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Global perspective of monitoring metal ions in Ganges river- A case study

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ABSTRACT

Water quality response in a river has often been assessed using datasets that provide dramatic over – or underestimate of actual picture at huge financial investment particularly in developing countries like India. A study has been undertaken to present how the level of metal ions in river water is influenced by suspended solids in response to spatial and seasonal conditions in Hugli estuary (India) which supports world's largest Mangrove system – The Sundarbans. To better elucidate actual degree of metal pollution, contamination sources, role of metal absorbance on TSS, environmental behavior of metals and distribution pattern over the stations, seasons, tides and depths; statistical analysis are employed to intensive datasets of Hugli estuary that discharges into the largest alluvial fan in the world. The enrichment factors of metal ions in TSS determine contamination level. Multivariate analysis identified anthropogenic and natural activities responsible for suspended metal contaminations in this tidal dominated river. Enrichment factor revealed level of contamination of Ni, Cr, Zn, Cu and Cd and their sources. Strong seasonal change, variable tidal energy level and irregular estuarine geometry in the study area played crucial role in governing the concentration of metals in TSS in water column. New database on suspended metal contamination will help to water quality management programme. Base on these findings existing monitoring programme can be refined.

Key words: river monitoring; Metal pollution; Suspended solids; multivariate analysis; monitoring practice.

INTRODUCTION

The estuary is a complex and dynamic environment. This complex environment suffers from intense anthropogenic perturbation and has been acting as regulators of contaminant inputs to the coastal areas [1]. Ongoing anthropogenic activities altered the environmental quality of aquatic system by accumulating large amounts of potentially hazardous contaminants [2] in the suspended solids. Among the various pollutants, metals are of particular concern due to their environmental persistence and biogeochemical recycling and ecological risks [3,4]. The estuary receives these metals both in dissolved and solid state through large volume of freshwater influx that transport agricultural runoff, storm water and wastewater. The relative distribution of these metals between the dissolved and particulate phases in the river depends on the nature and concentration of mineral and organic matter originating from the basin [5]. The metals in dissolved state are rapidly transferred to particulate state and ultimately get accumulated in bottom sediment by various processes such as adsorption onto mineral surfaces, absorption into organic matter, ions effects and salting out effects [6]. Eventual deposition of suspended sediment associated with metals on the bottom creates reservoir of metals in many estuaries [7]. The availability of Suspended solids (SS) in water column depends on influx of sediment during freshwater flow, tidal advection, seasonal winds, tidal energy associated with tidal cycle, depth etc [8]. Martin and Meyback [9] and Martin and Whitefield [10] have made the pioneer work on chemical composition of particulate matter. Viers et al [5] pointed out significant association of metals with SS and advocated the importance of quantitative and qualitative measurement of SS. Therefore total metal (dissolved and particulate) concentrations in water will obviously vary with the variation of the amount of suspended matter termed as TSS (0.45 μm) and thereby evaluation of spatial and temporal variation without relating them with the amount of TSS will mask actual variability of total metal ions in water. Despite investment of vast human and financial resources in different monitoring programs, this aspect is not always taken care off. Therefore, assessment of TSS metal composition is an emergent need to provide valuable information in understanding the status of metal pollution and their spatial and temporal variability in different rivers; role of absorbance of metal ions on TSS and their physical and chemical behavior in estuarine system; and transportation of metals to sea.

2.0 Study area

The study includes 240-km-long tidal stretch of the river Hooghly in West Bengal between the mouth of Bay of Bengal and confluence of Churni River (Figure. 1). Thirteen sampling sites were selected (Figure. 1) along the study stretch. The sampling locations selected in this study stretch are named as Sagar(G1), Auckland(G2), Mud Point(G3), Diamond Harbour(G4), Raichak(G5), Falta(G6), Uluberia(G7), Poojali(G8), Garden Reach(G9), Dakhineswar(G10), Palta(G11), Triveni(G12) and Churni(G13). The station G1 is located at the mouth of Bay of Bengal with maximum tidal influence and G13 at the extreme upstream with negligible tidal influence. All 13 stations are categorized into three groups based on sea water intrusion and tidal influence: I) G1-G5; ii) G6-G11; iii) G12-G13. The first group is located in the lower stretch which depicts sea water intrusion and maximum tidal influence; the second group indicated moderate tidal influence with no sea water intrusion and third group showed negligible tidal influence. The station G5 was included in the first group because of sea water intrusion during dry season. The sea water intrusion was investigated by the level of chloride concentration at all stations over the months.

