

Geochemical Characterization and Mineralogical Assemblage of Burhi-Dihing and Noa-Dihing—The Largest South Bank Tributaries of the Brahmaputra River

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Abstract: Mineralogical studies are valuable in understanding past weathering regimes induced by changing climatic conditions. Information about the bedrock lithology, weathering regimes, erosion and sedimentation rates are fundamental issues for better understanding of the river catchment behaviours. In this context, therefore, major ions, trace metals and clay mineral compositions of the sediment and water of Noa-Dihing and Burhi-Dihing rivers, the southbank tributaries of the Brahmaputra river, have been examined. Chemical index of alteration (CIA) values of both Noa-Dihing and Burhi-Dihing rivers suggests the prevalence of moderate chemical weathering events and formation of minerals such as muscovite, illite and smectite in the river catchment. Metal distribution in both rivers shows highly toxic metals, comprised of 32% of total mineral composition, and are less abundant with respect to moderately toxic metals (37%) except Zr, which comprises 37% and 32% respectively of the total mineral compositions. Comparison of sediment chemistry with composition of source rocks and average Upper Continental Crust (UCC) suggests higher depletion of CaO, Na₂O, P₂O₅, Al₂O₃, SiO₂, MgO and MnO signifying the dominance of mafic mineral phases. Loss of these metal oxides from the bed rocks during weathering and/or less abundance of clay in bed sediments compared to that in UCC may also be attributed to depleted values of these minerals. This is further substantiated by grain size analysis i.e. more abundance of sandy silt as compared to clay minerals in the overbank and channel sediments of Noa-Dihing and Burhi-Dihing rivers. Chemical Index of Alteration (CIA) varies significantly from 64.49 to 81.21, indicating large spatial variability in the intensity of chemical weathering of upper Brahmaputra basin. Multivariate analysis suggests that natural weathering processes of alkaline earth metals can be associated with release of trace metals in a riverine system and releasing mechanism of transition metal and their oxides are same and that of alkali and alkaline earth metal are similar.

Key words: Geochemistry, mineralogy, Noa-Dihing, Burhi-Dihing, grain size analysis, X-ray diffraction, cluster analysis.

Introduction

Changes in mineralogy of mainstream river bed sediments are often related to sediment dilution or concentration effects from tributary sediment and to

chemical weathering during transport (Eberl, 2004). Large rivers are most significantly impacted by their tributary junctions due to its vital role in the chemical properties, productivity and species diversity of the main river channel (Adedokun et al., 2008; Kaiser et

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al., 2015; Rice et al., 2001). The tributary junctions with unique hydrologic, geomorphic and biological attributes are very important as network nodes for regulating material flows in watersheds. Heterogeneity of water, sediment and organism communities is higher at tributary junctions. The interface main stream/tributary plays a crucial role for control of river metabolism, pollution and self-purification processes and water source management (Todorova and Topalova, 2014). Thus study of sediment-surface water interaction of different tributaries will help in providing insights regarding hydrodynamics of flows and also about depositional conditions. Relation between sedimentary processes and textural responses is a powerful tool for interpreting such genesis of depositional environments. Overall, tributaries play significant role in controlling the mineralogy as well as nutrient concentration of a river.

The Brahmaputra river and its tributaries bring millions of tons of sediments every year during storm events from the Himalayas and the adjoining areas (Nepal and Shrestha, 2015; Goswami, 1985). River sediments in general and the Brahmaputra river sediment in particular are rich source of nutrients as well as minerals. Weathering largely depends on the geology of a region, topographic setting, climate and anthropogenic activity (Vuba et al., 2015). Burhi-Dihing and Noa-dihing travel through diverse geological setting and climate of Assam and Arunachal Pradesh; therefore it is interesting to investigate the major and trace element composition of river sediments.

The study was carried out with the following objectives: (a) comparative analysis of physico-chemical characteristics of Noa-Dihing and Burhi-Dihing rivers, (b) mineralogical investigation through application of WD-XRF advance analytical techniques, and (c) assessment of surface geology in enhancement of trace metal distribution in surface water, sediments of Burhi-Dihing and Noa-dihing river through application of statistical techniques.

Methodology

Study Area

The Burhi-Dihing river is the biggest south-bank tributary of the Brahmaputra river in the North Eastern Region of India. The Burhi-Dihing originates in the Patkai hills at an elevation of 2375 m. After flowing for about 80 km, it meets the plains and runs through the alluvium of Assam Valley for about another 300 km before joining the Brahmaputra (Sarma et al., 2007).

Within the Assam Valley region the river cuts through a very narrow low ridge comprising tertiary rocks. The Burhi-Dihing basin occupies an area of about 6000 km² and receives an annual rainfall varying from 2100 mm to 3880 mm. Burhi-Dihing is formed by combination of two rivers Namphuk and Magaton, both having their source in Tirap District of Arunachal Pradesh. The river runs almost east-west direction and has its confluence with Brahmaputra at Dihingmukh about 25 km south west of Dibrugarh. Burhi-Dihing river bank and channel sediment samples were collected from Ledo, Margherita, Naharkatiya and Moran. Noa-Dihing river is a south bank tributary of the Brahmaputra which is a part of Dihing river that originates at 2275 metres (7792 ft) above sea level from Eastern Himalaya, Patkai mountain range, Arunachal Pradesh and bifurcates near Miao in Changlang district. Noa-Dihing flows through the Changlang and Lohit districts from east-west through the entire north-eastern and northern stretch of the district and meets with Lohit river near Namsai before merging with mighty Brahmaputra. Noa-Dihing river overbank and channel sediment samples were collected from Vijoypur, Mahadevpur and Mengkeng Miri.

Surface Water Analysis

Surface water and sediment samples were collected from Burhi-Dihing and Noa-Dihing rivers during 2014, as shown in Figure 1. Noa-Dihing river samples ($n = 4$) are collected from Vijoypur, Mahadevpur and Mengkeng-Miri (2) and Burhi-Dihing river samples ($n = 4$) are collected from Ledo, Margherita, Naharkatiya and Moran. Surface water samples from eight sites were collected and filtered using 0.45 μ m Millipore and collected in polyethylene bottles of 500 ml (for cation and anion analysis) and 125 ml (for metal analysis). Before sampling, the bottles were thoroughly rinsed 2-3 times with the surface water. For metal analysis, samples were treated with concentrated HNO₃ to preserve it. EC, pH and TDS were measured on-site using a multi-parameter probe (HANNA HI9828). Na⁺, K⁺ and Ca²⁺ were analyzed using a flame-photometer (Systronics Flame photometer 128), while the anions SO₄²⁻, PO₄³⁻ and H₄SiO₄ were analyzed using a UV-spectrophotometer (Shimadzu, UV-1700). Analyses were performed using different standard solutions and methods prescribed in American Public Health Association (APHA) 2005 for individual analytes.

