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EVALUATION OF THE STATUS OF HEAVY METAL CONTAMINATION IN SEDIMENT OF THE RIVER GANGA AT ALLAHABAD, INDIA

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ABSTRACT

Globally, aquatic ecosystems are highly polluted with heavy metals arising from anthropogenic and terrigenous sources. The river Ganges has been one of the major recipients of industrial effluent in India. The present paper deals with the study of occurrence of five heavy metals for sediment from the River Ganga at Allahabad, U.P., India. Mean concentration of heavy metal in the Sediment Pb: 23.80 mg/kg; Cu: 55.40 mg/kg; Zn: 100.6 mg/kg; Cd: 0.64 mg/kg; Cr: 131.8 mg/kg. The order of occurrence of heavy metal concentration in sediment: Cr>Zn>Cu>Pb>Cd. To assess metal contamination in the sediment, US Environmental Protection Agency's (USEPA) Guidelines were applied. The concentration of Cr and Cu in all sediment samples are above the EPA guideline for heavily polluted sediment and the concentration of Zn and Pb are fall in the criteria of moderately polluted and not polluted respectively. The heavy metals contamination in the sediments were also evaluated by applying Index of geoaccumulation (I_{geo}), contamination factor (CF), pollution load index (PLI), potential ecological risk index (RI).

KEYWORDS: Sediment; heavy metal; contamination; geoaccumulation index (I_{geo}), pollution load index (PLI); potential ecological risk index (RI); contamination factor (CF).

INTRODUCTION

Major rivers worldwide are threatened by effluent discharge from the sewage systems due to ever increasing anthropogenic activities in the nearby urban centers and catchment areas (Vörösmarty et al., 2000; Jackson et al., 2001; Singh et al., 2002; Vörösmarty et al., 2003; Dudgeon et al., 2006; Boran and Altinok, 2010; Huang et al., 2010; Vörösmarty et al., 2010; Zhang et al., 2014), primarily due to the release of the industrial waste (Poulichet et al., 2002; mauskar, 2008; Cazenave et al., 2014; Klaver et al., 2014) through sewage networks leading to large- scale ecological imbalance (Vorosmarty et al., 2003; Abell et al., 2008; IUCN 2010). A solution to this universal problem requires a paradigm shift in our approach to quantify the level of ecotoxicity for major rivers so that the remedial measures are better and rapidly implemented in local to regional scales (Jain, 2002; Wang et al., 2007). The geochemistry of river water and associated sediments in various forms (suspended, dissolved and bed load) are routinely investigated to monitor and assess river health (Chakrapani and Subramanian 1996; Konhauser et al., 1997; Dalai et al., 2004). The mass of suspended particulate matter in riverine systems is mainly dependent on natural and anthropogenic parameters (Viers et al., 2009)

The overall objectives of the present study are to assess the heavy metal contamination in sediments of Ganga River. Specific objectives of this study include:

(i) To assess the level of heavy metals (Pb, Cu, Zn, Cd and Cr) concentrations in the sediments at different

sites of Allahabad city and compare it with the USEPA quality guideline.

- (ii) Application of a advanced statistical technique such as correlation matrix in order to investigate the complex dynamic of pollutants, source of heavy metal concentration in sediments and relationships.
- (iii) To select different pollution indices such as contamination factor, contamination degree, pollution load index and geoaccumulation index to assess heavy metal contamination.
- (iv) To assess the ecological risk due to sediment contamination.

METHODS & MATERIALS

Sediments sample were collected from five sites along the River as showing in Figure 1, Latitude Longitude and Elevation for each site were illustrated in Table 1. The sediment samples were directly collected from different sites from the Ganga River at Allahabad. The samples were carried by polythene bag. After collection, the sediment samples were dried in a vacuum oven at 105°C until constant weight, lightly ground in an agate mortar for homogenization and prepared for analysis of heavy metal. For heavy metal test, 5 gm of dried sample was digested with acid and prepared 500 ml solution. Finally, five heavy metals (Pb, Cd, Cr, Cu, and Zn) concentration were determined by using atomic absorption spectrophotometer (AAS).