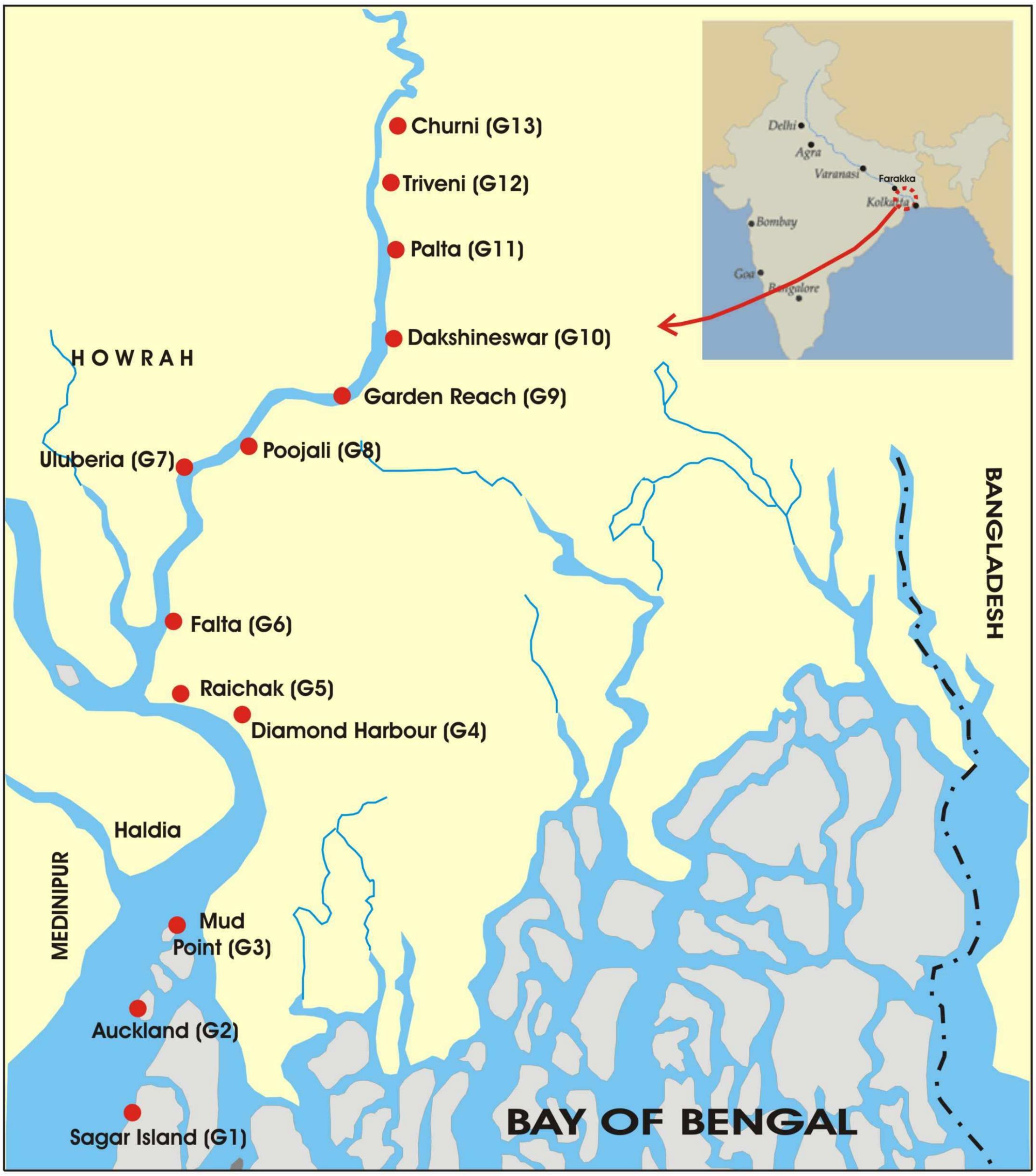
3.0 Characteristics of Ganges basin

The relevant information on geologic, geomorphic and hydrologic framework and evolution of the Ganga basin [11] are required for better understanding of the sources and behavior of metallic elements in particulate phase. The Ganga plain is one of the largest alluvial systems formed in response to the development of the Himalayas [12]. The Ganga basin has a good amount of smectite and a lower amount of kaolinite[13] derived from the low-temperature alteration of high-grade crystalline metasediments of the Himalayas by pedogenic processes within the Bengal basin[14,15].The heavy minerals in the ganga system are in the order of amphibole-garnet- epidote and dominated by unstable minerals[16,17]. The high-grade metamorphic terrains are the provenance of 40–46% of heavy minerals, followed by igneous terrains with 21–29% attribution [16, 17]. The Ganga is named as Hugli in West Bengal. The sediment load of Hugli River from natural weathering products and anthropogenic sources is estimated to be 520×10^6 T yr^{-1} [18-19]. Abbas and Subramanian [20] calculated that at Kolkata (former Calcutta), the Ganga annually supplies 411×10^6 T (i.e., 328×10^6 T Sediment $+83\times10^6$ T solute load) of total load to the Hugli estuary.

The hydrodynamic study focused that by discharge (15646 $m^3\ s^{-1}$) Ganga is the fifth largest river in the World [18]. The Ganga enters the basin from the northwest after draining Himalayas and most of north India for about 2500 km. The river after bifurcation below Farakka, flow southwards down the deltaic plain of West Bengal as the river Hugli and then empties into Bay of Bengal. The hydraulic character of the Ganga suddenly changes on entry into the tidal zone of the gangetic delta. The tidal stretch of river Hugli is up to Triveni from the Sagar islands. The tidal influence varies depending on upland flow with maximum amplitude of 5.5 m. The Hugli estuary is a well mixed type and vertically homogenous throughout the year except with slight stratification for a short period during south west monsoon (June – September) due to fresh water discharge [21]. Discharges from Farraka Barrage are 2975 ± 1144 m^3S^{-1} during monsoon with highest value (4000 m^3S^{-1}) during September, 1000 ± 81.6 m^3S^{-1} during pre-monsoon with minimum value (900 m^3S^{-1}) during May; and 1875 ± 985.5 m^3S^{-1} during post-monsoon [21]. Surface runoff (Km^3 $month^{-1}$) was reported to be 0.88, 4.02, 18.7, 8.47, 20.47 and 1.93 during May, June, July, August, September and October respectively [22]. The large tidal variation, irregular estuarine geometry, the presence of island and presence of navigation channel separated by shallow zone make the flow quite complicated.

In this soil, the values of total carbon (TC) were reported to be 8.2 ± 2.8 mg g^{-1} and bears good correlation with grain size of the sediments[23] . Sarin et al. [12] reported dominance of cation load (Na, Ca) in Ganga sediments. The river waters in the basin are circum-neutral to slightly alkaline [24,11], indicating chemical evolution associated with mineral weathering. The chemistry suggests dominance of carbonate dissolution, with some input of calcic plagioclase and pyroxene weathering [24].

Figure - 1: Study Stretch of River Ganga



MATERIALS AND METHODS

4.1 Sampling and Analysis

The water sampling strategy was designed to cover near surface (below 20 cm from surface) and deepest water (above 0.5m from the bed) of the water column during lowest low tide and highest high tide for the duration of two seasons. Meena M.V., a marine vessel equipped with relevant equipment/instruments, was put in use for collecting the samples and their pre-treatment. The acids used in any purpose were of high purity (suprapure, Merck, Germany). All materials coming in contact with the samples were acid washed. Water samples were collected by Niskin sampler and transferred directly into sample bottles. The metallic composition of TSS was determined by filtering through acid cleaned 0.45 μm cellulose nitrate membrane On Board immediately after collection to separate the solid matter. The sampled volume varied from 200 ml to 1000 ml depending on concentrations of suspended solids. The suspended solids collected in cellulose-membrane filters in duplicate for each sample were taken in two 50-ml vials covered with plastic polypack. Parallel series of filter blanks using ultra pure water (MilliQ®) were also taken systematically in the field to quash contamination due to filter quality and/or errors in the sampling protocol.

In the laboratory, all the elements except Hg and As were measured by AAS after dissolution in HNO_3-HF-$HClO_4$ (Merck suprapure). For measurement of Hg and As sample were digested with sodium chloride and a mixture og nitric acid and perchloric acid. The supernatant was taken in a precleaned plastic container. Cu, Mn, Zn, Fe, Ni, Cr, Pb were measured by Flame AAS; Al by nitrous oxide flame and Hg and As by AAS attached with vapor generation assembly. Parallel series of filtration was carried out for measurement of TSS. For TSS, approximately 100 ml samples were collected in 100-ml polyethylene bottle and filtration was done by transferring the whole aliquot in filtration assembly. The particulate adhered to the wall of the container were collected in filtration assembly by rinsing with distilled water. The volume of sample taken was measured by filling with distilled water up to the mark already put on the container in the field and recorded the volume for calculation. Salinity was determined by Mohr-Knudsen titration and standard sea water of chlorinity (19.374) obtained from National Institute of Oceanography (NIO), Goa, India was used for standardization.

4.2 Quality assurance protocol

For TSS sampling, care has been taken in site selection for sample consistency associated with uniform flow regime and a sediment transportation environment. The sampling plan included a duplicate sample at each sampling event for all analyses to ensure the homogeneity of the samples and rinse blank using decontaminated field equipment. The analytical results of the samples collected in duplicate at each sampling point ensure negligible differences except Cd(13%), Hg(13%) and Ni(10%). Results confirmed adequate precision in results and negligible cross-contamination.

