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Nutrient dynamics of the Brahmaputra (tropical river) during the monsoon period

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ABSTRACT

A rapid population growth and continuous migration to urban centers are posing serious challenges to urban water supplies and demands. Urban demands for continuous and secure water supplies relays on available water resources in quantity and quality. The same supplies of water in urban areas are associated with the uncontrolled releases of organic and inorganic chemical species, including nutrients. The lack of technologies or access to them reduces the ability of water systems to restore its original water quality. Further, areas driven by a single release of water in the form of summer precipitation such as the monsoon require water management strategies that allow assessments of water availability, in quantity and quality, all year long. This work aims to characterize the intra-seasonal drivers of contaminant dynamics in response to rainfall. The objective is to use a single precipitation pulse (intra-seasonal monsoonal rainfall) in a large-scale river basin [Brahmaputra River Basin (BRB)] to evidence water quality responses to hydro-climate forcings. The BRB is located in South East Asia, where summer rainfall influences nutrient replenishment, displacement, and dilution of unregulated pollutants through the basin. Results show that changes in nutrient concentration in streams respond to rainfall patterns and events, evidenced by nutrient displacement through surface runoff. Elevated nutrient concentrations found in some downstream sites can be associated to anthropogenic activities such as agriculture and urban sewage release from densely populated areas in the lower lands of the BRB. Multivariate analysis substantiated the probable source of nutrient release in the BRB. While the source of NO_3^- can be associated with anthropogenic inputs that of PO_4^{3-} could be attributed to point sources such as sewage from the ammonia/urea manufacturing industry present near the mainstream. Cluster analysis indicated the potential mobility of PO_4^{3-} carried by suspended solids in river water and subsequently to organisms some distance away from the source.

Keywords: Brahmaputra River; Nitrate; Phosphate; Monsoon; Redfield ratio

1. Introduction

Nutrient flux and speciation are the combined effects of physicochemical and biogeochemical processes occurring at various scales in a drainage basin. Thus, their integration could lead to identify the influence of climate and environmental forcings and the undermining changes in current and future water quality in river basins. The goal is to characterize the intra-seasonal drivers of contaminant dynamics in response to monsoonal rainfall. Nitrogen (N), phosphorus (P), and silicon (Si) are essential elements for both freshwater and marine organisms and their riverine inputs to marine system are considered to be one of the most important nutrient discharges [1–3]. The identifica-

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tion of river pollution by excessive nutrients discharge is crucial with respect to assessment of water quality, and environmental management, such as meeting the required standards of river water quality, assessment of the impact of various activities on the river ecosystem, and monitoring of pollution control for planning and policy making. With the growing population sewage generation was estimated to be 62000 million liters per day (MLD) approximately in India and sewage treatment capacity is currently only 23277 MLD from 816 sewage treatment plants (STPs)[4]. And in Assam treatment facilities are completely lacking. Because of the huge gap in sewage treatment capacity, about 38723 MLD of untreated sewage (62% of the total sewage) is discharged directly into nearby water bodies. Sewage treatment capacity of the Assam State is 1.37 MLD in contrast to sewage generation of 703 MLD. It suggest that 701.63 MLD untreated sewage is discharged to water bodies and is responsible for deteriorating water quality [5]. The Central Pollution Control Board (CPCB) had identified 29 river stretches at 42 locations as polluted in Assam under three categories – Priority I (>30 mg L^{-1}), Priority IV (6–10 mg L^{-1}) & Priority (3–6 mg L^{-1}), based on values of Biochemical Oxygen Demand (BOD). Although, nitrate (NO_3^-) and phosphate (PO_4^{3-}) are regarded as essential elements in the river ecosystem [6] yet the increasing concentrations can result into severe pollution such as eutrophication and to a great extent formation of carcinogenic compounds where species of nitrogen can act as substrate [7,8].

The hydrological processes controlling inorganic N and P export at the watershed scale have been the focus of a significant amount of research over the last decade due to concerns about increasing inputs of N and P into the environment by human activities [9,10]. Identification of pollution sources, evaluation of their magnitude and estimation of effects on the water body are crucial steps toward water quality management. Traditional assessment of river water pollution is characterized by the identification of contaminant concentrations but few studies identify the sources of such contaminants and their variability in response to seasonal changes in climate and environment in the Brahmaputra flood plain. Thus an assessment of the influences of discharge of pollutants in relation to the dilution capacity of the stream is essential through identifying the stretches in the stream where the entry of pollutants takes place [11]. Many researchers have reported pollution of water bodies due to pollutant transport through runoff along with uncontrolled discharge of untreated and partially treated sewage, and have identified effects of runoff on water bodies including nutrient enrichment and deterioration of water quality [12,13].

The Himalayan Rivers transport a large quantity of sediments in major basins, such as the Brahmaputra and the Ganges, the largest sediment producing basins and annually transport 900–1200 million tons of sediment. High sediment production in the Himalayan region is favored by monsoonal rains in the source areas. Heavy and intense rainfall, up to 11,000 mm/y, triggers extensive catchment erosion, thereby introducing high amounts of sediments [14]. Lithology, runoff, temperature, physical erosion, morphology, soil, ecosystems, and land use pattern play an important role in chemical weathering processes; which in turn are responsible for adding the ions and nutrients to water bodies [15]. Climate has a marked influence on weathering rates, and an increase in temperature and precipitation may increase weathering rates of minerals [16] producing dissolved Si, P and alkalinity.

Phosphate rock (phosphorite), which has approximately the same composition as the mineral fluorapatite $[3Ca_3(PO_4)_2CaF_2]$, is a major source of phosphorus. But these rocks have not been reported in the Brahmaputra plains. N occurs in both organic and inorganic forms in slate, whereas it is dominantly present in inorganic forms in the other lithologies. The inorganic N is assumed to be present as NH_4^+ incorporated into the interlayer of muscovite and sericite; these minerals are prevalent in all lithologies. N concentrations in a 10-cm thickness of phyllite, slate, biotite schist, and metavolcanic breccia contains 2,688, 2,592, 1,807, and 1,001 kg N ha^{-1}, respectively, based on the average total nitrogen (TN) concentration and rock density [17]. The weakly foliated pink granite around Guwahati, Assam is a product of magmatisation of biotite schist [18]. Phyllite is found around the western and northern part of the Mikir Hills across the Kopili valley which belongs to Shillong group. Muscovite and Biotite are reported to respectively contain 123–390 mg N kg^{-1} and 17–134 mg N kg^{-1} [19]. Several thin veins of pegmatite containing small books (10 cm × 7 cm) of muscovite along with feldspar, tourmaline and smoky quartz occur in Naga Langso and Mukjam Hills areas along Kaliani River, Mikir Hills and west of Abhayapuri, Goalpara district, of Assam. Biotite is also reported in the Goalpara district. In a study from USA it was found that feldspar may contains up to 2700–19000 N, mg kg^{-1} [20]. Assam estimated an inferred reserve of 2200 million tons of feldspar in pegmatite, which is located at Hahime in the Kamrup district [18]. In northern Germany coal were reported to contain 9000–17,000 mg N kg^{-1}. Assam is reported to have 515 million ton of coal reserve. Coal mining is done in Assam's hill ranges-Patkai, Tirap and Tikok. Weathering of these mineral resources may also add to the nutrient concentration in rivers.