Status of heavy metal contamination in sediment of the river Ganga



FIGURE I. Map showing the monitoring sites on the River Ganga at Allahabad city

| | | | - | |
|-------------|--------------------|-------------|--------------|----------------|
| Station No. | Location | Latitude | Longitude | Elevation (ft) |
| 1. | Shringwarepur ghat | 25 3522 N | 81 3821 E | 287 |
| 2. | Rasoolabad ghat | 25 2939 N | 81 5130.5 E | 335 |
| 3. | Daraganj ghat | 25 2633.7 N | 81 5251.96 E | 291 |
| 4. | Sangam | 25 25 16 N | 81 5318 E | 236 |
| 5. | Chatnaag ghat | 25 24 28 N | 81 5523 E | 309 |

TABLE I. Location of sediment sample collection

TABLE II. Concentration of heavy metals in sediments from River Ganga

| Locations | | Heavy Metals(mg/kg) | | | | | |
|--------------------|-------|---------------------|--------|-------|--------|--|--|
| | Pb | Cu | Zn | Cd | Cr | | |
| Shringwarepur ghat | 24 | 56 | 103 | 0.69 | 132 | | |
| Rasoolabad ghat | 27 | 59 | 108 | 0.75 | 139 | | |
| Daraganj ghat | 21 | 52 | 94 | 0.50 | 125 | | |
| Sangam | 18 | 48 | 87 | 0.47 | 121 | | |
| Chatnaag ghat | 29 | 62 | 111 | 0.91 | 142 | | |
| Mean | 23.80 | 55.40 | 100.60 | 0.644 | 131.80 | | |
| Max | 29 | 62 | 111 | 0.91 | 142 | | |
| Min | 18 | 48 | 87 | 0.47 | 121 | | |
| S.D | 4.44 | 5.55 | 9.964 | 0.182 | 8.93 | | |

RESULTS & DISCUSSION

A. Heavy metal concentration

The total metal concentrations for each sampling site found in sediments in this study are shown in the table II. Metal contents were ranging over following intervals: Pb: 18-29 mg/kg; Cu: 48-62 mg/kg; Zn: 87-111 mg/kg; Cd: 0.47-0.91 mg/kg; Cr: 121-142 mg/kg; dry weights. Mean concentrations of the metals were : Pb: 23.80 mg/kg ; Cu: 55.40 mg/kg ; Zn: 100.6 mg/kg ; Cd: 0.64 mg/kg ; Cr : 131.8 mg/kg dry weights , allowing to arrange the metals from higher to lower mean content in this area as : Cr>Zn>Cu>Pb>Cd. The range and mean values of the heavy metals concentration in the sediment shown in figure 2a.

Pearson's correlation coefficient matrix among the selected heavy metals is depicted in the Table III. Significant correlations between the contaminates of Pb and Cu (r = 0.999); Pb and Cr (r = 0.996); Zn and Cu (r = 0.994); Zn and Pb (r = 0.993); Cr and Cu (r = 0.991) could indicate the same or similar source input.

B. Assessment according to Geoaccumulation Index $(I_{\mbox{\scriptsize geo}})$

A common criterion to evaluate the heavy metal pollution in sediments is the geo-accumulation index. Geoaccumulation index proposed by Muller (1981) to determine metals contamination in sediments, by comparing current concentrations with pre-industrial levels and can be calculated using the following formula: $I_{geo} = log_2 [C_n / 1.5B_n]$

Where, C_n is the concentration of element "n" and B_n is the geochemical background value [In this study, consider B_n = world surface rock average given by Turekian and Weedpohl (1961)]. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The geoaccumulation index (Igeo) scale consists of seven grades (0 - 6) ranging from unpolluted to highly pollute (shown in Table IV). According to the Muller scale, the calculated results of I_{geo} values shown in Table V, for all the metals viz: Pb, Cu, Zn and Cr sediment quality was recorded unpolluted ($I_{geo} < 0$) for all the sites except Cd which indicates class 3 ranges from moderately to strongly polluted ($2>I_{geo}<3$) sediment quality for all the sites except two viz: Daraganj and Sangam sites, which depicted moderately polluted ($1>I_{geo} < 2$) sediment quality. The range and mean values Igeo of heavy metals in the sediment shown in figure 2b.