The standards traceable to NIST obtained from Merck, Germany were used to calibrate AAS (Varian, Spectr-20). In addition to the standard, SRM obtained from National Physical Laboratory, India was used to cross check the calibration standard. The difference was quite negligible (<0.2%). The amount of TSS collected from all sampling sites is maintained to produce signal of AAS lying within calibration range. The method detection limit was estimated in accordance with the standard methods [25]. Recalibration check was performed at regular interval. During calibration milli-Q water fortified with acid was measured as blank. All the blank values were close to zero. Inter-laboratory comparison was carried out among the laboratories accredited by NABL and recognized by MOEF, India to have better understanding of the possible dispersion. Dispersion among the values of all parameters did not exceed 7 percent except Hg and Cd. To test the accuracy of analysis, the certified reference material (MBSS) of comparable matrix prepared by Akademie der Wissenschafen der DDR, Institut fur Meereskunde and certified by analyzing in 42 laboratories in 18 states. There is fairly good agreement between reference values and the concentration of metal ions obtained in this study. This procedure ensures an analytical precision better than ±0.5 of the analyzed CRM.

The measurement uncertainties (MU) of all the metals were estimated considering all relevant sources of uncertainty based on 10 replicates of CRM(MBBS) in accordance with guide to the expression of uncertainty in measurement [26]. The estimated values of MU($C_{sample} \pm UC_{sample}$) were 8.4± 0.3 Pb µg Pb g^{-1}, 330± 8 µg Mn g^{-1}, 1.4± 0.2 µg Cd g^{-1}, 104± 4 µg Zn g^{-1} , 2.30± 0.34 µg Hg g^{-1} , 24000± 84µg Fe g^{-1}, 31400± 75, 5µg Al g^{-1}, 14.0± 0.7µg Ni g^{-1}, 22.1± 0.8 µg Cu g^{-1}, 1.4 ±0.1 µg As g^{-1}, 24.5± 1.7 µg Cr g^{-1}, 21.0± .7 µg Co g^{-1}, 340 ± 5 mg TSS l^{-1}.

4.3 Statistical technique

For statistical interpretation of data, including , mean, coefficient of variation, correlation coefficients, analysis of variance(ANOVA), analysis of means(ANOM), cluster analysis (CA) and factor analysis (FA) were performed. Factor analysis was performed by evaluation of principal components applying l varimax rotation and calculating the eigen factors higher than 1 [27] to evaluate environmental behavior of the measured metal ions and TSS. A probability of 0.05 or less was considered statistically significant.

RESULTS AND DISCUSSION

5.1 Distribution of Temperature, pH, DO and salinity

These parameters play important role in partitioning of metal ions between solid phase and liquid phase of water. The distribution pattern of these parameters over time and space are presented for understanding their influence on TSS metal concentrations. Maximum and minimum temperature of water were 32.3 ± 1.1° C and 21.0 ± 1.6° C during June and February respectively. Salinity of the coastal water at G1 decreased from 27.8 psu during May to 5.4 psu freshets (September); surface water remained un-saturated with respect to dissolved oxygen throughout the year (88.8 ± 6.0%) at G1 [28]. Vertical gradient in pH is almost negligible. DO in the surface and bottom water did not vary much during winter (4.5 to 5.1 mg L^{-1}) and during summer(5.1 – 5.8 mg L^{-1}) with small changes during post monsoon(5.0 to 6.2 mg L^{-1}) [22]. In this study vertical distribution of pH and DO clearly demonstrated no anoxic zone in the bottom water; thereby suggesting well mixed condition. The maximum depth of water column among the stations varied between 6.7 m (at G11) and 15 m (at G1) with average depth of water column 6 m. In this study, horizontal and vertical salinity measured during lowest low tide was found below 0.02 psu between G13 and G6 during wet and dry season. During wet season, salinity did not exceed 0.05 psu at G4 and during dry season salinity intrusion was observed up to G5. The water is more or less turbid and secchi disc transparency varied between 19 cm at G12 and 121 cm at G1 in the study stretch [28]. In the entire region, maximum turbidity was observed at G1.The prevailing concentrations of these parameters indicates conducive environment of the metal ions, in general, to be associated with suspended solids.

5.2 Distribution of particulate metal ions and TSS

Average concentrations and coefficients of variation (CV) of TSS measured from 13 sampling sites both at near surface and at deepest water during dry season and wet season are shown in Table-1 to capture the spatial variability of TSS. The surface runoff from the Ganga basin ultimately reaches to the river and accelerates production of TSS in situ within the fluvial environment as reported in other rivers [29-30]. The average values of TSS (Table-1) in near surface water (460 mgL^{-1} and 334 mgL^{-1}) are remarkably low compared to the values in deepest water (1010 mgL^{-1} and 975 mgL^{-1}) during both seasons. As fine sediments are winnowed from the beds, TSS concentrations are progressively increased with the increase of depth. CVs of TSS concentrations (Table-1) both in near surface (67% and 63%) and in deepest water (61% and 63%) during both the seasons indicate wide variations of TSS concentrations among the 13 sampling sites. Since the sampling sites are selected to be at different distances from the G1(Close to sea), each of them experiences different tidal energy. High tidal energy accelerates the resuspension of TSS and low tidal energy tends to encourage deposition of solids on the bed. Spatial variability of TSS is also influenced by transportation of suspended solids to main channel (sampling point) from shallow water due to tidal advection during spring tides. It may be inferred that tidal energy, upland flow, seasonal winds, irregular estuarine geometry are the key factors influencing spatial variability of TSS. In response to spatial condition it may be inferred that variability of metal ions is controlled by the amount of TSS. This aspect must be taken care off while reporting metal contamination in water.

5.3 Relation between particulate metal ions and TSS

Spatial variability of all the metal ions (Table-1) in particulate phase of water is investigated with the help of CV. CVs of all metal ion concentrations exceed 50 percent and largely identical to variability of TSS concentrations. The explanation is that the sediment enriched with minerals facilitates adsorption of metals on suspended solids in the fluvial environment and thereby major fraction (more than 90%) of total metal concentrations is associated with TSS as found elsewhere [5]. Therefore the factors responsible for variation of TSS concentrations influence the variation of particulate metal ion concentration in water. For better understanding of the relation between TSS and particulate metal ions in water, Pearson's correlation analysis at significance level of $p<0.005$ is employed. The correlation coefficients (Table-1) clearly reveal significant positive correlation of all the metals ions with TSS. To elucidate further the influence of TSS on particulate metal ion concentrations in water, the factor analysis was performed to represent degree of association of each variable. The factor-1 explains 91 percent of the total variance in datasets of dry season and wet season. Factor-1 portrays strong association of all metal ions among each other as well as between each metal and TSS. This association authenticates that TSS is an accurate surrogate for metal contamination in Hugli estuary.

5.4 Understanding of critical uncertainty in reporting total metal ions in water

In this context, it may be mentioned that reporting of high, moderate or low values of total metal ion concentrations in water and their spatial and temporal variability would not be realistic if total metal ion is not related with the amount of TSS. For example, G1 (close to Bay of Bengal) has relatively large TSS and therefore relatively high metal ions in particulate phase of water and G13 (relatively polluted stretch) has relatively low values of TSS concentrations and thereby relatively low concentrations of metal ions in particulate phase of water. Difference in total metal ion concentrations between G1 and G13 is mainly due to difference in TSS concentrations (based on raw dataset not shown here). Therefore, uncertainty in total metal ion concentrations in water always prevails if we investigate spatial variability without relating with the amount of TSS. This uncertainty in reporting total metal concentration must be addressed in the monitoring programme to capture actual spatial and temporal variability of metal ion in water. Though other factors such as pH, redox condition, DO, salinity play important role in solid-liquid partitioning of metal ions but significance level of correlation between TSS and metal ions in particulate phase needs thorough investigation of metallic composition of TSS as advocated by researchers [5,31,8].