There are various organic and inorganic pollutants that affect water quality, but monitoring NO_3^- and PO_4^{3-} is even more important as they are nutrients for aquatic life and under adverse environmental conditions pollute water bodies. Precise estimations of N and P concentrations is very important with respect to climate, land use patterns and population density in quality assessment and nutrient source apportionment research. This study was conducted to: (i) assess the impacts of rainfall on nutrient chemistry during the monsoon; (ii) estimate nutrient status across the Brahmaputra; and (iii) identify factors controlling nutrient dynamics.

2. Study area

The Brahmaputra River is the 6th largest tropical river in the world. The Brahmaputra River is characterized by high seasonal variability in flow, sediment transport, and channel configuration [21]. The catchment of the Brahmaputra occupies an area of 580,000 km^2, surrounded by an almost continuous chain of high hills and plateaus on the north, east, and south. The Brahmaputra River acquires a width of ~20 km [22]. The valley is bounded in the north by high Himalayan mountain ranges, in the east by the Patkai hill ranges, in the south by the lower (Assam) hill ranges and in the west, it is contiguous with the plains of Bangladesh. The southern (Assam) mountainous region under the basin is comprised of parts of Naga hills, Mikir hills, North Cachar hills, Khasi hills and Garo hills lying in continuity in the east-west direction from Patkai hill ranges up to the Bangladesh border.

The Brahmaputra valley is a part of North-East India which, in turn, is a part of sub-tropical South-East Asia. The region forms an integral part of the South Asiatic monsoon, but its peculiar orographic configuration plays a dominant role in causing deviations from normal weather conditions. According to W. Kopper, this region as a whole, excluding the high mountain barriers, enjoys 'Cwg' or humid meso-thermal Gangetic type of climate. Climatic conditions are generally characterized by temperature, rainfall variations, and the level of humidity, depending on such variations whole Brahmaputra basin is delineated into four micro-climatic zones: (a) North Bank Plain (NBPZ) 1000 mm and 80% (b) Upper Brahmaputra Valley (UBVZ) >2000 mm and >80% (c) Central Brahmaputra Valley (CBVZ) 1600 mm and <80% (d) Lower Brahmaputra Valley (LBVZ) 1700 mm and 80% respectively. 30% of the area under CBVZ receives less than 600 mm rainfall [11].

Basically, the climate of the Brahmaputra basin is humid subtropical and thus high monsoonal rainfall and humidity are the main dominating component of the climate in this area. The climatology when coupled with the hydrology can provide a basis for estimating ongoing surface phenomenon of different sites within a basin. Satellite data [16] provided an overview of the total basin land use pattern of the Brahmaputra; the forest cover (14.5%), grass land (44.0%), agricultural land (14.0%), crop land/natural vegetation mosaic (12.8%), barren/sparsely vegetated land (2.5%), water bodies (1.8%), snow and ice (1.1%), and urban built-up land (0.02%). According to the conventional system of soil classification the alluvium derived soils of the Brahmaputra valley have been grouped into new and old alluvial and forest soils. The Brahmaputra basin was formed during the Pleistocene and in recent periods from the sediments derived from the Assam plateau in the south and the Assam Himalayas in the north and brought down by the Brahmaputra River and its tributaries [11]. The major groups of alluvium-derived soils of the Brahmaputra valley are Entisols, Inceptisols and Alfisols. The soils of the Brahmaputra valley have wide textural variations ranging from sand to clay. The flood plain soils are predominantly silty loam to sand. The upland soils are loam to clay loam at the surface horizons and clay loam to clay at the lower horizons. The alluvium near the Brahmaputra River is newer and stratified. In the flood plain soils, coarser materials are deposited first, followed by finer materials. Chlorite, biotite, amphibole and pyroxene together constitute the major proportion of heavy minerals of sand fractions of soils of the basin. Clay mica is the dominant mineral in clay fractions of flood plain soils (53–61%). Chlorite constitutes 8 to 10% of the clay fractions of the flood plain soils of the basin. Kaolinite is another dominant mineral constituting 36–40% of the clays [11].

3. Material and methods

Water quality assessment of dynamic river systems requires multiple monitoring points to obtain representative concentration profiles. Therefore the river is divided into 3 segments; viz. Guijan, Rohmoria representing upstream, Nimatighat, Bhumuragudi represent midstream and Pandu, Jogighopa representing downstream from where monthly samples were collected likewise 11 tributaries were selected contributing to mainstream at upstream sites viz. Naharkatiya (Burhidihing river), Sivasagar (Dikhou river), at midstream sites viz. Jorhat (Bhogdoi river), Numaligarh (Dhansiri river), Nagaon (Kalang river), Tezpur (Jiabharali river), Dharamtul (Kopili river), and at downstream sites viz. Nalbari (Pagladia river), Barpeta (Manas river), Barpeta (Beki river) and Bongaingaon (Aie river) .

The monsoonal climate in India is characterized by high discharge variability with a period of high flood peaks during the summer monsoon and very low discharge during the remaining months. Therefore sampling was carried out during July to September 2014, and a total of 51 samples were collected to ensure proper representation of diverse environment. The sampling sites are shown in Fig. 1. The sampling sites were demarcated using a GPS set (Garmin GPS map 76CSX). The samples were filtered using 0.45 μm membrane filter and kept in 500 mL polyethylene bottles that were pre-washed for PO_4^{3-}, NO_3^-, H_4SiO_4 analyses. For cation and anion and total suspended solid (TSS) analysis raw samples were collected in 250 ml polyethylene bottles. All the samples are kept at 4°C until analyses. Dissolved-oxygen (DO), electrical conductivity (EC), total dissolved solid (TDS) and pH were measured in-situ with a sampling kit (H19828-Multiparameter Water Quality Portable Meter). Concentration of HCO_3^- was estimated by titrating 10 ml sample with 0.01 N HCl (standardized against sodium carbonate solution) to pH 8.3 (phenolphthalein indicator), then to pH 4.2–5.4 (methyl orange indicator). In all samples, phenolphthalein alkalinity was zero. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima DV2100) was used to analyse the Ca^{2+}, Mg^{2+}, Na^+ and K^+. The calibration standards were prepared using Perkin Elmer multi-element stock solutions of 100 ppm. For the multi-element calibration 2% HNO_3 was used as a blank. UV-Spectrophotometry (Shimadzu, UV-1700) was used to quantify PO_4^{3-}, NO_3^-, H_4SiO_4 and SO_4^{2-} while Cl^- was measured by Argentometric method NO_3^- calibration standards were prepared in the range of 0–7 mg NO_3^- N/L by diluting to 50 ml the volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, and 7.00 … 35.0 ml. NO_3^- standards were also treated with 1 N HCl. Acidification by HCl in samples and standards were done to prevent interference from hydroxide and carbonate. Absorbance or transmittance against re-distilled water set at zero absorbance or 100% transmittance is recorded. NO_3^- was measured at 220 nm and interference from dissolved organic matter was measured at 275 nm. PO_4^{3-} was measured at 690 nm and H_4SiO_4 at 410 nm. Total organic carbon (TOC) is analyzed using TOC-analyzer (Shimadzu TOC-VCSH).Analyses were performed using methods prescribed by the American Public Health Association [23] for individual analytes.