TABLE III. Correlation matrix of heavy metals in sediments from River Ganga

| Parameters | Pb | Cu | Zn | Cd | Cr | | |
|---|--------|--------|-------------|--------|----|--|--|
| Pb | 1 | | | | | | |
| Cu | .999** | 1 | | | | | |
| Zn | .993** | .994** | 1 | | | | |
| Cd | .971** | .973** | .960** | 1 | | | |
| Cr | .996** | .991** | $.988^{**}$ | .974** | 1 | | |
| **. Correlation is significant at the 0.01 level (2-tailed) | | | | | | | |

TABLE IV. Muller's classification for the Geo-accumulation Index

| Igeo Value | Class | Sediment Quality |
|------------|-------|--|
| 0 | 0 | Unpolluted |
| 0 - 1 | 1 | From unpolluted to moderately polluted |
| 1 -2 | 2 | Moderately polluted |
| 2 - 3 | 3 | From moderately to strongly polluted |
| 3 - 4 | 4 | Strongly polluted |
| 4 - 5 | 5 | From strongly to extremely polluted |
| >6 | 6 | Extremely polluted |

| TABLE | V: | Geoaccumulation | Index (| י (_{geo}) | values f | or th | e sediments | samples | s of tl | 1e Ganga R | liver |
|-------|----|-----------------|---------|----------------------|----------|-------|-------------|---------|---------|------------|-------|
|-------|----|-----------------|---------|----------------------|----------|-------|-------------|---------|---------|------------|-------|

| S.N | Parameters | | Geo-accumulation Index | | | | Mean |
|-----|------------|---------------|------------------------|----------|--------|----------|--------|
| | | Shringwarepur | Rasoolabad | Daraganj | Sangam | Chatnaag | |
| 1. | Pb | -1.32 | -1.15 | -1.52 | -1.74 | -1.05 | -31.45 |
| 2. | Cu | -5.79 | -5.72 | -5.88 | -9.97 | -5.64 | -6.60 |
| 3. | Zn | -7.16 | -6.97 | -7.38 | -7.38 | -6.96 | -5.48 |
| 4. | Cd | 2.35 | 2.47 | 1.88 | 1.64 | 2.75 | 2.22 |
| 5. | Cr | -6.38 | -6.51 | -6.64 | -6.79 | -6.38 | -4.62 |

Higher I_{geo} values are showed for Chatnaag site which sediment quality ranges from moderately polluted to strongly polluted for the Cd sediment. On the basis of the mean values of Igeo sediments are enriched for the metals in the following order Cd>Cr>Zn>Cu>Pb

C. Assessment According to Potential Ecological Risk Index

In 1980, Lars Hakanson reported an ecological risk index for aquatic pollution control; therefore, Hakanson's method has been often used in ecological risk assessment as a diagnostic tool to penetrate one of many possible avenues towards a potential ecological risk index, *i.e.*, to sort out which drainage area, reservoir, and substances should be given special attention [Hakanson, 1980].

The index is calculated as the following equations:

$$\mathbf{RI} = \mathbf{E}_{i}$$
$$\mathbf{E}_{i} = \mathbf{T}_{i} * \mathbf{f}_{i}$$
$$\mathbf{f}_{i} = \mathbf{C}_{i} / \mathbf{C}_{k}$$

Where RI is computed as the sum of all risk factors in the sediments, E_i is the monomial potential ecological risk

factor for individual factors, and T_i is the metal toxic factor. Based on the standardized heavy metal toxic factor developed by Hakanson(1980). f_i is the metal pollution factor, C_i is the concentration of metal in the sediments, and C_b is the reference value of a given metal in the earth's crust (Turekian and Weedpohl (1961)].)

The range and mean E_i values of the heavy metals in the sediment shown in figure 2c. The categorization related to

RI is also suggested by Hakanson (1980); RI<65 explicates low risk, RI=65 to 130 moderate risk; RI = 130 to 260 considerable risk, and RI>260 explicates very high risk. The results elucidate that Cd causes moderate risk, while the rest of the metals explicate low risk in the sediments. Overall, the cumulative potential risk index (RI= 60.44 to 109.47) reveals low risk of the sediments.