5.5 Spatial and temporal variation of metal ions in TSS

In the light of the above discussion an emergent need is to assess the metallic composition of TSS in near surface and in deepest water of river of 13 sampling sites during two seasons. All the datasets are used to compute metal ion concentration per gram of TSS and expressed as μg g^{-1}. These datasets are statistically processed to estimate mean, coefficient of variation (CV), skewness and kurtosis. These statistical parameters are shown in Table-2. Average values of

Table-1. Statistical parameters of metal ions in particulate phase of water

	Wet Season			Dry Season		
	Mean[4]	CV[3] (%)	r-value (TSS)	Mean[4]	CV[3] (%)	r-value (TSS)
Pb-S[1]	10	50	0.93	8	69	0.94
Pb-B[2]	24	51	0.91	24	71	0.92
Ni-S[1]	27	71	0.97	23	75	0.95
Ni-B[2]	54	56	0.93	63	65	0.92
Cu-S[1]	17	74	0.95	13	60	0.96
Cu-B[2]	34	57	0.94	35	69	0.97
Mn-S[1]	324	64	0.98	265	68	0.95
Mn-B[2]	713	56	0.97	701	63	0.92
Zn-S[1]	58	104	0.93	43	74	0.95
Zn-B[2]	138	69	0.91	134	74	0.95
Co-S[1]	8	83	0.96	6	65	0.93
Co-B[2]	16	56	0.94	17	72	0.95
Cd-S[1]	0.06	75	0.98	0.05	66	0.92
Cd-B[2]	0.13	51	0.95	0.11	71	0.98
Cr-S[1]	33	64	0.96	23	60	0.96
Cr-B[2]	69	45	0.93	62	71	0.94
Hg-S[1]	0.10	64	0.98	0.08	61	0.92
Hg-B[2]	0.24	60	0.99	0.21	73	0.92
As-S[1]	1.5	69	0.94	1.0	61	0.94
As-B[2]	3.1	55	0.92	2.4	70	0.95
Fe-S[1]	20454	45	0.95	12325	57	0.93
Fe-B[2]	38765	46	0.96	32836	71	0.96
Al-S[1]	32930.94	46	1	19870	60	0.9
Al-B[2]	63574.6	47	1	51530	72	0.98
TSS-S[1]	460	67	1	334	63	1
TSS-B[2]	1010	61	1	975	79	1

[1]Surface; [2]Bottom; [3]Coefficient Variation; [4]Metal concentration are expressed as μg L^{-1} and TSS as mg L^{-1}

TSS metal concentrations and their CVs reveal that TSS metal ion concentrations in near surface water are close to the concentrations in deepest water Variation of TSS metal ion concentrations is also reduced over 13 sampling sites.

Now distribution pattern of TSS metal ion concentrations is investigated by different statistical parameters. The closeness between mean and median values (Table-2) indicates normal distribution during both seasons. In both seasons, skewness values of TSS metal ion concentrations in near surface and in deepest water are less than 0.5 with few exceptions; thereby distribution of metal ions is symmetric. Kurtosis values of all metal ions are less than 3 indicating platy-kurtic distributions and thereby central peaks of all the metal ions are lower and broader. CVs varied between 13% and 40% clearly suggest spatial variability of TSS metal ion concentrations over 13 sites. Therefore, trend (inclined/declined) of these metal ions was investigated by Mann-Kendall test. This test (test results are not shown) indicates no systematic trend (inclined/declined) over the sites. Therefore spatial variability appears to be of random.

Table-2. Statistical parameters of metal ions in TSS

	Wet Season							**Dry Season**						
	Mean (μg g^{-1})	Median (μg g^{-1})	Min (μg g^{-1})	Max (μg g^{-1})	CV[3] (%)	Skew [4]	Kurt[5]	Mean (μg g^{-1})	Median (μg g^{-1})	Min (μg g^{-1})	Max (μg g^{-1})	CV[3] (%)	Skew[4]	Kurt[5]
Pb-S[1]	25	25	15	33	21	-0.2	-0.9	26	26	18	37	20	0.1	-0.8
Pb-B[2]	26	26	16	37	27	0	-1.5	26	28	17	34	22	-0.3	-1.5
Ni-S[1]	58	58	32	89	19	0.3	2.2	66	67	43	88	21	0.1	-1.2
Ni-B[2]	57	57	37	86	18	0.4	1.9	72	76	42	97	21	-0.4	-1
Cu-S[1]	36	38	20	46	22	-0.8	-0.2	40	39	32	52	13	0.4	0
Cu-B[2]	35	35	25	51	18	0.3	0	37	37	28	47	14	0	-1
Mn-S[1]	717	736	450	898	18	-0.7	-0.4	868	878	528	1260	22	-0.1	-0.4
Mn-B[2]	735	761	477	866	13	-0.9	0.7	807	774	512	1189	24	0.4	-0.7
Zn-S[1]	115	95	61	201	40	0.8	-0.8	124	128	88	171	21	0.2	-1.1
Zn-B[2]	129	119	80	193	28	0.4	-1.2	141	144	96	182	21	-0.1	-1.8
Co-S[1]	17	16	10	24	27	0	-1.4	17	17	9	25	26	0.2	-0.9
Co-B[2]	17	17	11	27	22	0.8	1.5	18	17	9	25	26	-0.2	-1
Cd-S[1]	0.14	0.14	0.10	0.17	15	0	-1.0	0..19	0.19	0.10	0.25	24	-0.2	-1.2
Cd-B[2]	0.14	0.14	0.09	0.20	19	0	0.1	0.16	0.16	0.11	0.24	22	1.0	0.3
Cr-S[1]	75	79	46	97	19	-0.8	0	73	69	57	111	20	1.4	1.5
Cr-B[2]	73	70	45	107	28	0.3	-1.2	67	66	47	96	20	0.1	-0.8
Hg-S[1]	0.23	0.23	0.14	0.26	12	-1.8	4.4	0.25	0.22	0.13	0.41	24	0.8	1.1
Hg-B[2]	0.24	0.24	0.20	0.26	7	-0.7	0.1	0..19	0.21	0.07	0.24	25	-0.9	-0.2
As-S[1]	3.4	3.5	1.98	4.97	23	0.2	0	4.26	4.01	3.25	6.05	19	0.7	-0.3
As-B[2]	3.2	3.32	1.97	4.25	21	-0.2	-1.3	2.66	2.54	0.22	5.32	34	0.3	4
Fe-S[1]	48998	52587	33242	66272	22	-0.2	-1.6	39079	39103	26301	48858	17	-0.3	-1.1
Fe-B[2]	41093	37252	23786	72711	32	1	0	36516	35039	26359	49010	20	0.3	-1.3
Al-S[1]	80800	90181	53754	103405	24	-0.3	-1.8	61906	64644	41688	80986	22	-0.2	-1.5
Al-B[2]	69361	64081	41162	118380	31	1	0	59749	56827	46145	79089	19	0.4	-1.4