3.1. Statistical analyses

One-way ANOVA was used to determine significant differences in spatial and temporal variation in nutrient concentration and physiochemical parameters in the Brah-

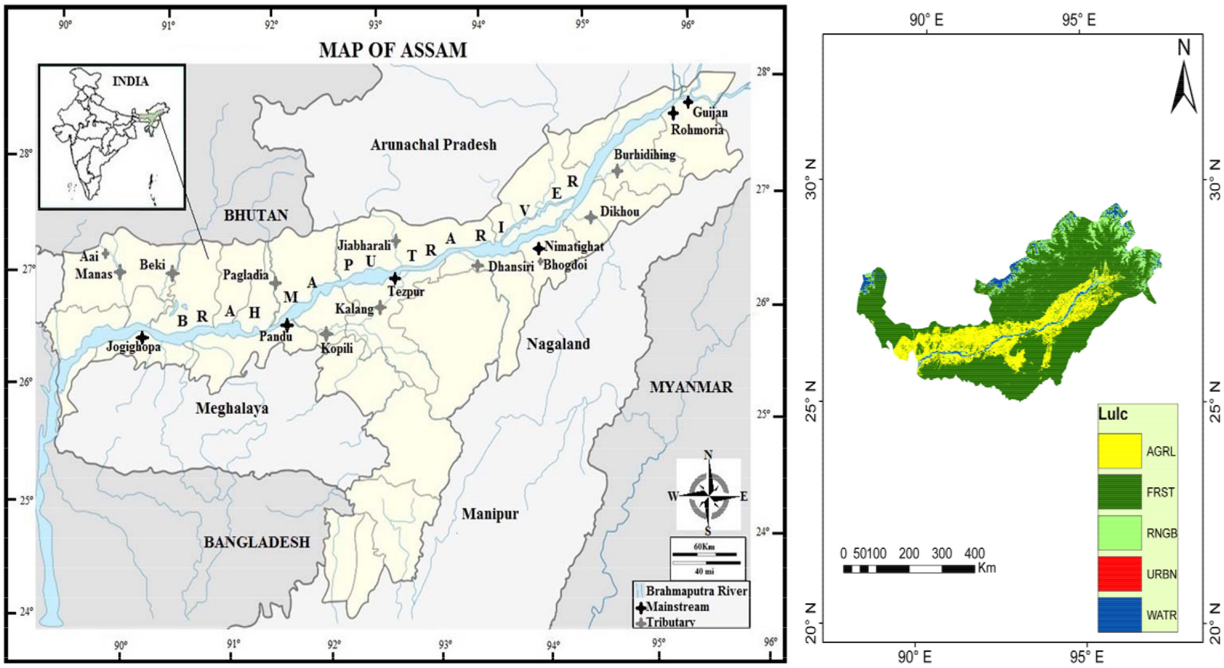

Fig. 1. Sampling sites along the stretch of Brahmaputra River and land-use land-cover patterns.

maputra river system. ANOVA results are reported as $F_{critical} = F_{calculated}$ with P level and the null hypothesis rejected if $F_{calculated} > F_{critical}$.

Multivariate analyses were performed using Statistical Package for Social Sciences (SPSS) version 21 after data standardization. Factor analysis was carried out for all the parameters to identify the factor controlling the nutrient chemistry in the river basin. Factor analysis is very useful for explaining temporal and spatial variation caused by natural and human factors linked to seasonality [24]. Hierarchical Cluster Analysis (HCA) for water samples is used widely in the classification of hydrochemical data of rivers. In this study, cluster analysis was performed using Ward's method with squared Euclidean distances as a measure of similarity for linkage and it produces the most distinctive groups.

4. Results and discussion

4.1. Descriptive analysis of dissolved nutrients and physicochemical attributes

The river carries a variety of ions, introduced from the atmosphere, land surface, and from the anthropogenic sources [25,26]; and hence are required to be monitored on regular basis. The composition of dissolved nutrients and physiochemical parameters in Brahmaputra River during the study period is given in Table 1. The pH was alkaline during the monsoon because the Brahmaputra floodplain is rich in weather able minerals, especially micas. The dissolved oxygen (DO) concentration was less than the minimum desirable limit of 4 mg L^{-1} at few sites indicating increase in the aquatic species. Midstream and downstream sites are more depleted with dissolved oxygen. A minimum of 5 mg L^{-1} DO is recommended as the optimum value for healthy environment for aquatic dwellers [8]. Decreased DO levels are indicative of bacterial abundance and excess biological oxygen demand (BOD) particularly due to untreated sewage, partially treated sewage, organic discharges, and anoxic discharges which consume DO. Parameters such as EC, TDS, HCO_3, Cl,SO_4, Na and K are below desirable limits of ambient water quality and hence decrease suitability of the water for recreational use.

Upstream PO_4^{3-} concentrations varied little during all months while midstream concentration was lower in July and August but increased in September (Fig. 2). Higher midstream PO_4^{3-} concentrations during periods of less rainfall implies that source of PO_4^{3-} is not agricultural runoff, instead it is a point source. The NO_3^- concentration is highest in the downstream during July. NO_3^- concentration in August remains more or less same from upstream to downstream. Overall higher NO_3^- concentrations were found at the end of the monsoon in September. Fig. 2 shows that the NO_3^- concentration is lowest in the midstream and highest downstream. Downstream sites are mostly located in the regions with high agricultural activities and that received more rainfall during monsoon; hence agricultural runoff can be the reason for elevated NO_3^- levels. The maximum NO_3^- found at site MS5 in Guwahati may be attributed to release of sewage from densely populated urban settlements. The relatively recent industrial growth and urbanization has led to pollution caused by disposal of industrial and municipal waste in and around Guwahati city which has consequently increased threat to the river Brahmaputra [26].