Concentration of HCO₃⁻ was analyzed using the titrimetric method. HCO₃⁻ was estimated by titrating 10 ml sample with 0.01N HCl (which is standardised

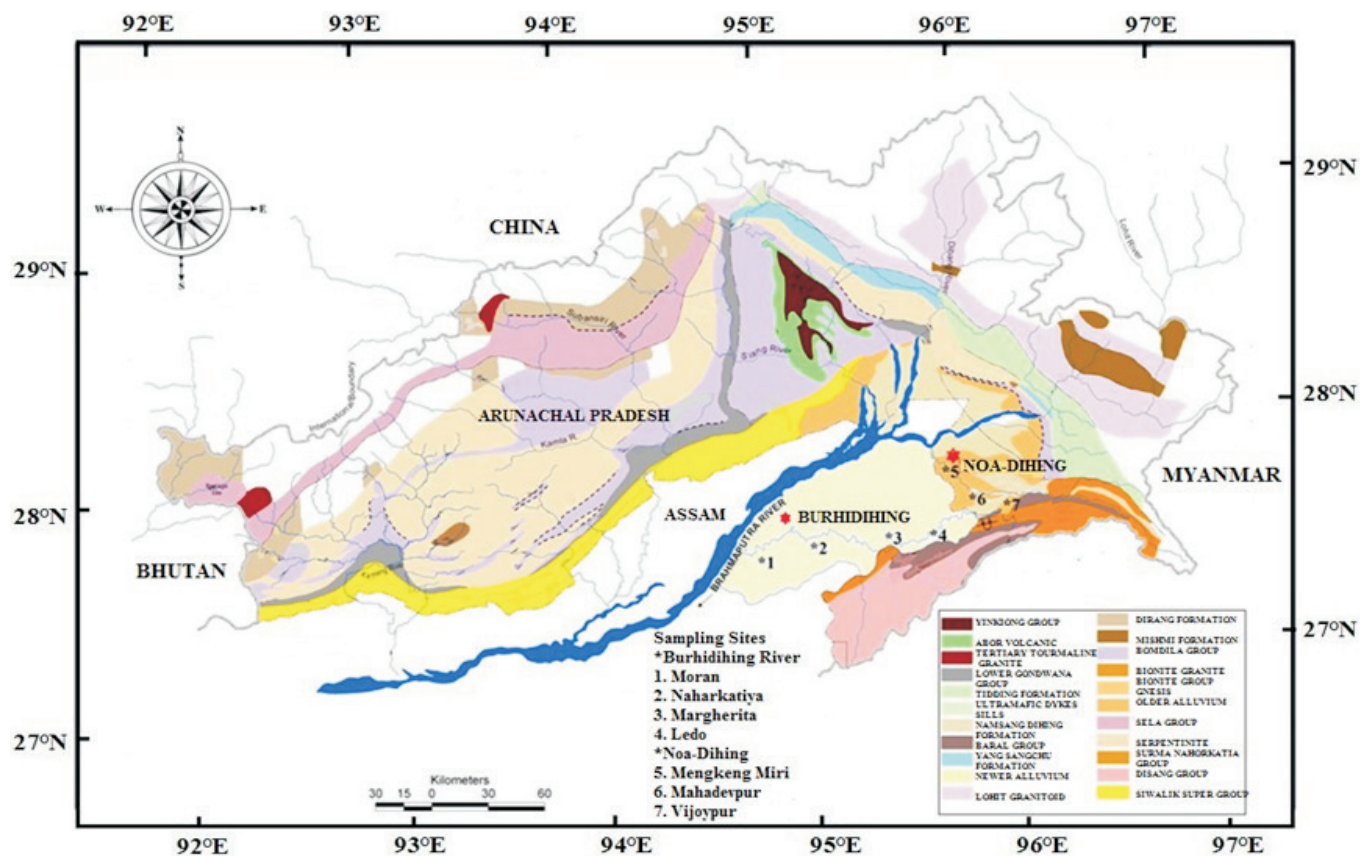


Figure 1: Map showing sampling sites and geology of the study area.

against sodium carbonate solution) first to pH 8.3 using phenolphthalein as an indicator and then further to pH between 4.2 and 5.4 with methyl orange. In all samples, phenolphthalein alkalinity was found to be zero. Cl^- was measured using Argentometric method. Mg^{2+} , Co, Cu, Mn, Ni, Sr and Fe were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima DV2100). The calibration standards were prepared using Perkin Elmer multi-element stock solutions of 100 ppm. For the multi-element calibration 2% nitric acid (HNO_3) was used as blank. The detection limit of the instrument is 0.001 mgL^{-1} . The accuracy of the analytical methods was checked by calculating the charge balance, which is $(\text{Tz}^+ - \text{Tz}^- / \text{Tz}^+ + \text{Tz}^-) \times 100$, where Tz^+ and Tz^- are total cations and total anions respectively calculated in meqL^{-1} (Farooqi et al., 2007). The charge balance of the data is within $\pm 10\%$.

Sediment Analysis

A total of eight sediment samples from Burhi Dihing and eight sediment samples from Noa-Dihing (overbank and channel sediments) were collected by channel (a groove of 0.5 to 1 m length and 10-20 cm depth and thickness)

sampling method, after removing the upper few centimetres layer with a plastic shovel. Approximately 2 kg of sediment sample was taken after homogenizing the collected material from selected locations along the river. The collected sediment samples were then packed and sealed in polyethylene bags and transferred to the laboratory after naming and coding.

Grain size analysis was performed using dry sieving method in a mechanical shaker (Ro-Tap mechanical sieve shaker, ASTM). Dry sieving method is used to fractionate a sediment/soil into its proportion of coarse sand, fine sand, very fine sand, silt and clay. A total of three for Noa-Dihing and four for Burhi-Dihing surface sediment samples were taken for textural analysis. For these analyses sieves of 2.36 mm, 1.18 mm, 0.6 mm, 0.3 mm, 0.18 mm and 0.063 mm were used. Dry samples (50 g) were placed in the uppermost sieve and covered in a set of stacked sieves. The stack of sieves arranged in order so that the coarse sieves at the top with finer one below. The sieves set are placed on shaking machine. The samples were then sieved for 20 minutes in Ro-Tap mechanical shaker. The sample that has retained on each sieve and the pan were collected and weighed using a balance having an accuracy of 0.001 gm and cumulative

weight percentage was calculated. The calculations were made for weight percentage and cumulative percentage. The major (SiO_2 , TiO_2 , Al_2O_3 , FeO , MnO , MgO , CaO , Na_2O , K_2O and P_2O_5) and trace (Ba, Co, Cr, Ni, Pb, Rb, Sr, V, Zn, Zr and Cu) elements of sediment samples were analyzed by using WD-XRF (PANalytical, Axios).

Results and Discussion

Assessment of Grain Size Distribution and Sediment Mineralogy

Grain size distribution can be used for describing a site's geomorphic setting, interpreting the geomorphic significance of fluid dynamics in the natural environment, sample permeability and stability under load; kinetic reactions and the affinities of fine-grained particles and contaminants (McCave and Syvitski, 1991).

Table 1 shows the summary of results obtained from grain size analysis and its interpretation. Graphic

mean distribution for the sediment ranges 2.18-5.19 for Noa-Dihing and 2.53-4.70 for Burhi-Dihing. It is a function of the size range of the sediments and amount of energy impacted to the sediments which depends on current velocity or turbulence of transporting medium. Analyzed results show sorting range of 1.53-2.56 for Noa-Dihing and 2.03-2.33 for Burhi-Dihing. It measures the spread of the grain size distribution with respect to mean and thus signify effectiveness of the depositional medium (water) in separating grains of the different classes. Skewness value ranges -0.36-1.52 for Noa-Dihing and -0.04-1.05 for Burhi-Dihing. It is a measure of symmetry of the distribution, which suggests the energy of deposition. Range of kurtosis are 1.37-4.13 for Noa-Dihing and 1.55-2.60 for Burhi-Dihing. In natural environments kurtosis value reflects the fluctuation in the velocity of depositing medium. A value greater than unity suggests greater fluctuation (Verma and Prasad, 1981).