[1]*Surface;* [2]*Bottom;* [3]*Coefficient Variation;* [4]*Skewness;* [5]*Kurtosis*

Now General Linear Model of Analysis of variance (ANOVA) was employed to evaluate significance of variation of metal ions in TSS due to sites, seasons, depths and tides. The output of ANOVA shown in Table-3 reveals that there is no variation of any metal ion due to tides. Therefore measured metal ions in TSS during lowest low tide and highest high tide do not exhibit any difference indicating similar character of TSS during the tidal cycle. Significant variation of Zn, Fe and Al are noted due to depths. This difference may be attributed to grain size sorting of suspended solid between near surface and deepest water due to variable tidal energy. In deepest water, coarser mineral grains are relatively concentrated due to removal of clay minerals. Fine particles associated with TSS increase concentrations of Zn, Fe and Al in TSS. Few metal ions such as Ni, Mn, Al and Fe depict significant variation due to seasons. Influx of sediment with minerals and other coarse detritus from the basin during wet season alters the chemical characteristics of TSS. During dry season, when influx of sediment is ceased, characteristics of TSS in the estuary undergo alteration due to primary productivity and physico-chemical processes. Significant variation of Pb, Cu, Zn, Cr, Fe and Al in near surface water due to locations indicates spatial variability of these metals. But no systematic changes (inclined/declined) of TSS metal ion concentrations were observed with the increasing distances from G1 to G13 as observed earlier by Mann-Kendall test.

Table-3. Output (p-value) of ANOM

Source	Pb	Ni	Cu	Mn	Zn	Co	Cd	Cr	Hg	As	Fe	Al
Season	0.51	0.00	0.13	**0.00**	0.31	0.22	0.08	0.47	0.07	0.21	**0.00**	**0.00**
Tide	0.88	0.16	0.93	0.63	0.70	0.60	0.35	0.13	0.12	0.37	0.34	0.78
Station	**0.01**	0.07	**0.02**	0.40	**0.00**	0.74	0.15	**0.00**	0.17	0.74	**0.00**	**0.00**
Depth	0.88	0.35	0.40	0.41	**0.00**	0.71	0.16	0.06	**0.09**	**0.08**	**0.00**	**0.03**

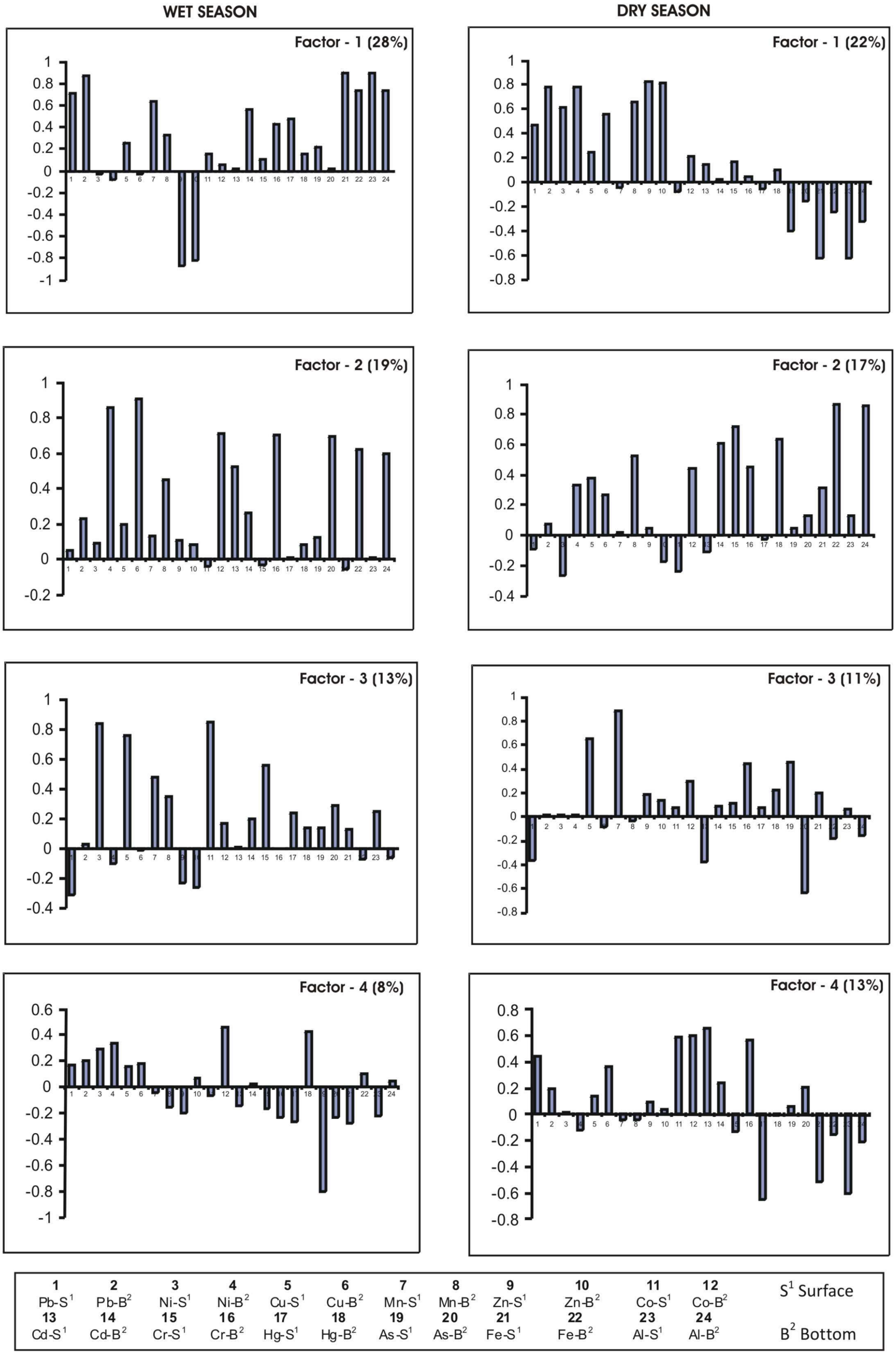
Considering these spatial variability, ANOM (Analysis of Mean) is applied to determine the deviation of the mean concentrations of Pb, Cu, Zn, Cr, Fe and Al at each site from the grand mean. The output of ANOM reveals negative deviation from the grand mean of Pb, Cu, Cd, Mn, Fe and Al at the stations in the lower stretch (G1 to G5) and positive deviation from the grand mean in the upper stretch (G6 to G13). Two distinct groups emerge from 13 stations with respect to above six metals in wet season. Mean concentration of Zn during the wet season is found just opposite to the mean concentration of other metals. It indicated that basin input of Zn to river is relatively low during wet season. Therefore dilution of prevailing TSS due to sediment influx decreases Zn concentration in the upper stretch. During dry season no distinct group is observed and distribution pattern is random. A significant deviation from the grand mean is found in case of Pb (at G3), Cu (at G11), Ni (at G6 and G4), Zn (at G1 and G4), Cr(G9), Fe (G2 and G10) and Al (G2 and G10). The possible explanation is that the relatively high and variable energy level and transportation of TSS with pendulum movement at active tidal zone concentrate the coarser mineral grains and wash out clay minerals enriched with metals [32] at the lower stretch. During dry season, characteristics of TSS undergo spatial alteration due to shift of chemical composition of suspended matter due to primary productivity, precipitation, grain size fractionation etc.