H_4SiO_4 concentration was higher in midstream during all the months as than in upstream and downstream. H_4SiO_4 is present in upstream in higher concentration except for the month of August where H_4SiO_4 is highest in downstream site (MS5). H_4SiO_4 is a major component of the total dis-

Table 1
Descriptive summary of nutrients and physicochemical parameters of the Brahmaputra and its tributaries

	July				August				September			
Parameter	Range		Mean ± Std. Dev		Range		Mean ± Std. Dev		Range		Mean ± Std. Dev	
pH	6.51	8.64	8.04	0.55	7.2	9.1	7.97	0.68	5.27	8.66	7.50	0.77
DO	3.4	8.86	6.82	1.74	3.53	9.77	6.39	1.6	3.41	9.06	6.55	1.36
ORP	–104	43.4	–32.99	38.34	–86.4	83.2	17.86	51.66	–83.4	80.5	1.75	59.30
EC	27	182	91.65	35.53	17	430	107.94	93.47	39	156	91.65	41.20
TDS	14	91	45.88	17.75	9	214	54.35	46.7	20	79	46.47	21.23
TSS	11	1098	240.12	250.36	4	256	102.88	80.94	4.0	256	97.53	82.53
Temp	22.82	32.9	27.38	2.78	23.22	33.83	27.34	2.71	25.47	31.13	28.10	1.65
HCO_3	5	115	51.76	29.68	35	190	75.88	34.74	30	175	86.18	42.67
PO_4^{3-}	0.1	0.6	0.3	0.2	0.1	0.6	0.3	0.1	BDL	0.5	0.2	0.2
NO_3^-	0.1	13.8	2.0	3.3	0.4	4.5	2.1	1.1	2.0	7.1	3.9	1.4
H_4SiO_4	2.55	11.86	6.81	2.68	3.9	17.9	8.84	3.56	3.97	18.17	7.08	3.25
SO_4^{2-}	12.13	87	29.37	19.1	13.63	48.88	23.61	8.86	12	40.88	22.43	8.48
Cl^-	35.5	120.7	49.28	19.68	28.4	63.9	48.86	11.47	14.2	42.6	25.48	7.96
Ca^{2+}	3.26	29.38	14.99	7.55	7.49	48.41	19.31	10.44	6.09	33.1	17.63	8.90
Mg^{2+}	1.41	12.11	4.7	2.99	2.11	27.36	6.86	5.8	1.9	18.05	6.31	3.95
Na^+	2.8	9.6	5.6	2.0	2.4	11.1	4.9	2.0	3.2	8.1	4.9	1.4
K^+	1.2	5.2	3.6	1.3	0.1	3.4	1.6	0.9	1.2	4.3	2.6	0.7
DIN/DIP	0.4	156.1	13.6	36.9	2.1	29.4	11.5	7.25	6.4	454.5	122.2	127.1
DSi/DIN	0.1	87.9	11.2	20.84	1.1	10.3	3.9	3.24	0.6	2.5	1.3	0.69

Note: All units are mg L^{-1}, except pH, EC (μS cm^{-1}) and temperature(°C). BDL = Below detection limit

solved solids found in waters resulting from the chemical weathering of soils and surficial rocks, which has important relationships with major nutrients and phosphorus in particular [27]. And it is also an essential nutrient for a group of microalgae, the diatoms. The H_4SiO_4 concentration is higher in tributaries in the mid region of the Brahmaputra mainstream.

TSS concentration is higher in upstream during beginning of monsoon while the concentration increases in midstream in August and September. Downstream have lower TSS concentration as compared to upstream and midstream. The downstream increase in the concentration of TSS is seen in the month of July but the trend is not observed in August and September. Heavy rains and fast-moving water are erosive and cause higher TSS concentrations, unless the additional particles are dispersed throughout large volumes of flood water [28]. Fig. 2 also suggests that TSS has highest concentration in both upstream and downstream tributaries probably because of higher flow rate as rainfall events are more in these regions as compared to tributary sites at TS5 and TS6 (Jiabharali and Kalang) which experienced little rainfall in 2014. Rivers originating in orogenic belts are characterized by very high suspended load (>80%) and much smaller bed load (2–15%) and have frequent, sinuous channels in small to medium size rivers, often alternating with straight reaches. The Brahmaputra is a multi-channel system, with moderate sinuosity in selected reaches [29].

Rainfall varies from the month of July to September. Fig. 2 shows downstream receive more rainfall except for the month of August. Midstream received more rainfall in July and August and low in September. Mountains act as an orographic barrier to the incoming air masses, thereby increasing rainfall. The southern (Assam) mountainous region under the basin where midstream portion of our study flows is comprised of parts of Naga hills, Mikir hills, North Cachar hills, Khasi hills and Garo hills. High relief and heavy concentrated precipitation produce high sediment yield in mountainous basins, which in turn acts as a carrier for adding the ions and nutrients to water bodies (Fig. 2). Fig. 3 shows the variation in the discharge of the Brahmaputra River at MS-4 during monsoon rainfall. It suggests that during May to September highest rainfall is received and subsequently highest discharged is recorded during these months.

4.2. Monthly and spatial variation in physiochemical attributes and nutrient concentrations

The monthly variation in the physicochemical parameter and nutrient concentration in the Brahmaputra river system is shown in Fig. 4. One way ANOVA analysis was conducted to determine the significance of monthly and spatial variation and results are presented in Table 2. The pH shows significant monthly variation (P = 0.006) due to different rainfall pattern across the entire stream. TDS and EC have shown no significant temporal variation with higher concentration in August (Table 2). Relatively higher concentration in August was may be due to low river flow compared to other months (Fig. 4). DO in Brahmaputra River shows no significant monthly variation. High concen-