Table 1: Summary of results obtained from grain size analysis and its interpretation

Site	Mean	Sorting	Skewness	Kurtosis	Interpretation
Noa-Dihing river sediments					
Site 1-BS	4.07	2.55	0.02	1.37	Very fine sand, very poorly sorted, symmetrical, Platykurtic
Site 1-CS	2.22	2.22	0.81	2.37	Fine sand, poorly sorted, fined skewed, Mesokurtic
Site 2-BS	2.84	1.80	1.52	4.10	Fine sand, poorly sorted, very fine skewed, Leptokurtic
Site 2-CS	2.98	1.69	1.34	4.13	Fine sand, poorly sorted, very fine skewed, Leptokurtic
Site 3-BS	5.19	1.99	-0.36	1.52	Very coarse silt, poorly sorted, very fine skewed, Platykurtic
Site 3-CS	3.72	2.19	0.47	1.88	Very fine sand, very poorly sorted, fine skewed, Leptokurtic
Site 4-BS	3.82	2.56	0.15	1.43	Very fine sand, very poorly sorted, symmetrical, Platykurtic
Site 5-CS	2.18	1.53	1.39	5.06	Fine sand, poorly sorted, fine skewed, very Platykurtic
Burhi-Dihing river sediments					
Site 1-BS	2.53	2.33	1.05	2.60	Fine sand, poorly sorted, very fine skewed, Mesokurtic
Site 1-CS	4.70	2.06	-0.040	1.56	Very coarse silt, poorly sorted, very fine skewed, Mesokurtic
Site 2-BS	4.22	2.21	0.17	1.57	Very fine sand, very poorly sorted, fine skewed, Leptokurtic
Site 2-CS	3.32	2.03	0.77	2.45	Very fine sand, poorly sorted, symmetrical, Mesokurtic
Site 3-BS	3.48	2.03	0.72	2.32	Very fine sand, poorly sorted, fine skewed, Leptokurtic
Site 3-CS	4.22	2.17	0.18	1.61	Very fine sand, very poorly sorted, fine skewed, Leptokurtic
Site 4-BS	3.48	2.14	0.65	2.10	Very fine sand, poorly sorted, fine skewed, Mesokurtic
Site 4-CS	4.19	2.23	0.17	1.55	Very fine sand, very poorly sorted, fine skewed, Mesokurtic

Note: Mean size unit (ϕ) Skewness unit (ϕ) (Folk and Ward, 1962) method of grain size of the river sediments, BS – Bank sediment and CS – channel sediment.

Figure 2 shows that all the sediment samples of Noa-Dihing river are composed of Silty-Sand type, while one sample is Sandy silt type and one sample represents Sand type. It is observed that as we move along the river, the sediments become finer in size. These suggest that as the sediments are transported from upstream to downstream water action makes them finer in size. Figure 2 shows that 100% sediment samples of Burhi-Dihing river are composed of Silty-Sand type. It is also important in distinguishing local versus regional sediment transport mechanisms because grain size is a dominant controlling factor in sediment geochemistry. Cations derived from mineral weathering and pollution sources are preferentially adsorbed onto clay, which has the highest surface area to volume ratio of any particle size class.

Comparison of the Major-element Composition of the Upper Continental Crust and Weathering Profiles

The upper continental crust, being the most accessible part of our planet, has long been the target of geochemical investigations (Hartmann et al., 2012). There are two basic methods employed to determine the composition of the upper crust: (i) establishing weighted averages of the compositions of rocks exposed at the surface and (ii) determining averages of the composition of insoluble elements in fine-grained clastic sedimentary

rocks or glacial deposits and using these to infer upper-crust composition.

The concentrations of the major and trace elements in the investigated samples have been normalized to their average contents in the Upper Continental Crust (UCC) reported by Taylor and McLennan (1985) and Rudnick and Gao (2003). Mean abundances of major-element oxides for sediments is expressed as ratios to upper continental crust (UCC) means. Values < 1 indicate depletion relative to the UCC mean; values > 1 indicate enrichment.

Upper continental crust normalized ratio of major element oxides of Burhi-Dihing sediments are shown in Figure 3 Burhi-Dihing bank sediments have the normalized ratio for CaO, Na₂O, K₂O, MgO, P₂O₅ and Al₂O₃ less than 1. The Burhi-Dihing channel sediments have the normalized ratio for CaO, Na₂O, P₂O₅, K₂O, MgO, Al₂O₃, FeO and MnO less than 1. This can be because of loss of these metal oxides from bed rocks during weathering and/or less abundance of clay in bed sediments compared to that in UCC (Dalai et al., 2004) which is substantiated by the finding of grain size analysis that sandy silt is found in more abundance as compared to clay minerals in the bank and channel sediments of Burhi-Dihing river. It is observed that relative to the bulk rocks, groundmass compositions are typically enriched in SiO₂ and alkalis, but depleted in MgO, MnO, FeO and TiO₂, while Al₂O₃ and CaO are either mildly enriched or depleted which indicates the dominance of mafic mineral phases (Gomez-Tuena et al., 2014). Mafic refers to silicate *mineral* or rock that is rich in magnesium and iron. Silica clastic sediment compositions are controlled by numerous processes such as chemical and physical weathering, abrasion, and hydrodynamic sorting active during soil formation, erosion, transport and deposition (Peter and Kamp, 2010). These processes and their effects are further controlled by climate and topography, residence time, distance of transport, and the depositional environment. Composition of muds and silts are of much importance since they are the repository of the minerals derived from the parent rocks. Weathering process is important since during weathering and erosion some trace elements are removed from the parent rock to solution.

The chemical composition of weathering products in a sedimentary basin is expected to reveal concepts on mobility of various elements during weathering (Wekeil and Anwar, 2013). During chemical weathering, Ca, Na and K are largely removed from source rocks. Since in feldspars Al is the least mobile element, Nesbitt and

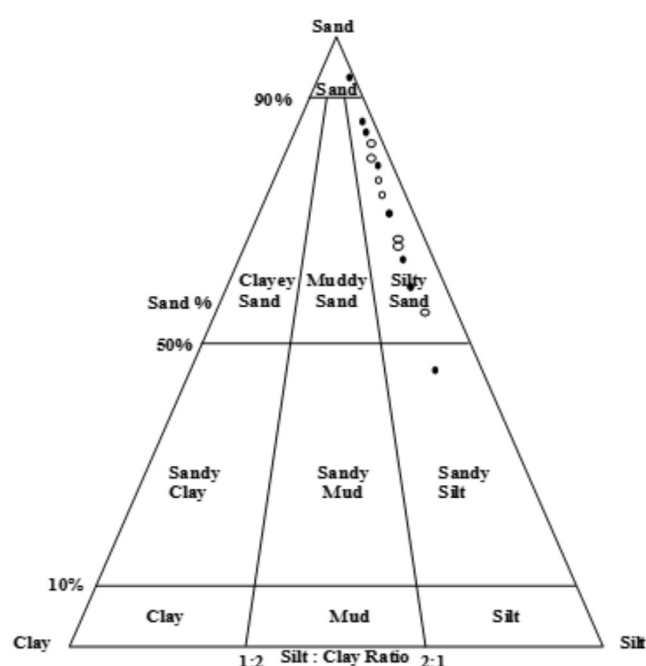


Figure 2: Sediment grain size analysis of Noa-Dihing river (black circle) and Burhi-Dihing river (white circle).