5.6 Inter-metal relationship in TSS

The Pearson' analysis (Pearson-Product Moment Coefficient) was performed to investigate inter-metal relationship to assess their common characteristics (behavior, origin etc). at significance level of $p<0.005$ (table not shown). The correlation coefficients of Pb(r-0.67), Mn(r-0.51), Fe(r-0.57) and Al(r-0.64) depicted good relation between near surface and deepest water during wet season and Zn (0.85 and 0.67) during both seasons. The high turbulence during wet season enables a complete physical mixing of TSS in entire water column due to high inland flow and tidal energy. Suspended solids distributed uniformly in the entire water column are enriched with Fe, Al, Mn and Pb. Interestingly, Zn depicted strong negative correlation with Fe and Al during both seasons. The explanation is that Zn may not be associated with transported sediment because of its different chemical phase. Strong positive interrelation among Co-Cu-Ni both in near surface and in deepest water indicates influence of anthropogenic sources. The strong positive correlation between Mn and Cu at bottom showed association of Cu with Mn-carbonate. The strong positive correlations of Fe and Al with Cu, Co and Cr at bottom TSS determine association of Cu, Co and Cr with Fe and Al. Therefore it may be inferred that Cu, Co and Cr in TSS at surface are effectively removed by adsorption on Fe/Al oxide in aerobic condition. During dry season, strong negative correlation of Pb with Fe and Al both at surface and bottom exhibits removal of clay minerals enriched with Fe and Al by transporting to sea.

Factor Analysis was conducted for metals ions in TSS in near surface water and in deepest water collected in two seasons. The varimax normalized method was used to rotate the loading matrix for better explanation of FA in relation with the behavior of all metal ions. Figure 2 depicted loadings for four factors during wet season that explained 68% of total variance. Factor-1 accounted for 28% of total variance is mainly characterized by strong positive loadings of Fe, Al and Pb and strong negative loading on Zn both in near surface and in deepest water. Factor-2 accounted 19% of the total variance and is characterized by strong positive loadings on Ni, Co, Cd and Cr and moderate positive loadings on Fe and Al at bottom. Pattern of loadings in Factor-1 and 2 clearly represents physical and chemical weathering of the soil enriched with Fe and Al. Chemical weathering becomes more intense at high surface run-off rates with a high proportion of soluble rock components being leached from the rock and thereby concentrating Al and Fe in TSS. TSS of this river consists mainly of quartz, feldspar and

Figure-2 : Factor loadings of Metal ions in TSS during wet and dry seasons



illite as main minerals [13] with dominance of mica as clay minerals [32]. Clay minerals exhibit selective affinity for different metals. Pb is preferentially adsorbed over other metals. Pb, originating from natural and anthropogenic sources adsorbed on the surface of the minerals as oxyhydroxide coatings both at surface and bottom. Ni, Co, Cd and Cr are moderately associated with Fe and Al in deepest water. The dissimilar and independent behavior of Zn among all the metals exhibits negligible basin input to river because abundant clay minerals have poor affinity to Zn. The clay mineral, which is dominant in TSS exhibit poor affinity for Zn ions. Fresh input of suspended solids dilutes permanent TSS enriched with Zn and reduces the level of Zn in TSS during wet season. Hochella and White [33] advocated that most important carriers for metals in particulate form are clay minerals, Fe, Al and Mn oxides / hydroxides as well as particulate organic matter. Continuous basin input during wet season increases the concentration of Fe, Al, Clay, Organic matter and lowers the oxygen saturation (< 4 mg L^{-1}) in near surface water. This condition augments degree of association of different metals in TSS with Al and Fe. Factor-3 demonstrated metal contamination from natural and anthropogenic sources because Ni, Co, Cu and Cr are associated with Mn. These metals derived from adjacent landmass are concentrated in oxides and other non-aluminous silicate minerals. In this case, Mn oxides in the TSS partly control the level of Ni, Co, Cu and Cr. Factor loading on As in Factor-4 indicates independent behavior of As in surface water during wet season. It is pertinent to mention that use of arsenic contaminated ground water mainly for agricultural and domestic purposes in the Ganga basin enhances As level in surface water. This finding is the clear evidence of adverse impact of arsenic contaminated groundwater in the adjacent landmass on water quality of river Hugli.

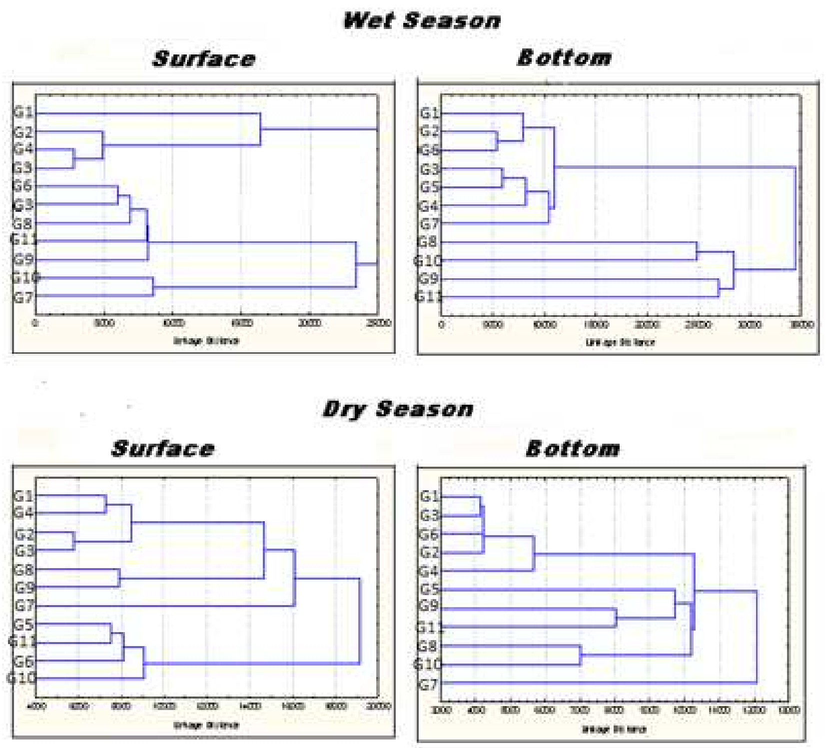
During the dry season, four significant factors accounting for 63% of the total variance are distinguished for the analyzed data (Figure-2). Factor-1 accounted for 22% of the total variance is mainly characterized by strong positive loadings on Zn both at surface and bottom; and on Pb at bottom, moderate positive loading of Mn and Cu at bottom , moderate positive loadings on Fe and Al at surface. Factor 1 clearly represents the absence of basin input as mean concentrations of Fe and Al are relatively low (Table-1). Input of Pb, Fe and Al associated with clay minerals to the river during wet season are removed during dry season by physical, chemical and biological processes. Active aeration of water during transport of suspended solids in tidal energetic zone from the estuary to the outer shelf enhances it oxygen saturation (>5mg/l in deepest water) that invokes active oxidation and accelerates the formation of Mn oxy- hydroxides particles as reported in other rivers [34]. These particles are ultimately transported to sea. Also growth of these particles accelerated their settling rate on the bed. It is also possible that under oxic condition, organic bound Fe, Al and Pb can be oxidized and metal ions are released into water. In near surface water, presence of fine particles is responsible for moderate association of Fe and Al with Zn. Moderate to strong association among Zn, Pb, Mn and Cu in deepest water indicates formation of Mn-oxides/hydroxides that adsorbs Pb, Zn and Cu.Factor-2 accounted for 17% of the total variance is characterized by strong positive loadings on Ni, Co, and Cr in deepest water suggesting dominance of anthropogenic contamination. Factor-3 exhibited 11% of total variance is characterized by moderate loadings on Cu, Mn, and As at surface. Factor-4 accounted 13% of total variance is characterized by moderate loading on Co both at surface and bottom. Factor-4 represents uniform distribution of Co at different depths. During dry season, the behavior of Hg was similar in both the season. The dissimilar behavior of metal ions in TSS during dry season indicates changes due to various physical, chemical and biological processes during transportation and retention of suspended matter for a long time in tidal energetic zone. The pattern of factor loadings shows good agreement with interrelation of particulate metal ions obtained by Pearson's analysis.