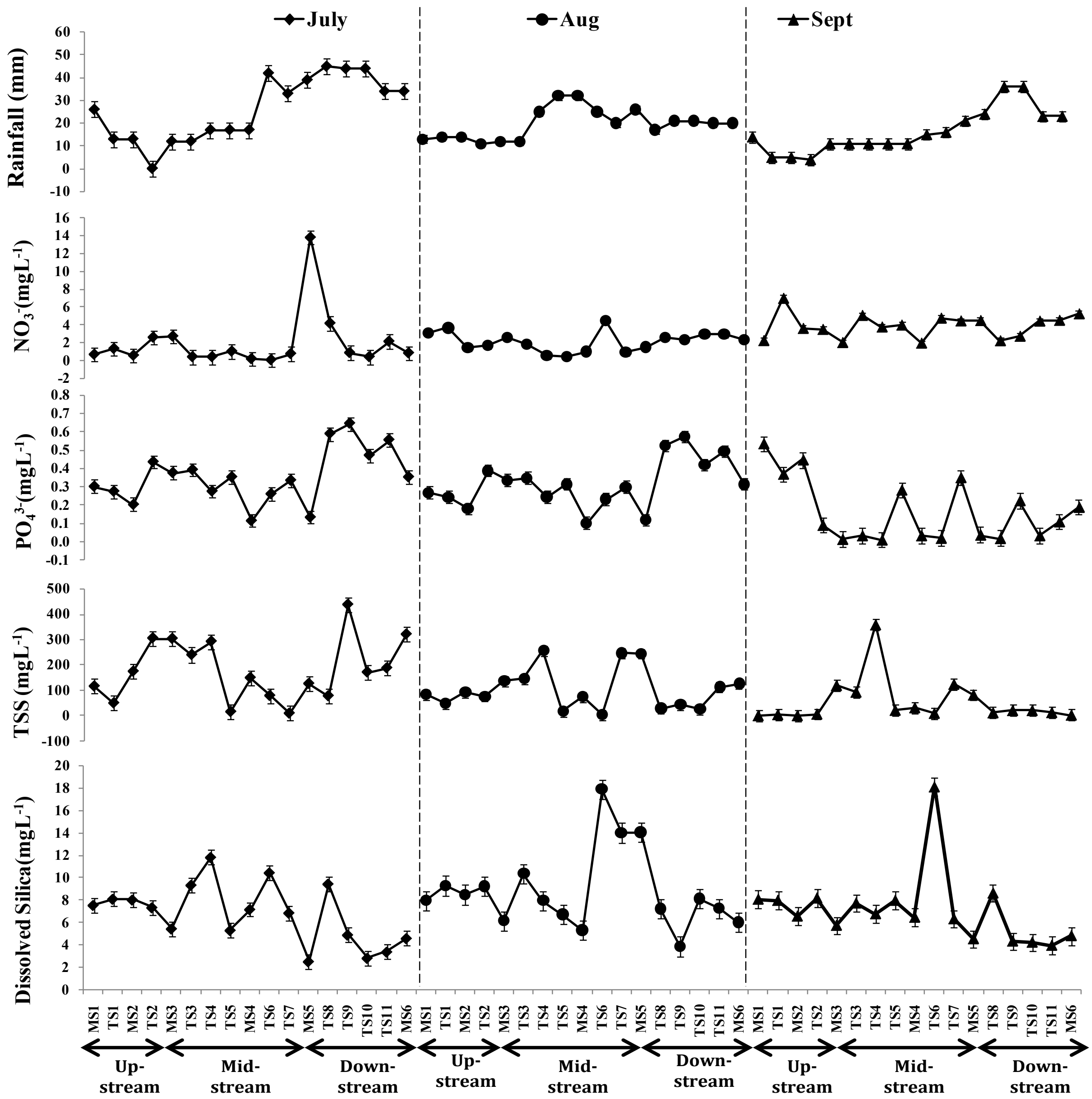

Fig. 2. Relationships between rainfall events and nutrient chemistry in the Brahmaputra River and its tributaries.

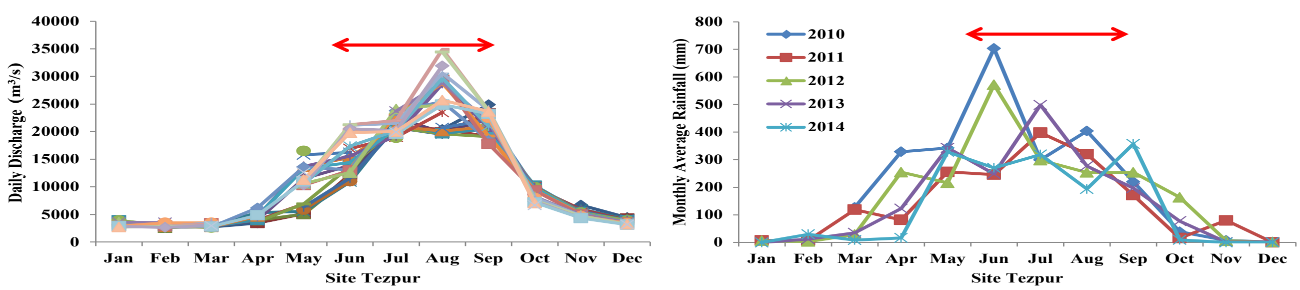

Fig. 3. Discharge-rainfall patterns in Tezpur (Brahmaputra River at mainstream site-4) during the Monsoon.

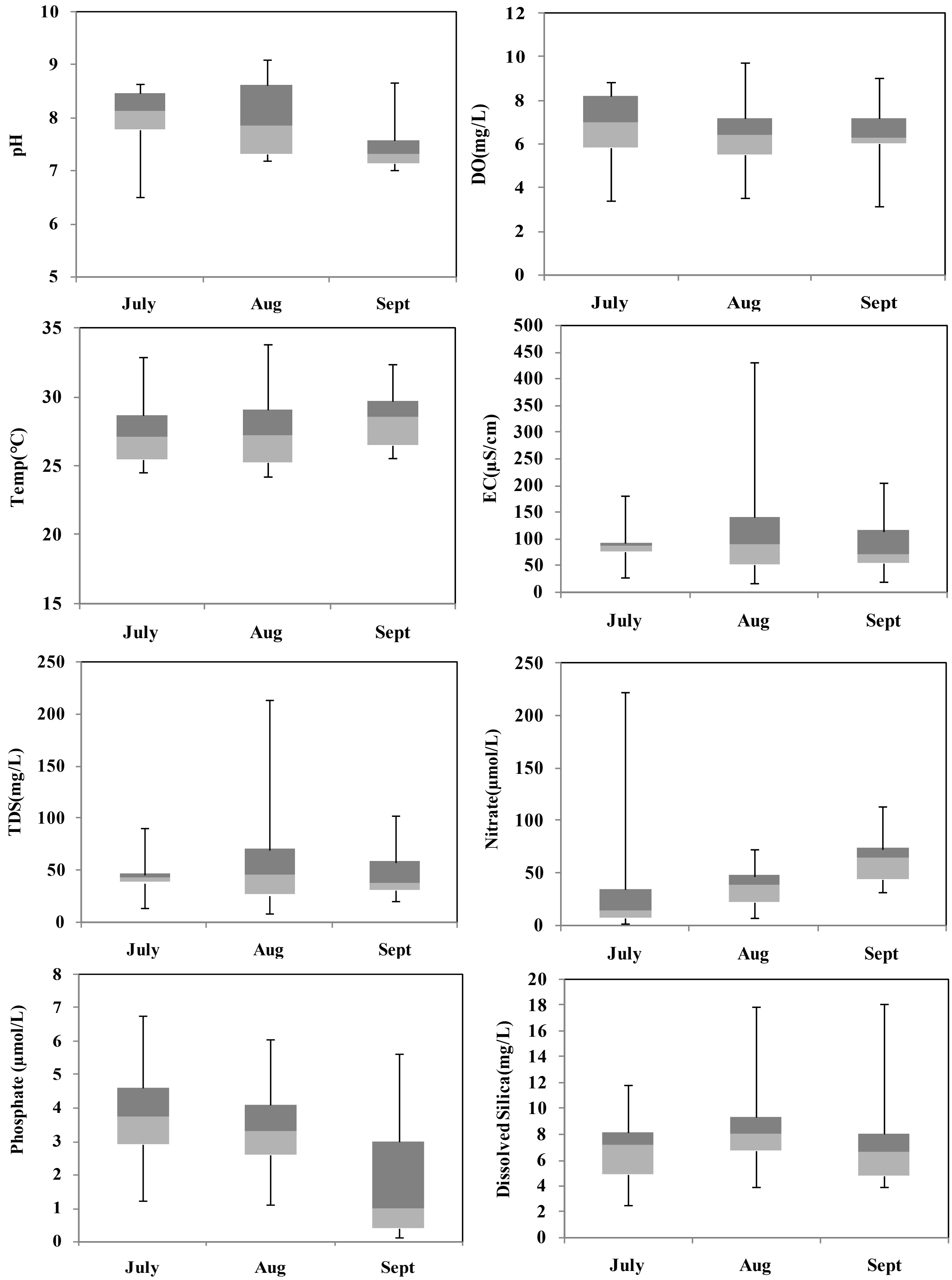

Fig. 4. Monthly variation in nutrient and associated physicochemical parameters in the Brahmaputra River and its tributaries.

