for metal EF of sediment and surface soil (0-10cm), whereas EF of metals and Igeo of metals along vertical soil profile showed significant relation indicating their primary sources are same(industrial dispose and effluents discharge).

## CONCLUSIONS

The present study concludes that the channel water, sediment and soil samples are considerably polluted with heavy metals due to the industrial processes and anthropogenic activities along the monitored channel. pH, TSS, COD values and concentrations of Fe, Pb, and Hg in the channel water exceeds BIS standard. The high alkaline nature of channel water leads to metal deposition through the channel sediments. Total metal concentration in the channel sediments followed in the order of Fe >Mn> Cr >Pb> Cd > Cu > Ni > Hg. Most of the metals studied except Cu and Ni are much higher in concentration than the recommended sediment quality guidelines. Total $C_f$ value in channel water samples followed in the order of Hg >Pb> Fe > Cr > Cd > Cu >Mn> Ni while EF and $I_{geo}$ values of metal in channel surface sediments follow the order of Hg > Cd > Fe >Pb>Mn> Cr > Ni > Cu. Strong positive correlations ($p < 0.05$) are found for $C_f$ values of channel water with sediment $I_{geo}$ values for metal content. Heavy metals contentalong the vertical profiles of channel adjacent soil shows mostly decreasing trends with increasing depth. Heavy metal concentration in the channel soil profile follow the order of Fe >Mn> Cr >Pb> Cu > Cd > Ni > Hg. Among the studied metals, Hg has high EF and $I_{geo}$ values in soil layers even at 50-60cm depth indicates mercury has significant downward mobility which can entail potential risk at large scale contamination of ground water in the studied region. The results of multivariate statistical analysis indicates that heavy metal contamination in water and sediments may be related to two major sources i.e. industrial sources or surface runoff (influences by lithogenic processes). Presentstudy also reveals the strong positive correlation between metal EF of sediment and surface soil (0-10cm), while significant correlation between metal EF and $I_{geo}$ of metal along vertical soil layers suggesting heavy metal contamination and accumulation mainly associated with industrial discharge (anthropogenic factors). The result of the present study suggests that the channel should be given priority for effective treatment and management to reduce the potential large scale risk to the environment.

## ACKNOWLEDGEMENTS

We wish to acknowledge the Head of the Department of Chemistry, National Institute of Technology, Durgapur, for supporting with infra-structure, and Dr Srimanta Gupta, Dept. of Environmental Science, The University of Burdwan, for his valuable suggestions. Thanks are also due to all reviewers and editor of this manuscript for their valuable comments and suggestions.

## REFERENCES

Abrahim, G.M.S. and Parker, R.J. 2008.Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environmental Monitoring and Assessment 136: 227–238.

Amin, B.; Ismail, A.; Arshad, A.; Yap, C.K. and Kamarudin, M.S. 2009. Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. Environmental Monitoring and Assessment 148: 291–305.

APHA. 2000. Standard Methods for the Examination of Water and Wastewater. 10th edition. American Public Health Association, Washington, DC. 1200 pages.

Atkinson, B.W.; Bux, F. and Kasan, H.C. 1998. Considerations for application of biosorptiontechnology remediate metal-contaminated industrial effluents. Water SA 24(2): 129-136.

Backman, B.; Bodis, D.; Lahermo, P.; Rajpant, S. and Tarvainen, T. 1997.Application of ground water contamination index in Finland and Slovakia. Environmental Geology 36: 55–64.

Barman, S.C.; Sahu, R.K.; Bhargava, S.K. and Chatterjee, C. 2000. Distribution of heavy metals in wheat, mustard, and weed grown in fields irrigated with industrial effluents. Bulletin of Environmental Contamination and Toxicology 64: 489–496.

Barman, S.C.; Kisku, G.C.; Salve, P.R.; Misra, D.; Sahu, R.K.; Ramteke, P.W. and Bhargava, S.K. 2001.Assessment of industrial effluent and its impact on soil and plants. Journal of Environmental Biology 22(4): 251-256.

Blinova, I.; Bityukova, L.; Kasemets, K.; Ivaska, A.; Käkinena, A.; Kurvet, I.; Bondarenkoa, O.; Kanarbika, L.; Sihtmäea, M.; Aruojaa, V.; Schvede, H. and Kahrua, A. 2012. Environmental hazard of oil shale combustion fly ash. Journal of Hazardous Materials 229–230: 192–200.