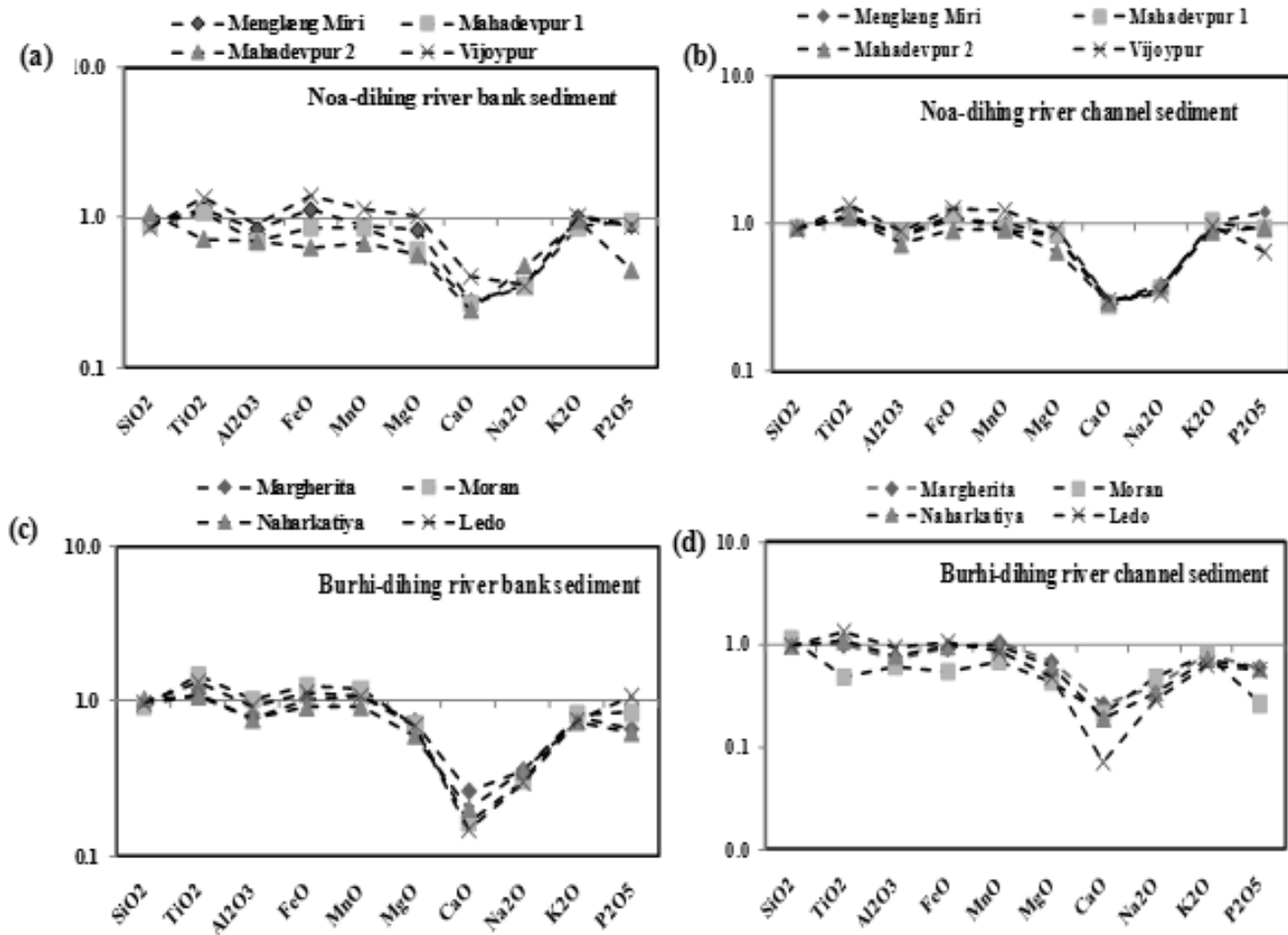


Figure 3: Upper continental crust (UCC) normalized ratio for major ions in (a) Noa-Dihing river bank sediment, (b) Noa-Dihing river channel sediment, (c) Burhi-Dihing river bank sediment and (d) Burhi-Dihing river channel sediment.

Young (1982) proposed a chemical index of alteration (CIA) which enables determining the intensity of weathering in source areas using the formula:

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$$

where CaO* represents CaO associated with the silicate fraction of the rock. The CIA value is thought to quantify the state of chemical weathering of the rocks by referring to the loss of mobile elements such as Ca and K. Samples with CIA values below 60 reflect low chemical weathering of the source rocks, between 60 and 80 indicate moderate weathering whereas more than 80 indicate intensive weathering (Bandopadhyay and Ghosh, 2015). The recorded CIA values (Figure 4) for the Noa-Dihing samples range from 64.5 to 70.9 and for Burhi-Dihing samples it is from 64.8 to 81.2 which suggests moderate weathering events except for site 4 where CIA is greater than 80. CIA values range 70–75, indicating moderate chemical weathering and the formation of muscovite, illite and smectite during

weathering (Nesbitt and Young, 1989; Bandopadhyay and Ghosh, 2015).

Figure 5 (a) shows the distribution of trace metal in the Noa-Dihing river bank sediment where it is observed that bank sediments are abundant with metals such as Ba (37%), Cr (12%) and Zr (10%) in comparison to Cu (1%) and Co (3%). In Figure 5 (b), distribution of trace metal in the Noa-Dihing river channel sediment shows that the sediments are carrier of metals such as Ba (25%), Zr (19%) and Cr (17%) as compared to Co (1%), Pb (1%) and Cu (2%). Presence of moderately toxic metal Cr and highly toxic metal Zr may be hazardous in comparison to Ba which is less toxic but more abundant in the sediment.

Figure 5 (c) shows trace metal concentration in Burhi-Dihing river bank sediment, where it is observed that Ba comprises 32%, Zr (14%) and Cr (13%) of the total trace metal concentration while in Figure 5 (d) trace metal concentration in Burhi-Dihing river channel sediment shows that Ba has highest percentage

of 25% and Zr and Cr shares equal share of 17% each in the distribution chart. Ba is present in the sediment through the natural process of sediment formation, which includes the breakdown of parent rocks by weathering. Ba levels are high in sediments formed from limestone, feldspar and biotite micas of the schists and

shales (Clark and Washington, 1924). When soluble Ba-containing minerals weather and come into contact with solutions containing sulphates, Ba-sulphate is deposited in available geological faults. If there is insufficient sulphate to combine with Ba, the sediment material formed is partially saturated with Ba. Ba replaces other cations in the sediments particles by ion exchange. Colloidal clays have been found to decompose insoluble Ba-sulphate by binding Ba. Bradfield (1932) found that, in the reaction between purified sodium clay and Ba sulphate, the sulphate ion became much more soluble, thus releasing the Ba into the clay. Zr and Cr are found in minerals that are heavy and stable enough to be mechanically concentrated.