Table 2
Analysis of variance (ANOVA) for spatial and temporal variation of measured parameters in Brahmaputra River water

Parameters	Unit	Spatial variation		Monthly variation	
		$F_{calculated}$*	p-value	$F_{calculated}$**	p-value
pH	–	0.721	0.75	5.676	0.006
TDS	mg/L	3.594	0.001	0.516	0.60
EC	µs/cm	3.679	0.001	0.594	0.56
DO	mg/L	5.066	3.53E-05	0.437	0.65
ORP	mV	0.950	0.53	10.92	0.001
Temperature	°C	6.297	3.53E-06	0.548	0.58
Nitrate	µmol/l	0.850	0.63	4.278	0.02
Phosphate	µmol/l	1.143	0.36	7.614	0.001
Silicate	mg/L	3.300	0.001	2.018	0.15

*$F_{critical}$ = 1.952; **$F_{critical}$ = 3.191

tration of TOC and low concentration of DO in downstream region reflects the high discharge of sewage waste into the river (Fig. 5a and Fig. 5b). In surface waters, TOC concentrations are generally less than 10 mg/L, unless the water receives wastes or is highly coloured due to natural organic material. Fig. 5b suggests that most of the sites have TOC concentration greater than 10 mg/L, which implies surface water is contaminated with organic wastes discharged by anthropogenic inputs. H_4SiO_4 and temperature showed no significant variation while oxidation reduction potential (ORP) (P = 0.001) showed significant monthly variation. Monthly variation in NO_3^- and PO_4^{3-} (P = 0.001) were significant and may be due to differential runoff conditions (Fig. 2). Elevated nutrient concentration found in some downstream sites may be related to anthropogenic activities such as agriculture (Assam is an agriculture-dominant state) and release of sewage from densely populated areas (Fig. 6), which is carried downstream by flood waters during extreme rainfall events.

The pH showed no significant spatial variation in Brahmaputra river system with relatively lower pH value was observed in upstream region (Fig. 7). EC showed significant spatial variation (P = 0.001) in Brahmaputra river system with relatively lower EC in midstream and decreasing downstream due to additions from both natural and anthropogenic sources in the catchment area by the tributaries (Fig. 7). TDS showed significant spatial variation (P = 0.001) in study area. The tributaries showed similar increasing trend for TDS as for EC in Brahmaputra river system (Fig. 7). Dissolved oxygen concentration showed significant spatial variations (P = 3.53E-05) with lowest oxygen concentration in midstream (Fig. 5). ORP value shows no significant variation. Significant spatial variation is shown by temperature (P = 3.53E-06). Elevated water temperature enhances phytoplankton community diversity, which is further supported by nutrient concentrations.

The spatial variation of dissolved nutrients NO_3^-, PO_4^{3-} and H_4SiO_4 is shown in Fig. 7. Variation in the NO_3^-, PO_4^{3-} and H_4SiO_4 data can be attributed to the relative change in the contribution from the anthropogenic sources and biological activities. H_4SiO_4 showed high spatial variability (P = 0.001 while that of NO_3^- and PO_4^{3-} show no significant variation (Table 2). Moving upstream to downstream there is a change in the catchment area geology, along with changes in the relative contribution from anthropogenic sources including agricultural activities, industrial effluents and domestic sewage discharge, resulting into wide spatial variation of nutrient concentration in river system

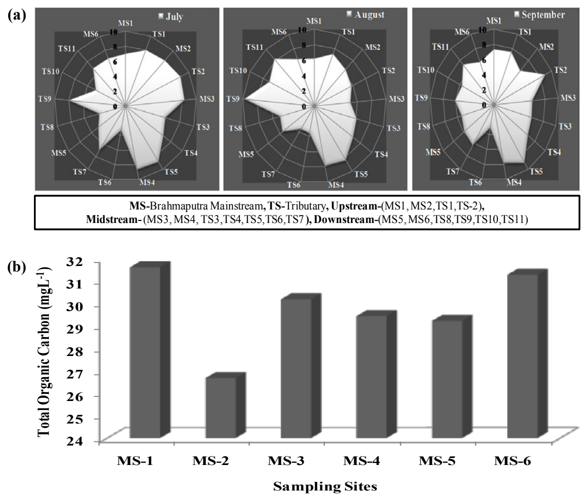

Fig. 5. Variation in (a) dissolved oxygen concentration and (b) total organic carbon distributionin the Brahmaputra River.

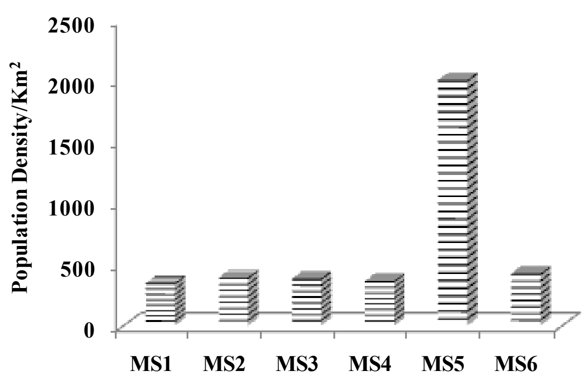

Fig. 6. Population density along the Brahmaputra River basin (2011 census).