Calmano, W.; Ahlf, W. and Forstner, U. 1990.Exchange of heavy metals between sediment components and water. Pages 503-522, In: Broekaert, J.A.C.; Gucer, S. and Adams, F. (Editors), Metal Speciation in the Environment, NATO ASI Series 23. Springer-Verlag Berlin

Edet, A.E. and Offiong, O.E. 2002. Evaluation of water quality pollution indices for heavy metal contamination monitoring.A study case from Akpabuyo–Odukpani area, Lower Cross River Basin (southeastern Nigeria). Geo Journal 57: 295–304.

Gao, H.; Bai, J.; Rong Xiao, R.; Peipei Liu, P.; Jiang, W. and Wang, J. 2013. Levels, sources and risk assessment of trace elements in wetland soils of a typical shallow freshwater lake, China. Stochastic Environmental Research and Risk Assessment 27: 275–284.

Gao, X. and Arthur Chen, C.T. 2012. Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water research 46: 1901-1911.

Ghosh, A.K.; Bhatt.M.A. and Agrawal, H.P. 2012.Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in Northern India. Environmental Monitoring and Assessment 184: 1025–1036.

Gibb, H. and O'Leary, K.G. 2014. Mercury exposure and health impacts among individuals in the artisanal and small-scale gold mining community: a comprehensive review. Environmental Health Perspectives 122: 667– 672.

Guagliardi, I.; Apollaro, C.; Scarciglia, F. and Rosa, R.D. 2013. Influence of particle-size on geochemical distribution of stream sediments in the Lese river catchment, southern Italy. Biotechnology, Agronomy, Society and Environment 17: 43–55.

Gupta, S.; Nayek, S. and Saha, R.N. 2010. Temporal changes and depth wise variations in pit pond hydrochemistry contaminated with industrial effluents with special emphasis on metal distribution in water–sediment system. Journal of Hazardous Materials 183: 125–131.

Gupta, S.; Nayek, S.; Saha, R.N. and Satpati, S. 2008. Assessment of heavy metal accumulation in macrophyte, agricultural soil, and crop plants adjacent to discharge zone of sponge iron factory. Environmental Geology 55: 731–739.

Gupta, S.; Satpati, S.; Saha, R.N. and Nayek, S. 2013. Assessment of spatial and temporal variation of pollutants along a natural channel receiving industrial wastewater. Internnational Journal of Environmental Engineering 5(1): 52-69.

Hakanson, L. 1980. Ecological risk index for aquatic pollution control. A sedimentological approach. Water Research 14: 975–1001.

Harguinteguy, C.A.; Cirelli, A.F. and Pignata, M.L. 2014. Heavy metal accumulation in leaves of aquatic plant Stuckeniafiliformis and its relationship with sediment and water in the Suquíariver (Argentina). Microchemical Journal 114: 111–118.

Iwegbue, C.M.A.; Isirimah, N.O.;Igwe, C. and Williams, E.S. 2006. Characteristic levels of heavy metals in soil profiles of automobile mechanic waste dumps in Nigeria. Environmentalist 26: 123–128

IS 2490 Part I: 1981. Tolerance Limits for Industrial Effluents Discharged into Inland Surface Waters. Part I. General Limits, Bureau of Indian Standards, New Delhi. 12 pages

Jaradat, Q.M.; Masadeh, A.;Zaitoun, M.A. and Maitah, B.M. 2005.Heavy Metal Contamination of Soil, Plantand Air of Scrapyard of Discarded Vehiclesat Zarqa City, Jordan. Soil and Sediment Contamination, An International Journal 14: 449–462.

Keith, L.H. and Telliard, W.A. 1979. Priority pollutants. Environmental Science and Technology 13: 416-424.

Lara-Martín, P.A.; Renfro, A.A.; Cochran, J.K. and Brownawell, B.J. 2015. Geochronologies of pharmaceuticals in a sewage-impacted estuarine urban setting (Jamaica Bay, New York). Environmental Science and Technology 49: 5948–5955.