| Parameter | Cd | Cr | Cu | Pb | Zn |
|--|------|----|----|----|----|
| Pre-industrial background values | 0.30 | 90 | 45 | 20 | 95 |
| [Turekian and Weedpohl(1961)], C _b | | | | | |
| Toxic Response Factor, T _f ⁱ | 30 | 2 | 5 | 5 | 1 |
| [Hakanson (1980)] | | | | | |

| FABLE VII: Potential ecological risk index (RI) values for the sediment | s samples of the | Ganga River |
|--|------------------|-------------|
|--|------------------|-------------|

| Location | Pb | Cu | Zn | Cd | Cr | RI | Grade Hakanson (1980) |
|--------------------|-------------|-------------|-------------|-------------|-------------|--------|-----------------------|
| | $T_i * f_i$ | | |
| Shringwarepur ghat | 6.0 | 6.22 | 1.08 | 69 | 2.93 | 85.23 | Low |
| Rasoolabad ghat | 6.75 | 6.56 | 1.14 | 75 | 3.09 | 92.54 | Low |
| Daraganj ghat | 5.25 | 5.78 | 0.99 | 50 | 2.77 | 64.79 | Low |
| Sangam | 4.5 | 5.33 | 0.92 | 47 | 2.69 | 60.44 | Low |
| Chatnaag ghat | 7.25 | 6.89 | 1.17 | 91 | 3.16 | 109.47 | Low |

D. Assessment according to United States Environmental Protection Agency (USEPA)

The chemical contaminations in the sediments were evaluated by comparison with the sediment quality guideline proposed by US EPA; these criteria are shown in the Table VIII. Present study shows that all the sites are not polluted for the Pb and all the sites are heavily polluted for the Cu while moderately polluted for the Sangam site and for the Zn, all the sites are moderately polluted except Sangam site, which is not polluted.

| TABLE VIII. EPA C | Guidelines for the sediment |
|-------------------|-----------------------------|
|-------------------|-----------------------------|

| | Metal | Not polluted | Moderately polluted | Heavily polluted | Present study |
|---|-------|--------------|---------------------|------------------|---------------|
| 1 | Pb | <40 | 40 - 60 | >60 | 23.80 |
| 2 | Cd | | | >6 | 0.64 |
| 3 | Cr | <25 | 25 - 75 | >75 | 131.80 |
| 4 | Cu | <25 | 25 - 50 | >50 | 55.40 |
| 5 | Zn | <90 | 90 - 200 | >200 | 100.60 |

E.Assessment according to Contamination Factor (C.F), Contamination Degree (CD) and Pollution Load Index

Contamination factor (Cf) is an arithmetically calculated index, depending on a linear proportion between the concentrations of the metal in the sample taken from study area and earth crust (Hakanson, 1980; Pekey *et al.*, 2004). Concentration values of each surface sample were compared to the background values of average rocks of earth crust (Turekian and Wedepohl, 1961) and according to following formula (Hakanson, 1980; Pekey *et al.*, 2004). CF for each metal was determined by-

$$CF = \frac{Observed metal Concentration}{Background concentration of the same metal}$$

CD for each site was calculated as sum of all contamination factors (Ahdy and khaled, 2009).

In the present study, maximum contamination factor was found at the site 5 (Chatnaag ghat), where the degree of contamination is 8.61 shown in Table IX. All the sites has a contamination factor (CF>1) for the all tested heavy metals except two sites *viz*: site 2 (Daraganj) and site 3 (Sangam) for Zn and Pb. The mean values of the CF are found: Pb: 1.19; Cu: 1.23; Zn: 1.06; Cd: 2.21; Cr: 1.46, all the values are comes under the class 2, according to the Hakanson(1980) which shows moderate contamination.

On the basis of the mean values of the CF sediments are enriched for metals in the following order: Cd>Cr>Cu> Pb>Zn. The range and mean CF values of the heavy metals in the sediment shown in figure 2d.

Pollution Load Index

Pollution load index for each site was determined following the method proposed by Tomlinson *et al.* (1980). The PLI for a single site is the n^{th} root of *n* number multiplying the factors (CF values) together. PLI for each site was determined by-

PLI = n (CF₁ * CF₂ * CF₃*....* CF_n)

Where, CF is the contamination factor and n is the number of parameters.