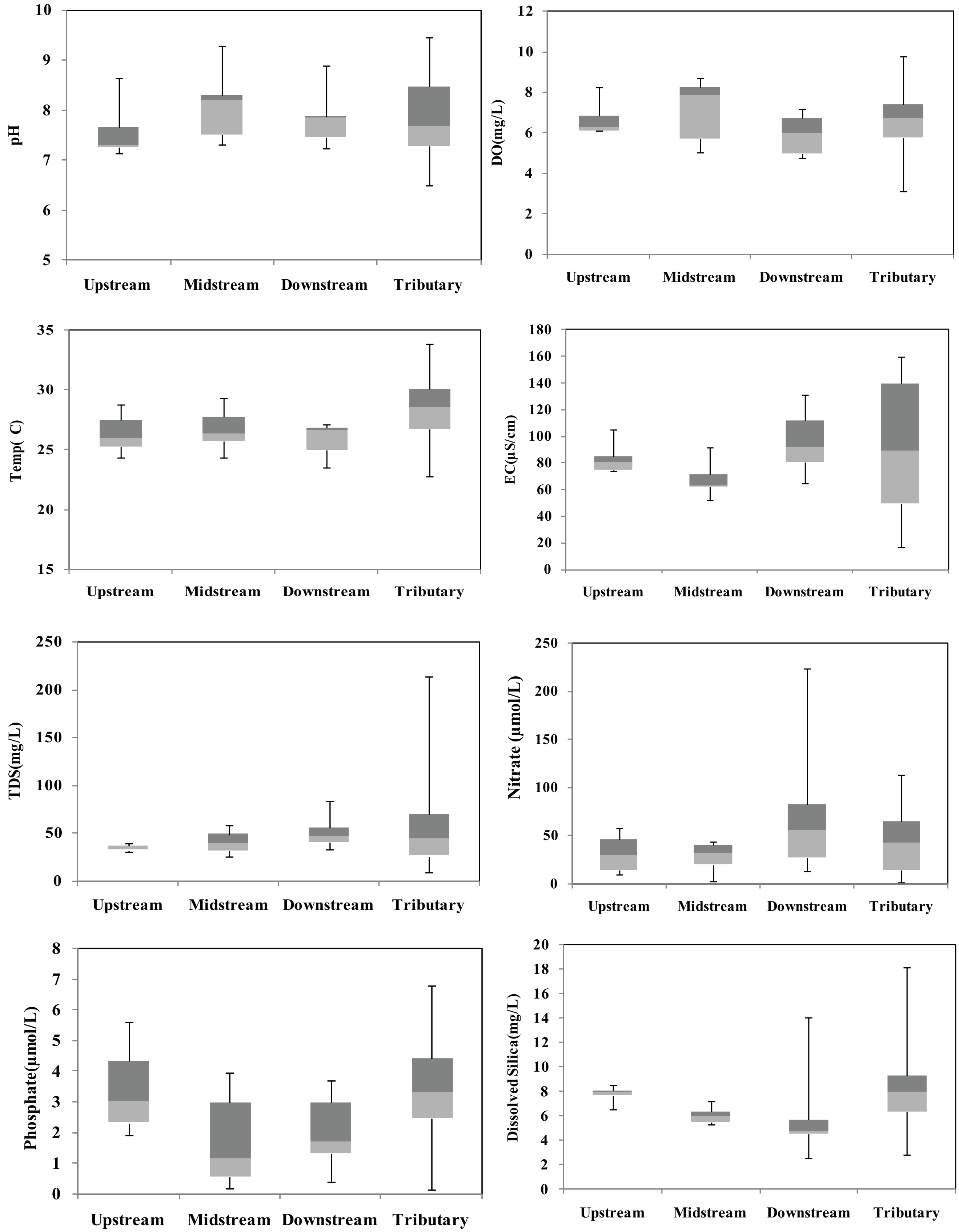

Fig. 7. Spatial variation in nutrient and associated physicochemical parameters in the Brahmaputra River and its tributaries.

[30]. NO_3^- concentration is relatively higher in downstream as compared to PO_4^{3-} contributed from high agricultural activity (fertilizer application) in that region. Runoff from land containing fertilizer and sewage contributes to high concentration of NO_3^- and PO_4^{3-} in the river water. H_4SiO_4 concentration was relatively lower downstream compared to the upstream stretch and tributaries (Fig. 7).

4.3. Factors controlling nutrient chemistry of Brahmaputra River

Four distinct factors were found to govern nutrient chemistry of the Brahmaputra surface water (Table 3). Factor 1 account for 25.03% of the variance, with highest loading by EC, TDS, HCO_3, Mg and Ca. This factor reflects processes responsible for imparting alkalinity to the river water. Factor 2 represents 16.08% of the variance with positive loading by temperature and H_4SiO_4, it is indicative of dissolution of H_4SiO_4 is affected by temperature variations and show negative loading for DO. Factor 3 shows variance of 15.10 % with loading by TSS, PO_4 and SO_4. This factor is indicative of sorption process as many organic (such as carbon) and inorganic pollutants (such as PO_4^{3-}) sorb to suspended solids, thus increasing pollutant concentration. Thus, sorbed pollutants (and solids) can be transported elsewhere in river and lake systems, subsequently resulting in the exposure of organisms to pollutants away from the point source. Factor 4 accounts for 8.64% of the variance and is loaded by pH, Cl, Na and K, indicating weathering of Feldspar.

Various approaches are being used to interpret the concealed variables that determine the variance of observed water chemistry of different surface water systems. The use of multivariate statistical techniques such as cluster analysis is useful when the number of variables are large and for easy and robust evaluation. In the present study the variables are clustered in three major groups based on maximum similar attributes among them (Fig. 8). The first cluster has EC, TDS, and Mg in close association while HCO_3 and Ca are distantly related,indicating the dominance of alkaline earth metal as major ions in the river. The second cluster is comprised of pH, PO_4, Cl and DO. This is indicative of phosphate dissolution as a pH-dependent process. The third cluster is formed between two large sub-groups comprising of NO_3, K and ORP; it suggests the source of NO_3 in surface water can be application of nitrogenous fertilizer such as potassium nitrate. TSS, SO_4, temperature, H_4SiO_4 and Na are clustered in the other subgroup, indicating the temperature dependent nutrient dissolution processes through chemical weathering of suspended solids [31], which are a rich source of various organic and inorganic species.

Table 3
Major factors governing nutrient chemistry of the Brahmaputra

	Component			
Parameter	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.03	–0.46	0.32	0.50
DO	–0.09	–0.76	–0.09	0.09
ORP	0.19	–0.08	–0.45	–0.75
EC	0.93	0.14	0.10	0.09
TDS	0.92	0.14	0.11	0.10
TSS	–0.02	0.08	0.78	0.38
TEMP	0.13	0.67	0.23	–0.16
HCO_3	0.84	–0.06	–0.26	–0.01
PO_4^{3-}	0.14	–0.29	0.53	0.08
NO_3^-	0.21	0.02	–0.13	0.33
H_4SiO_4	–0.07	0.81	–0.14	0.04
SO_4^{2-}	–0.11	0.23	0.85	–0.08
Cl^-	0.11	–0.03	–0.07	0.82
Ca^{2+}	0.87	–0.25	–0.02	0.05
Mg^{2+}	0.91	0.08	–0.09	–0.03
Na^+	–0.15	0.43	0.24	0.57
K^+	0.05	–0.06	0.12	0.96
Eigen value	4.25	2.73	2.57	1.47
% of variance	25.03	16.08	15.10	8.64
Cumulative %	25.03	41.11	56.21	64.85