Lee, C.L.; Fang, M.D. and Hsieh, M.T. 1998.Characterization and distributing of metals in surficial sediments in southwestern Taiwan. Marine Pollution Bulletin 36: 464–471.

Loska. K. and Wiechuya, D. 2003. Application of principle component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere 51: 723–733

MacDonald, D.D.; Ingersoll, C. and Berger, T. 2000.Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology 39: 20–31.

Muller, G. 1981. The heavy metal pollution of the sediments of Neckars and its tributary: a stocktaking. Chemiker Zeitung 105: 157–164.

Rai, P.K. 2009. Heavy metal phytoremediation from aquatic ecosystems with special reference to macrophytes. Critical Reviews in Environmental Science and Technology 39: 697–753.

Salati, S. and Moore, F. 2010. Assessment of heavy metal concentration in the Khoshk River water and sediment, Shiraz, Southwest Iran. Environmental Monitoring and Assessment 164: 677–689.

Silva, C.; Ya´n˜ez, E.; Martı´n-Dı´az, M.L.; Riba, I. and DelValls, T.A. 2013. Integrated ecotoxicological assessment of marine sediments affected by land-based marine fish farm effluents: physicochemical, acute toxicity and benthic community analyses. Ecotoxicology 22: 996–1011.

Singh, M.; Ansari, A.A.; Muller, G. and Singh, I.B. 1997. Heavy metals in freshly deposited sediments of Gomti river (a

tributary of the Ganga river): effects of human activities. Environmental Geology 29: 246–252.

Thornton, J.A.; McComb, A.J. and Ryding, S.O. 1975. The role of sediments. Pages 205-223, In: McComb, A.J. (Editor), Eutrophic Shallow Estuaries and Lagoons. CRC Press, Boca Raton, FL, USA.

USEPA, 2007. Method 3051a. Microwave Assisted Acid Dissolution of Sediments, Sludges, Soils, and Oils. Revision 1, United States Environmental Protection Agency,Washington, DC.

Wakawa, R.J.; Uzairu, A.; Kagbu, J.A. and Balarabe, M.L. 2010. Seasonal variation assessment of impact of industrial effluents on physicochemical parameters of surface water of River Challawa, Kano, Nigeria. Toxicological & Environ-mental Chemistry 92(1): 27–38.

Walkley, A. and Black, I.A. 1934. An examination of degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Science 37: 29-37.

Zahra, A.; Hashmi, M.Z.; Malik, R.N. and Ahmed, Z. 2014. Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-Feeding tributary of the Rawal Lake Reservoir, Pakistan. Science of the Total Environment 470–471: 925–933.

Zhang, J. and Liu, C.L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China: weathering features, anthropogenic impact and chemical fluxes. Estuarine Coastal and Shelf Science 54: 1051-1070.

*Received 20 March 2017*
*Accepted 12 September 2017*

Supplementary 1.Correlation matrix of physicochemical parameter and heavy metals of the channel soil.

| Variables | pH | EC | OC | Pb | Cd | Cr | Fe | Cu | Ni | Mn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | **1** | | | | | | | | | | |
| EC | **0.974** | **1** | | | | | | | | | |
| OC | 0.471 | 0.510 | **1** | | | | | | | | |
| Pb | **0.986** | **0.991** | 0.442 | **1** | | | | | | | |
| Cd | **0.981** | **0.986** | **0.587** | **0.973** | **1** | | | | | | |
| Cr | **0.967** | **0.965** | **0.658** | **0.951** | **0.983** | **1** | | | | | |
| Fe | **0.938** | **0.925** | **0.722** | **0.910** | **0.971** | **0.966** | **1** | | | | |
| Cu | **0.989** | **0.993** | 0.508 | **0.987** | **0.995** | **0.971** | **0.946** | **1** | | | |
| Ni | **0.956** | **0.957** | 0.405 | **0.969** | **0.951** | **0.891** | **0.908** | **0.964** | **1** | | |
| Mn | **0.989** | **0.989** | **0.556** | **0.987** | **0.989** | **0.988** | **0.949** | **0.990** | **0.940** | **1** | |
| Hg | **0.911** | **0.887** | **0.735** | **0.871** | **0.948** | **0.941** | **0.995** | **0.918** | **0.882** | **0.916** | **1** |

Note: Values in bold are different from 0 with a significance level alpha=0.05