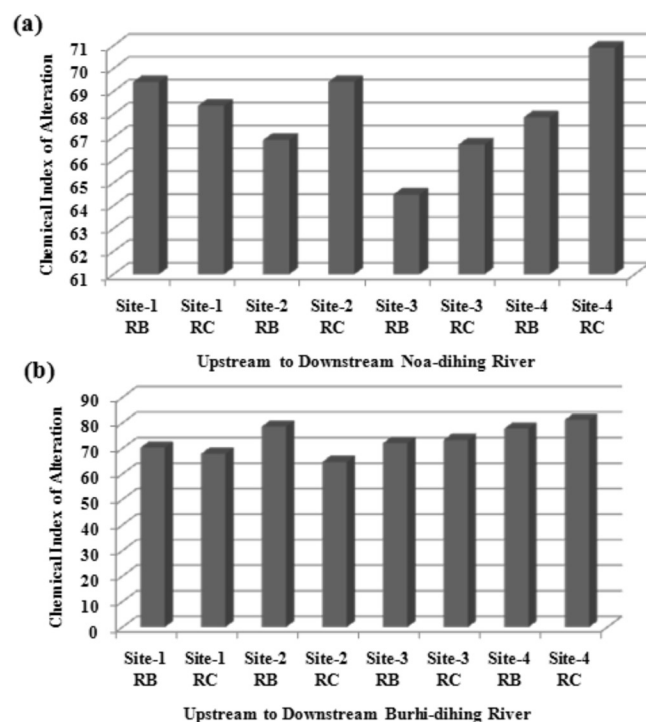


Figure 4: Chemical mobility and weathering trends analysis using Chemical Index of Alteration (CIA).

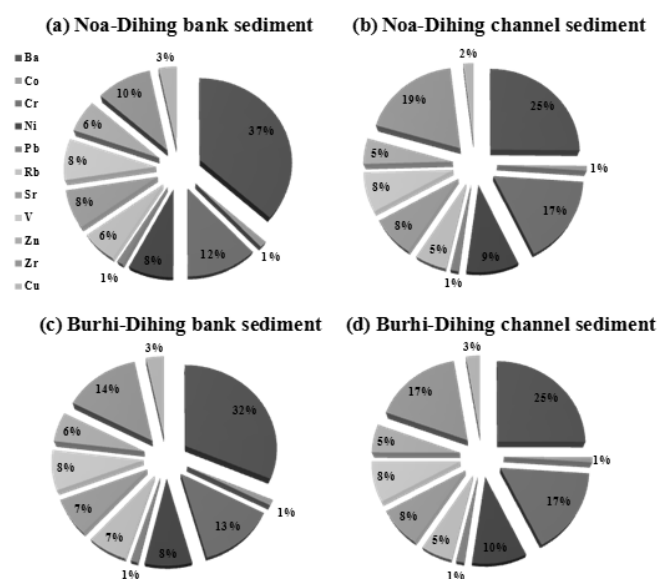


Figure 5: Trace metal concentration in (a) Noa-Dihing river bank sediment, (b) Noa-Dihing river channel sediment, (c) Burhi-Dihing river bank sediment and (d) Burhi-Dihing river channel sediment.

Assessment of Interactive Mechanism of Chemical Parameters in Surface Water

Cation and anions are analysed in order to discuss about the geochemical process associated with surface water and sediment interaction, mainly exhibited by cations (Na^+ , Ca^{2+} , Mg^{2+} and K^+) and anions (HCO_3^- , NO_3^{2-} and PO_4^{3-}). The comparative statistical data of the hydrochemical parameters of both river water in terms of maximum, minimum, average, and standard deviation has been given in Table 3.

According to the results, pH of Burhi-Dihing river was found to be neutral to that of Noa-Dihing which is slightly alkaline. EC of Noa-Dihing river is found to be slightly more than that of the Burhi-Dihing river on an average EC value is $86.67 \mu\text{S}/\text{cm}$. TDS was determined to measure the dissolved ion concentration in a solution. The TDS of the Noa-Dihing river shows an average of 58.07 mgL^{-1} whereas for Burhi-Dihing river, 54.27 mgL^{-1} is observed. It has been found that the sites Mahadevpur and Mengkeng-Miri of Noa-Dihing river and Margherita and Naharkatiya of Burhi-Dihing have lesser values of TH compared to the other sites of both the rivers. The average concentration of NO_3^- of the Noa-Dihing river, on an average, is 0.14 mgL^{-1} and that of Burhi-Dihing is 0.12 mgL^{-1} . SO_4^{2-} concentration is less at Burhi-Dihing with an average concentration of 3.23 mgL^{-1} and for Noa-Dihing 3.40 mgL^{-1} . The average concentration of PO_4^{3-} is 0.12 mgL^{-1} at Burhi-Dihing river which is higher in comparison to Noa-Dihing river with average concentration of 0.09 mgL^{-1} . The Ca^{2+} is found to be higher at Nao-Dihing (9.18 mgL^{-1}) as compared to Burhi-Dihing river (9.05 mgL^{-1}) and Mg^{2+} concentration is high at Burhi-Dihing river (6.71 mgL^{-1}) to that of Noa-Dihing (3.72 mgL^{-1}). In case of trace metal Co, Cu and Ni the average concentration found in Burhi-Dihing river is 0.002 mgL^{-1} , 0.001

Table 2: Distribution of physical parameter and heavy metals in the Noa-Dihing and Burhi-Dihing river sediments

<i>Parameters</i>	<i>Noa-Dihing</i>				<i>Burhi-Dihing River</i>			
	<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Std. Dev</i>	<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Std. Dev</i>
pH	7.3	6.9	7.1	0.1	7.2	7	7.1	0.1
EC	208	133	176	27.0	216	138	184	24.7
Ba	664	532	597	48.4	549	186	389	110
Co	22	9.5	16.3	4.1	20.5	8.7	15.8	3.6
Cr	231	160	200	20.9	345	166	262	49.6
Ni	143	89.3	120	23.9	184	127	153	18.4
Pb	22	19.9	21.7	0.8	23.1	21.2	21.8	0.6
Rb	137	111	121	11.4	101	76.5	88.8	7.5
Sr	158	129	145	9.9	153	90.3	120	19.8
V	143	97.8	126	13.5	144	82.4	121	18.6
Zn	116	62.2	89.6	21.0	111	70.3	89.3	16.6
Zr	372	175	241	77.2	285	116.1	242	53.3
Cu	58.9	31.3	47.8	9.7	68.1	29.2	46.9	13.4

All the units are in μgg^{-1} , except for pH and EC (μScm^{-1})

Table 3: Summary table of the chemical parameters of Noa-Dihing and Burhi-Dihing river water