The above findings reveals that combined effect of the basin characteristics (relief, geology, climate, vegetation, size of the drainage area etc) and anthropogenic activities (urban development, promotion of industries, mining, agriculture, deforestation etc) govern the type (composition of metals) and quantity of TSS. The industrial solid wastes containing Pb, Ni, Co, Cd and Cr scattered over industrial area and road side during dry season reaches to the river through surface runoff during wet season. During transportation, the abundant organic matter, Fe and Al originating from basin accelerates the binding of these metals [35-37] with the formation of authigenic particles in the fluvial environmental [29,38]. The nature of interrelationship of metals indicated that discharge of wastewater form mega city - Kolkata is not the major cause of metal pollution in the lower stretch of Ganges though several researchers advocated these inferences [39].

5.7 Grouping of stations

The distribution pattern of TSS metal ions exhibits overall distinction between upper stretch and lower stretch of estuary as reflected by ANOM analysis. Now the level of salinity over the study stretch is determined to investigate the occurrence of marine TSS in study stretch. During wet season, salinity intrusion was observed up to G4 with highest occurrence at G1 (7.15 ppt). During dry season, salinity intrusion is noted up to G5 with highest occurrence at G1 (24.3 ppt). The salinity in the remaining stations does not exceed 0.02 ppt. Seasonal variation of salinity level is pronounced in lower stretch of this estuary. The hierarchical cluster analysis using the ward's method with Euclidian distances is applied for better understanding of similarity among the stations at surface and bottom for both seasons. The dendrograms (Figure-3) display three clusters of near surface TSS metal ions : i) G1-G2-G4-G6; ii) G3-G8-G11-G9-G10; iii) G5-G7 and four clusters of deepest water TSS metal ions: i) G1-G2-G6; ii) G3-G5-G4-G7; iii) G8-G10; and iv) G9 – G11 during wet season. Dendrograms (Figure-3) display 5 clusters of near surface TSS metal ions: i) G1-G4; ii) G2-G3; iii) G8-G9 iv) G7; and v) G5-G11-G6-G10, and five clusters of deepest TSS metal ions : i) G1-G3-G6-G2-G4; ii) G5; iii) G9-G11; iv) G8-G11; and v) G7 during dry season. During wet season, first cluster of near surface TSS metal ions covers the stations located in lower stretch except one i.e. G3. The remaining stations are covered in second and third clusters in random order. The clusters of TSS metal ions indicate that G1 to G7 are covered by first and second clusters. Remaining stations are covered by third and fourth clusters in random order. During dry season, the stations at lower stretch are placed in first two clusters with respect to near surface TSS metal ions but all these stations are placed in first cluster with respect to deepest TSS metal ions. The nature of the clusters indicated that G1 and G2 stations located in the saline zone in the first cluster have influence of marine TSS in both seasons. Therefore stations located in the lower stretch have been separated from the stations located in upper stretch. That separation cannot be strictly attributed to the influence of saline zone except G1 and G2. It may be inferred that high energy level removed the clay minerals enriched with the metals from estuarine zone to sea. This causes decrease of TSS metal ion concentrations. Therefore unique behavior of TSS metal ions in this tidal dominated estuary may be attributed to different energy level due to large tidal variation, irregular estuarine geometry, navigation channel separated by shallow zones, large influx of sediment during wet seasons and various chemical and biological processes.

Figure-3 :Dendrogram of 11 Stations using Single Linkage Euclidean Distance



5.8 Status of metallic composition of TSS in global perspective

The amount of suspended solids in the river is controlled by strong seasonal changes in accordance with annual hydrological cycle [40]. The maximum input was in wet season (July - Sept). The lower stretch is subject to rapid change by incoming tides that created turbulence resulting high suspension load in the water column. The variable tidal energy has made significant difference of TSS concentrations between near surface and deepest water over entire study stretch except G12 and G13. The metal ions in TSS at two different seasons were compared with the metal profiles in the upper continental crust proposed by Taylor and Mc Lennen [41] and by other researchers. The comparative statement are presented in Table-4 .The average concentrations of the metal ions are lower than that of upper crust. The overall metallic composition of TSS did not match exactly with any other composition reported by the researchers but more or less close to the average values proposed by Savenko[42] and Stummeyer et al [30]. The overall metal content in TSS is relatively low compared to other world rivers. But, this finding cannot ensure that input of metals from natural and anthropogenic sources to river is not cause of concern because the inherent and unique environmental processes going on in this tidal dominated estuarine system which discharges TSS metals to sea.

5.9 Enrichment factor

Apportionment of metal origin between anthropogenic and natural weathering is an essential part of geochemical studies. According to Nolting et al[43], normalizing the metal content relative to Al is a powerful tool to determine enrichment factors (EFs). EF is calculated by using the following formula to focus the magnitude of metal contamination in this study stretch:

EF = [X] / [Al] Sample / [X] / [Al] upper crust

Table-4. Average metal ions in TSS of Present Study and of Other World Rivers and Upper Crust