The Pollution Load Index (PLI) at different locations for the river Ganga is depicted in Table IX. For the Ganga River, all locations are polluted as per PLI proposed by Mohiuddin *et al.*, (2010).

| TABLE IX: | Contamination | factor, con | itamination | degree an | d PLI | values |
|------------------|---------------|-------------|-------------|-----------|-------|--------|
|------------------|---------------|-------------|-------------|-----------|-------|--------|

| Contamination Factor | | | | | | | Mean |
|----------------------|------------|---------------|------------|----------|--------|----------|------|
| S.N | Parameters | Shringwarepur | Rasoolabad | Daraganj | Sangam | Chatnaag | |
| 1. | Pb | 1.20 | 1.35 | 1.05 | 0.90 | 1.45 | 1.19 |
| 2. | Cu | 1.24 | 1.31 | 1.16 | 1.07 | 1.38 | 1.23 |
| 3. | Zn | 1.08 | 1.14 | 0.99 | 0.92 | 1.17 | 1.06 |
| 4. | Cd | 2.30 | 2.50 | 1.66 | 1.56 | 3.03 | 2.21 |
| 5. | Cr | 1.47 | 1.54 | 1.39 | 1.34 | 1.58 | 1.46 |
| (CD) | | 7.29 | 7.84 | 6.25 | 5.79 | 8.61 | 7.16 |
| PLI | | 1.40 | 1.51 | 1.22 | 1.13 | 1.62 | 1.38 |

TABLE X: Contamination Factor, Contamination Degree and Pollution Load Index classifications of sediment quality

| CF values | Class | Sediment quality | | | |
|----------------------|-------|---|--|--|--|
| Hakanson (1980) | | | | | |
| CF < 1 | 1 | Low CF | | | |
| 1 CF <3 | 2 | Moderate CF | | | |
| 3 CF < 6 | 3 | Considerable CF | | | |
| CF 6 | 4 | High CF | | | |
| | | | | | |
| CD values | Class | Sediment quality | | | |
| Ahdy & Khaled (2009) | | | | | |
| CD < 6 | 1 | Low CD | | | |
| 6 CD < 12 | 2 | Moderate CD | | | |
| 12 CD < 24 | 3 | Considerable CD | | | |
| CD 24 | 4 | High CD | | | |
| | | | | | |
| PLI values | Class | Sediment quality | | | |
| Mohiuddin (2010) | | | | | |
| PLI=0 | 1 | Perfection/Not polluted | | | |
| PLI=1 | 2 | Only baseline levels of pollutant present | | | |
| PLI>1 | 3 | polluted | | | |









FIGURE II. Description of the different parameters. Description of (a) heavy metals concentration(mg/kg); (b) geoaccmulation index (I_{geo}); (c) potential ecological risk factor (E_i); (d) contamination factor (Cf)

CONCLUSION

USEPA guideline, Geo-accumulation index, Ecological risk index, contamination factor and degree of contamination, pollution load index and Multivariate statistical analysis were successfully applied for the assessment of heavy metal contamination of Ganga river sediments. Metal concentrations ranged between Pb: 18-29 mg/kg; Cu: 48-62 mg/kg; Zn: 87-111 mg/kg; Cd: 0.47-0.91mg/kg; Cr: 121-142 mg/kg in the Ganga river sediments and the order of mean concentration of tested heavy metals: Cr>Zn>Cu>Pb>Cd. As per USEPA sediment quality guideline for Cu and Cr the sediment samples are heavily polluted whereas for the Zn sediment samples are moderately polluted for Ganga River.

Significant correlation found between the contaminants of Pb and Cu (r = 0.999); Pb and Cr (r = 0.996); Zn and Cu (r = 0.994); Zn and Pb (r = 0.993); Cr and Cu (r = 0.991) in Pearson's correlation for the heavy metals of the Ganga river. This concludes that those contaminants may have same or similar source input. According to geo-accumulation Index, Ganga River is unpolluted with all the tested heavy metals *viz*: Pb, Cu, Zn and Cr except Cd which shows moderately polluted to strongly polluted. According to ecological risk index, on the whole, RI shows low risk of contamination in the sediments.

According to contamination factor (CF): Pb, Cu, Cr, Zn and Cd are responsible for moderate contaminations. According to Pollution load index (PLI): all the sites are polluted as per proposed by Mohiuddin et al. (2010). Considering all the assessment criteria, Cr, Zn and Cu are responsible for considerable or significant amount of heavy metals while Pb and Cd are responsible for minor contaminations. Site 5 (Chatnaag ghat) contains highest amount of heavy metal contamination and site 4 (Sangam) contains lowest amount of heavy metal contaminations.

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