<i>Parameter</i>	<i>Units</i>	<i>Noa-Dihing</i>				<i>Burhi-Dihing</i>			
		<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Std.Dev</i>	<i>Max</i>	<i>Min</i>	<i>Avg</i>	<i>Std.Dev</i>
pH	-	7.4	7.2	7.3	0.1	7.2	7.1	7.2	0.1
EC	μScm^{-1}	96	73	86.6	10.6	90	67	81	9.7
TH	mgL^{-1}	56	44	49.3	5.4	92	43	58	22
TA	mgL^{-1}	170	50	123	56	340	140	219	84.4
TDS	mgL^{-1}	64.3	48.9	58.0	7.1	60.3	44.9	54.3	6.5
Cl^{-}	mgL^{-1}	32	24	28.3	3.6	30	22	26.8	3.4
NO_3^{-}	mgL^{-1}	0.2	0.1	0.1	0.0	0.2	0.1	0.1	0.0
SO_4^{2-}	mgL^{-1}	3.7	3	3.4	0.3	3.9	2.2	3.2	0.8
PO_4^{3-}	mgL^{-1}	0.1	0.0	0.1	0.0	0.2	0.1	0.1	0.0
Na^{+}	mgL^{-1}	5.6	4.2	4.9	0.6	6.2	3.0	4.8	1.4
K^{+}	mgL^{-1}	2.5	2.0	2.3	0.2	3.0	1.5	2.3	0.7
Ca^{2+}	mgL^{-1}	10.7	6.4	9.2	2.1	15.1	6.2	9.0	4.0
Mg^{2+}	mgL^{-1}	3.7	3.7	3.7	0.02	13.3	4.2	6.7	4.2
Fe	μgL^{-1}	2531	1275	1981	570	693	180	389	229
Co	μgL^{-1}	5	2	3	1	3	BDL	2	1
Cu	μgL^{-1}	5	5	5	BDL	3	BDL	1	1
Mn	μgL^{-1}	82	50	71	15	398	17	120	176
Ni	μgL^{-1}	8	BDL	3	4	2	BDL	1	1
Sr	μgL^{-1}	43	29	38	7	89	38	52	23

All the units are in mgL^{-1} , except for pH and EC (μScm^{-1}), BDL – Below Detection Limit

mgL⁻¹ and 0.001 mgL⁻¹ whereas for Noa-Dihing the average concentration is 0.003 mgL⁻¹, 0.005 mgL⁻¹ and 0.003 mgL⁻¹ respectively. The concentration of Fe is found above permissible limit at Nao-Dihing with an average concentration of 1.981 mgL⁻¹ whereas in the Burhi-Dihing the average concentration is 0.389 mgL⁻¹. Average Mn concentration is 0.071 mgL⁻¹ and 0.12 mgL⁻¹ for Noa-Dihing and Burhi-Dihing rivers respectively. The average Sr concentration is 0.038 mgL⁻¹ and 0.052 mgL⁻¹ for Noa-Dihing and Burhi-Dihing rivers respectively.

The changes in hydrogeochemical phases of river water in the study area can be interpreted by various standard methods. The geochemical evolution can be described from the Piper plot, which has been divided into six sub categories viz. A. (Ca-Mg-Cl-SO₄ type); B. (Ca-Mg-Na-Cl type); C. (Na-Ca-HCO₃ type); D. (Na-K-HCO₃ type); E. (Ca-Mg-HCO₃ type) and F. (Na-K-Cl-HCO₃ type). Major ion compositions plotted on a Piper (1994) trilinear diagram shows that maximum samples are clustered at group-E (Ca-Mg-HCO₃ type)

except one sample which is present in group-B (Ca-Mg-Na-Cl mixed type). From the plot as shown in Figure 6, it is observed that in the river water samples alkaline earth metal exceeds the alkali and Ca²⁺ and Mg²⁺ play a dominant role in controlling the cation chemistry. Dissolution of calcite and dolomite is the most important chemical process in the generation of Ca-Mg-HCO₃ type water.

Application of Multivariate Statistical Analyses for Determination of Association among Releasing Mechanisms of the Minerals

In the last decade the application of multivariate statistical tools have been used for the characterization and evaluation of geochemical sample (Guler et al., 2002; Simeonova et al., 2003; Singh et al., 2004; Astel et al., 2006; Kowalkowski et al., 2006; Papatheodorou et al., 2006; Shin and Fong, 1999; Shrestha and Kazama, 2007; Zhou et al., 2007). Statistical technique of principal component analysis is widely applied for classification of variables with common attributes and

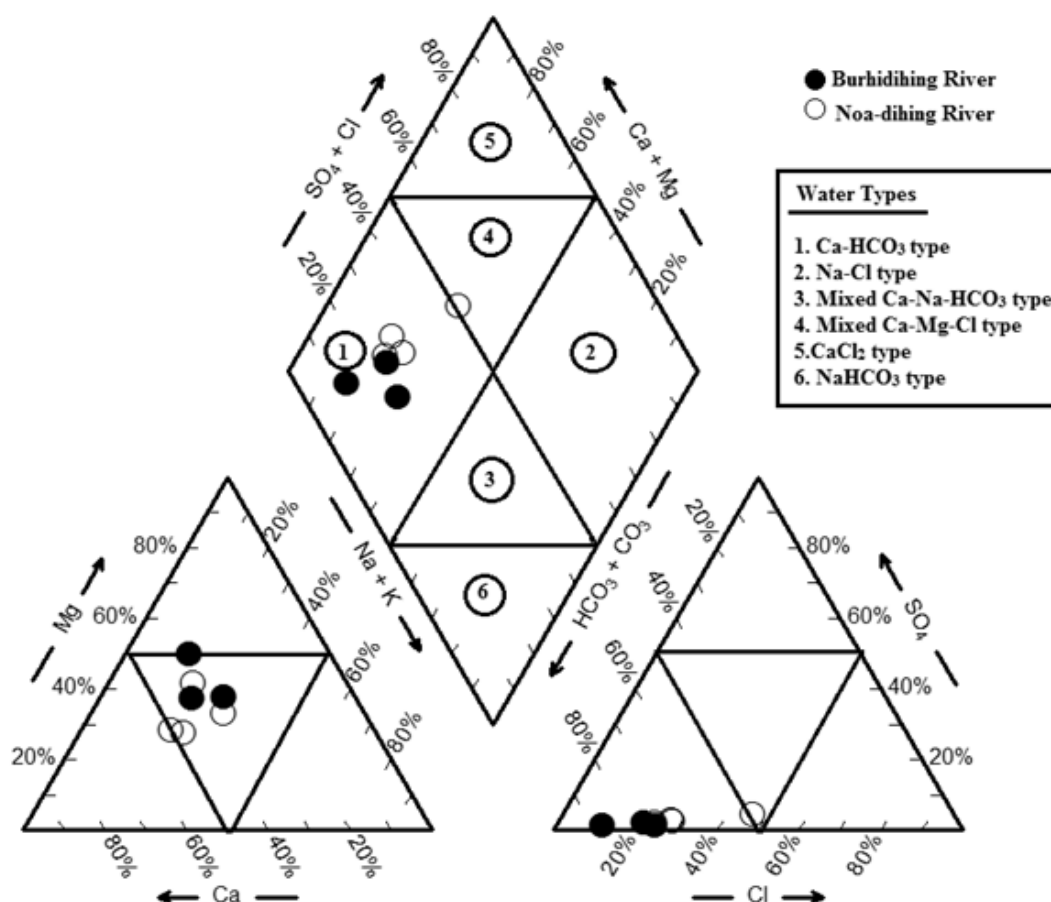


Figure 6: Trilinear diagram illustrating hydrochemical facies.

for evidencing temporal and spatial variation caused by natural and human factors linked to seasonality (Helena et al., 2000; Zhao et al., 2011, Kumar et al., 2006).