Element	South America[1]	North America[1]	Asia[1]	Russia[1]	Central Africa[1]	Europe[1]	Viers		Upper Crust[2]	M& M[3]	Sav[4]	Stummeyer[5]		Present Study			
														Wet Season		Dry Season	
							AV[6]	SD[7]				AV[6]	SD[7]	AV[6]	SD[7]	AV[6]	SD[7]
Al	91000	83000	71000	95000	113000	61000	87200	6010	80400	94000	86300	101000	5	67267	18498	56136	11508
As	-	-	-	-	-	-	36.3	27	-	5	14	15	1.5	3.32	0.73	3.46	1.17
Cd	-	-	-	-	-	-	1.55	4.15	0.098	-	0.5	-	-	0.14	0.02	0.17	0.04
Co	15	15	30	21	23	16	22.5	19.6	10	20	19	21	1	16.7	4.1	17.3	4.4
Cr	79	115	260	117	130	164	130	155	35	100	85	120	3	75.3	18.2	69.9	14.4
Cu	59	34	145	53	53	172	75.9	135	25	100	45			35.5	7	38.4	5.4
Fe	52900	45000	78800	46000	75000	43000	58100	4810	35000	48000	50300	56000	10	41423	11184	35268	6524
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	0.23	0.02	0.22	0.06
Mn	700	1430	5767	970	1478	1884	1679	5011	600	1050	1150	940	25	726	112	838	192
Ni	46	50	123	68	78	66	74.5	100	20	90	50	69	4	57.2	10.6	68.5	14.6
Pb	76	22	35	64	46	71	61.1	91.2	20	100	25	30	3	25.4	6.1	26.1	5.5
Zn	184	137	300	145	130	346	208	237	71	250	130	120	10	122	41	132	29

[1] Viers et al (2009); [2] Proposed by Taylor and McLennan (1985) ; [3] Martin & Maybeck (1979); [4] Savenko (2006); [5] Summeyer et al (2002)
[6] Average; [7] Standrad Deviation; - not available

Table-5. Enrichment Factor of metal ions in TSS of the Present Study and of Other World Rivers

Element	Present Study EF				M& M[1]	Sav[2]	Viers[3]	South America[3]	North America[3]	Asia[3]	Russia[3]	Central Africa[3]	Europe
	Wet Season		Dry Season										
	AV[4]	SD[5]	AV[4]	SD[5]									
Pb	1.4	0.15	1.4	0.12	[6] NA	[6] NA	[6] NA	3.64	1.16	2.15	2.94	1.77	5.07
Cu	1.5	0.19	2	0.17	3.71	1.82	3.04	2.26	1.43	7.12	1.95	1.64	9.84
Mn	1.3	0.12	1.8	0.26	1.62	1.94	2.80	1.12	2.50	11.80	1.48	1.90	4.49
Ni	3.1	0.96	4.3	1.58	4.17	2.53	3.73	2.20	2.63	7.55	3.12	3.01	4.72
Cd	1.5	0.25	2.3	0.60	0.00	5.16	15.82	0.00	0.00	0.00	0.00	0.00	0.00
Cr	2.3	0.83	2.6	0.68	2.65	2.45	3.71	2.16	3.45	9.12	3.07	2.87	6.70
Co	1.8	0.55	2.3	0.69	1.86	1.92	2.25	1.44	1.58	3.68	1.93	1.77	2.29
Fe	1.4	0.35	1.4	0.19	1.17	1.34	1.53	1.34	1.25	2.55	1.11	1.52	1.62
Zn	2	0.93	2.5	0.70	3.27	1.85	2.93	1.03	0.33	0.61	0.83	0.50	1.43

[1] Martin & Maybeck (1979); [2] Savenko (2006); [3] Viers et al (2009); [4] Average; [5] Standard deviation; [6] Not available

[X] Represents the concentration of the metals and [Al] the Al concentration. In this estimation, Al has been assumed to be solely of terrigenous origin because the geological basement of this basin is formed due to assemblage of heavy minerals such as amphibole, epidote, smectite etc. those contains Al, Fe, Mn, Ca, Mg etc. Initially EFs were calculated separately for surface and bottom of both seasons but no significant differences were observed between near surface and deepest water. Therefore, EFs were further calculated for both the season merging all the values of near surface and deepest water and presented along with EFs reported for other world rivers (Table-5). The average values of EFs of Pb, Cu, Mn, Ni, Cd, Cr, Co, Fe and Zn during the dry season are shown in Table-5. The EFs of all the metals are ranked by decreasing order of magnitude - Ni > Cr> Zn> Ni> Co> Cu & Cd> Pb & Fe > Mn. Among all the metals, Ni, Cr and Zn exceeded 2 during wet season and Cu, Ni, Cd, Cr and Zn exceeded 2 unit during dry season. EFs of these elements are relatively low compared to the EFs reported for other world rivers. The level of EFs during dry season is relatively high. The metals with a EF values greater than unity reveal contamination of suspended solids. The relatively high EF values for Cu, Ni, Co, Cr and Zn suggest the contamination of TSS with metals derived from various activities of atmospheric inputs, mines, thermal power plants, vehicle, electroplating industries, metallurgical industries, municipal drains etc. Due to transportation of metals to sea with the clay and accumulation of metals in river sediment in variable energetic estuary the EFs do not reach to alarming level. During dry season, most interesting observation is that relatively high enrichment of Fe with respect to Al indicates the presence of primary ferromagnesian silicates or Fe-rich secondary phases as reported in other river [44] . However intense run off accelerates the chemical weathering of soluble rock component and incorporate these metal ions in particulate phase. These observations exhibit good agreement with the observations of coefficient and factor analysis. EF clearly revealed that major source of metal contamination in this estuary is large influx of sediment due to natural activities and moderate source of anthropogenic sources over the years.

CONCLUSION

The discussion made above established the importance of evaluating metallic composition of TSS to address the environmental issues of the estuarine system related to metal contamination. The reporting of total metal concentrations appears to be misleading for formulation of water quality management if interpretation of datasets is not done in relation with amount of TSS. Re-suspension of sediment due to high energy at tidal dominated estuary may provide dramatic over- or under estimate of metal contamination in river depending on the prevailing TSS concentrations. The study of metallic composition of TSS clearly reveals that the metal contamination is mainly governed by natural and anthropogenic activities. Normalization of metal ions in TSS to Al and their ratios with crustal average demonstrate higher EF for Cu, Cd, Ni, Cr and Zn indicating contamination of suspended solids by these metals from anthropogenic activities related to poor land uses for urbanization and industrialization. Environmental behavior of Fe and Al signals natural weathering in the basin. Level of metal contamination clearly reflects upset of the natural terrestrial system leading to severe soil erosion mainly due to anthropogenic activities in the basin. The inherent physical and chemical conditions accelerate transportation of metals to sea. These actions restrict increase of metal ions in water column despite continuous metal input to the estuary. It may be inferred that metal pollution causes irreparable loss of coastal ecosystem. It is pertinent to mention that implementation of various monitoring programmes is unable to address the complex dynamic environmental behavior of metal ions in estuarine ecosystem. This study clearly reveals the necessity to redesign the monitoring network in India. The enforcement agencies generally put emphasis on controlling the metal contamination at the source stipulating certain environmental norms. The environmental behavior of metal ions associated with TSS clearly indicates inadequacy of preventive measures taken by enforcement agencies. Overall management of industrial solid waste (Particularly foundries, electroplating, galvanizing industries, Pb-smelting unit, sponge-iron, mines, steel industry etc) dumped on the different areas of the basin and implementation of eco-friendly urban development to control erosion of soil will play key role to control metal contamination of river Ganges. The monitoring of TSS and its composition would be less costly and more easily measured surrogate to assess metal contamination in river and help to answer fundamental questions confronting enforcement agencies**.**

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