Cluster analysis can be used to discover structures in data without providing an explanation/interpretation (Sharma, 1996). Cluster analysis comprises a series of multivariate methods which are used to find true groups within the data. Hierarchical clustering is the procedure which joins the most similar observations first, followed by the next most similar observations successively. The levels of similarity at which observations are merged are used to construct a Dendrogram. Cluster analysis was performed on standardized parameter values and using Euclidian distance as the measure of difference between variables.

Figure 7 shows hierarchical clustering between the variables using Euclidean distance as a measure of similarity between them. In our study three distinct clusters are formed. The first cluster comprises Co, FeO, V, TiO₂, Zn, Al₂O₃, MnO, MgO, P₂O₅, Cr, Ni and Zn. The results showed close association of metals of similar chemical characteristics. Transition metals such as Co, Zn, V, Cr, Ni and Zn are associated with metal oxides of transition metal and are further linked with alkaline earth metals and post transition metal. Correlation of other metals with FeO and MnO may be due to their association with iron and manganese minerals or their sequestration with iron oxy-hydroxides. The second cluster is consisting of Rb, K₂O, Ba, Sr and CaO, suggesting close linkage of alkali metal with alkaline earth metal. The third cluster is associated with SiO₂, Na₂O, Pb, Cu and pH. Here close linkage of alkali metal

with metalloid and transition metal is observed. Thus these groups can be further analysed through principal component analysis for understanding the relation or association of occurrence of these minerals and their releasing mechanisms.

Principal component analysis provides basic, independent dimensions of variables (Kouping Chen et al., 2006; Kumar et al., 2009). The eigenvectors that are used to compute the scores of the observations are called principal component loadings. The first principal component loading explains the most variance, each subsequent component explaining progressively less. The principal component loadings can thus provide further insight into the processes that are responsible for similarities in the elemental concentrations.

The result of principal component analysis is depicted in Figure 8. The first two components with highest loading are used for this analysis. The first component exhibits variance of 40% with variables such as Co, V, Zn, SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO and Na₂O. The second component exhibits variance of 30% with variables such as Ba, Cr, Rb, Sr and K₂O. Thus it can be ascertained from the results that releasing mechanism of transition metal and their oxides are same and that of alkali and alkaline earth metals are similar.

Conclusion

Comparative analysis of physicochemical characteristics of Noa-Dihing and Burhi-Dihing Rivers reveals that the surface water contaminants including heavy metals are within the desirable limit. The mineralogy and grain size

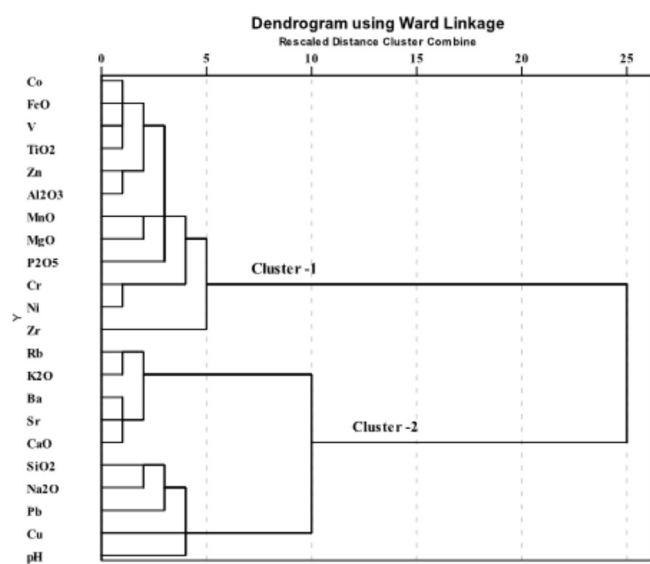


Figure 7 : Dendrogram showing the hierarchical clustering between the variables.

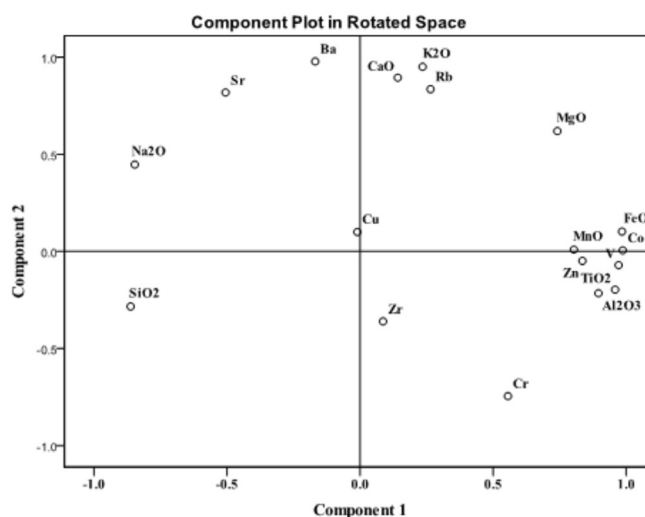


Figure 8: Principal Component Analysis of sediment samples to delineate the association among releasing mechanisms of the minerals.

characterization of river bank and channel sediments of Noa-Dihing and Burhi-Dihing rivers suggests that all the sediment samples of Noa-Dihing river are composed of Silty-sand type, while few samples are Sandy silt type and few represent Sand type. In case of Burhi-Dihing river 100% sediment samples are composed of Silty-sand type. It is observed that as we move along the river, the sediments become finer in size with the action of river flow from upstream to downstream. The mineralogy of both the rivers indicates the abundance of trace metals such as Ba, Cr and Zr in varying percentage in the sediment samples. In Noa-Dihing sediments and Burhi-Dihing sediments, the normalized ratio for CaO, Na₂O, P₂O₅, Al₂O₃, SiO₂, MgO and MnO is less than 1 except for SiO₂, which is enriched in the Burhi-Dihing sediment samples indicating the dominance of mafic mineral phases.

Depleted values can be because of loss of these metal oxides from bed rocks during weathering and/or less abundance of clay in bed sediments compared to that in UCC. The metal distribution in the surface water shows that all metals are within permissible range and hence the surface water is potable. The metal distribution in sediments of Noa-Dihing and Burhi-Dihing rivers suggests that highly toxic metals are less abundant in comparison to moderately toxic metals except for Zr, which comprises 37% and 32% in the river bank sediments of the Noa-Dihing and Burhi-Dihing rivers respectively. Multivariate analysis of hydrologic and geological data of Noa-Dihing and Burhi-Dihing rivers suggests that natural weathering processes of alkaline earth metals can be associated with release of trace metals in a riverine system and releasing mechanism of transition metal and their oxides are same and that of alkali and alkaline earth metals are similar.

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References

- Adedokun, O.A., Adeyemo, O.K., Adeleye, E. and R.K. Yusuf (2008). Seasonal Limnological Variation and Nutrient Load of the River System in Ibadan Metropolis, Nigeria. *Eur. J. Sci. Res.*, ISSN 1450-2160, **23(1)**: 98-108.
- APHA, AWWA and WEF (2005). Standard methods for the examination of water and waste water, 21st ed. American Public Health Association, Washington DC.
- Astel, A., Biziuk, M., Przyjazny, A. and J. Namiesnik (2006). Chemometrics in monitoring spatial and temporal variations in drinking water quality. *Water Res.*, **40(8)**: 1706-1716.
- Bandopadhyay, P.C. and B. Ghosh (2015). Provenance analysis of the Oligocene turbidites (Andaman Flysch), South Andaman Island: A geochemical approach. *J Earth Syst Sci*, **124(5)**: 1019-1037.
- Bradfield, R. (1932). The concentration of cations in clay soils. *J Phys Chem*, **36**: 340-347.
- Clarke, F.W. and H.S. Washington (1924). The composition of the earth's crust. *U.S. Geol. Survey Prof. Paper*, **127**: 117.
- Dalai, T.K., Rengarajan, R. and P.P. Patel (2004). Sediment geochemistry of the Yamuna River System in the Himalaya: Implications to weathering and transport. *Geochemical Journal*, **38(5)**: 441-453.
- Eberl, D.D. (2004). Quantitative mineralogy of the Yukon River system: Changes with reach and season, and determining sediment provenance. *Am Mineral*, **89**: 1784-1794.
- EL-Wekeil, S.S. and E.A. Abou El-Anwar (2013). Petrology, geochemistry and sedimentation history of Lower Carboniferous shales in Gebel Abu Durba, southwestern Sinai. *Egypt Jappl Sci Res*, **9(8)**: 4781-4798.
- Gomez-Tuena, A., Straub, S.M. and G.F. Zellmer (2014). Orogenic Andesites and Crustal Growth. *Geol Soc London Sci*, 414.
- Goswami, D.C. (1985). Brahmaputra River, Assam, India: Physiography, Basin Denudation and Channel Aggradation. *Water Resour Res*, **21(7)**: 959-978.
- Guler, C., Thyne, G.D., Mccray, J.E. and A.K. Turner (2002). Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrol J*, **10**: 455-474.
- Hartmann, J., Dürr, H.H., Moosdorf, N., Meybeck, M. and S. Kempe (2012). The geochemical composition of the terrestrial surface (without soils) and comparison with the upper continental crust. *International Journal of Earth Sciences*, **101(1)**: 365-376.
- Helena, B., Pardo, R., Vega, M., Barrado, E., Fernandez, M.J. and L. Fernandez (2000). Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga river, Spain) by principal component analysis. *Water Res*, **34**: 807-816.
- Kaiser, D., Kowalski, N., Bottcher, M.E., Yan, B. and D. Unger (2015). Benthic Nutrient Fluxes from Mangrove Sediments of an Anthropogenically Impacted Estuary in Southern China. *J Mar Sci Eng*, **3**: 466-491.
- Kouping, C., Jiu, J.J., Jianmin, H. and H. Runqiu (2006). Multivariate statistical evaluation of trace elements in

- groundwater in a coastal area in Shenzhen, China. *Environ Pollut*, **147**: 771-780.
- Kowalkowski, T., Zbytniewski, R., Szpejna, J. and B. Buszewski (2006). Application chemometrics in river water classification. *Water Res*, **40**: 744-752.
- Kumar, M., Kumari, K., Singh, K.U. and AL. Ramanathan (2009). Hydrogeochemical processes in the groundwater environment of Muktsar, Punjab: Conventional graphical and multivariate statistical approach. *Environ Geol*, **57**: 873-884.
- Kumar, M., Ramanathan, AL., Rao, M.S. and B. Kumar (2006). Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India. *Environmental Geology*, **50**(7): 1025-1039.
- McCave, I.N. and J.P.M. Syvitski (1991). Principles and methods of particle size analysis. In: J.P.M. Syvitski (ed.), Principles, Methods, and Applications of Particle Size Analysis. Cambridge University Press, New York.
- Nepal, S. and A.B. Shrestha (2015). Impact of climate change on the hydrological regime of the Indus, Ganges and Brahmaputra river basins: A review of the literature. *Int J Water Resour*, **D31**(2): 201-218.
- Nesbitt, H.W. and G.M. Young (1989). Formation and diagenesis of weathering profiles. *J Geol*, **97**: 129-147.
- Nesbitt, H.W. and G.M. Young (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*, **299**: 715-717.
- Papatheodorou, G., Lambrakis, N. and G. Panagopoulos (2006). Application of multivariate statistical procedures to the hydrochemical study of a coastal aquifer: An example from crete. *Greece Intern J Hydrol Process*, **21**(11): 1482-1495.
- Peter, C. and Van de Kamp (2010). Arkose, subarkose, quartz sand, and associated muds derived from felsic plutonic rocks in glacial to tropical humid climate. *Journal of Sedimentary Research*, **80**: 895-918.
- Rice, S.P. and M. Church (2001). Longitudinal profiles in simple alluvial systems. *Water Resour Res*, **37**: 417-426.
- Rudnick, R.L. and S. Gao (2003). Composition of the continental crust. The Crust In: Treatise on Geochemistry Vol. 3, (Holland, H.D. and Turekian, K.K., eds), Elsevier, Oxford.
- Sarma, J.N., Borah, D. and U. Goswami (2007). Change of River Channel and Bank Erosion of the Burhi Dihing River (Assam) Assessed Using Remote Sensing Data and GIS. *J Indian Soc Remote*, **35**(1): 94-100.
- Sharma, S. (1996). Applied Multivariate Techniques. John Wiley & Sons, United States.
- Shin, P.K.S. and K.Y.S. Fong (1999). Multiple discriminant analysis of marine sediment data. *Mar Pollut Bull*, **39**: 285-294.
- Shrestha, S. and F. Kazama (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of Fuji river basin, Japan. *Environ Modell Softw*, **22**: 464-475.
- Simeonov, V., Stratis, J.A. and C. Samara (2003). Assessment of the surface water quality in Northern Greece. *Wat Res*, **37**: 4119-4124.
- Singh, K.P., Malik, A. and D. Mohan (2004). Multivariate statistical techniques for the evaluation of spatial and temporal variation in water quality of Gomti River (India): A case study. *Wat Res*, **38**: 3980-3992.
- Taylor, S.R. and S.M. McLennan (1985). The Continental Crust: Its Composition and Evolution. Blackwell, Oxford.
- Todorova, Y. and Y. Topalova (2014). Importance of Main Stream/Tributary Interface for Nutrient Dynamics and Microbial Communities in Upper River Sub-catchment. *Annu. Res. Rev. Biol.*, **4**(2): 399-411.
- Vuba, S., Ahmad, S.M. and N.R. Anipindi (2015). Geochemical and mineralogical studies in recent clastic sediments from upper Godavari river in peninsular India. *Journal of the Geological Society of India*, **86**(1): 107-114.
- Zhao, J., Fu, G., Lei, K. and Y. Li (2011). Multivariate analysis of surface water quality in the Three Gorges area of China and implications for water management. *J Environ Sci (China)*, **23**(9): 1460-1471.
- Zhou, F., Liu, Y. and H. Guo (2007). Application of multivariate statistical methods to water quality assessment of the watercourses in North-western New Territories, Hong Kong. *Environ Monit Assess*, **132**(1-3): 1-13.