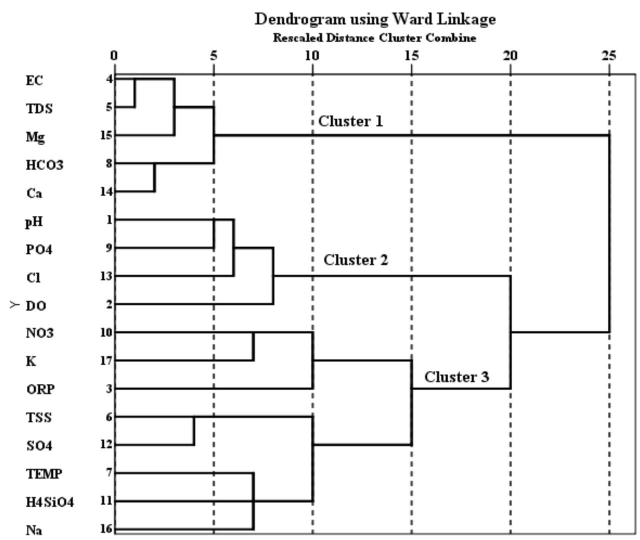

Fig. 8. Q–mode hierarchical cluster analysis to identify closely associated variables with nutrients.

4.4. Assessment of dissolved nutrient elemental ratio

Huge fluxes of particulate organic and inorganic P, around 0.2 and 1.5 million tonnes, respectively, is transported from the Indian rivers to the ocean each year [32,33]. According to Meybeck [34] particulate P (organic and inorganic) constitutes 95% of the total P transported by rivers. Global particulate N transport by rivers amounts to 33 million tonnes per year, more than 80% of which occurs in rivers with high suspended matter concentrations such as the Ganges, Brahmaputra, Mekong and Huang he [35]. Galloway [36] predicted that by the year 2020 two-thirds of the increase in anthropogenic N-fixation will take place in Asia, accounting for over half of the global anthropogenic N-fixation during that time. Thus, considering the rapidly changing land use pattern in the tropics and unequal population distribution, substantial transport of N by the rivers to the sea can be anticipated. Table 4 shows the variation in nutrient chemistry in the world's major river systems. Higher NO_3 and PO_4 concentrations are reported in tropical/subtropical and temperate rivers and are mostly derived from human activities [33], with a minor contribution from natural sources. NO_3^- and PO_4^{3-} are generally low in relatively pristine river basins with less anthropogenic influence.

Phytoplankton requires DIN and DIP to sustain growth, and a DIN/DIP elemental ratio of 16:1 is termed as Redfield ratio [37]. A 1:1 DSi/DIN ratio is optimum for diatom growth [38]. Increase in loading of nutrient in water body not only affects the phytoplankton biomass but also deteriorate its quality [3]. Increased human activities leading to nutrient pollution, often elevates the DIN:DIP ratio.

In the Brahmaputra River and its tributaries the DIN/DIP molar ratio ranged from of 0.4–156, with an average of 13.6 ± 36.9 in July, while DIN/DIP molar ratio decreased to 2.1–29.4 with an average of 11.5 ± 7.25 in August and the ratio is 6.4–454.5 with an average of 69.0 ± 66.39 in September (Table 1). The average DIN/DIP ratio was above the Redfield ratio (16:1) in the Brahmaputra river system, however a few locations showed relatively lower DIN/DIP ratios (<10). On an average the DIN/DIP ratio calculated for the Brahmaputra River (excluding tributaries) was greater than 22 in July and September (Fig. 9).

The DSi/DIN molar ratio varied from 0.1 to 87.9 with average of 11.2 ± 20.84 in July, and from 1.1–10.3 with an average of 3.9 ± 3.24 in August and in September the DSi/DIN molar ratio is 0.6–2.5 with an average of (1.3 ± 0.69) of the Brahmaputra River system (Table 1).The average DSi/DIN molar ratio was greater than 1. When the DSi/DIN molar ratio decreases below 1:1, growth of harmful phytoplankton species becomes more prominent over diatom [39]. Most of the stretches of the Brahmaputra River had DSi/DIN molar ratios greater than 1.

Table 4
Average nutrient (N, P, Si) concentrations in the Brahmaputra and other major world rivers

River	NO_3 (μM)	PO_4 (μM)	$Si(OH)_4$ (μM)	DIN/DIP Ratio	Reference
Amazon	10	0.7	115	14	[40]
Changjiang	70.3	0.83	102	84	[41]
Lena	0.7–10	0.46	66	<10	[42,43]
Mackenzie	2.42	0.10	48	24	[44,45]
Mississippi	114	7.7	127	15	[46,47]
Ob	56	2.3	164	24	[42]
Trinitya	39.2	1.85	82 ± 35	21	[48]
Yenisei	26	0.4	107	65	[42]
Yukon	1.4–10.7	0.25–8.75	25–125	–	[49]
Yukon	2.43	0.05	82	69	[50]
Brahmaputra	42.9	2.96	78.9	30.65	Present study

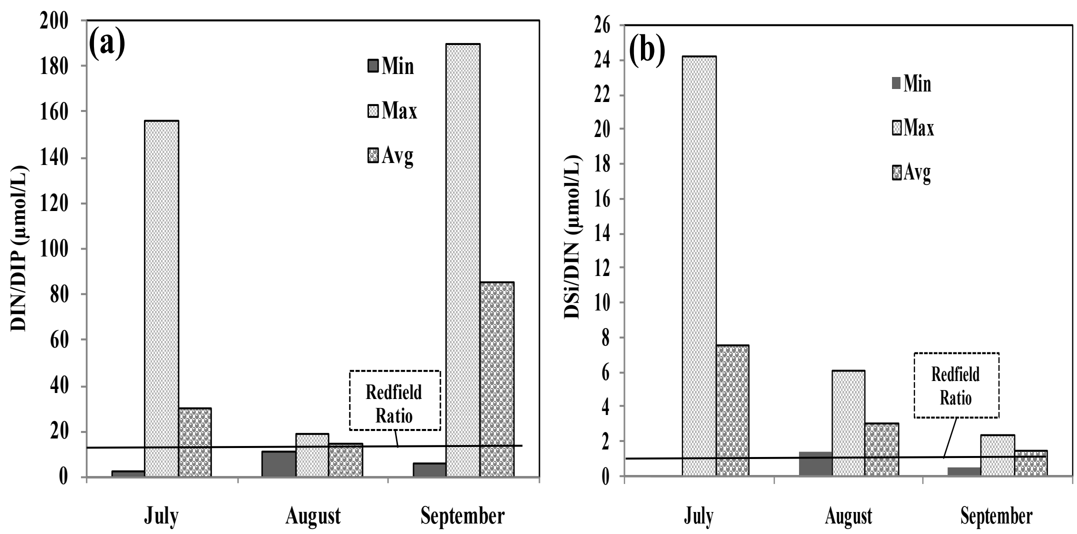

Fig. 9. Redfield (2014) (a) DIN:DIP (μmol/l) and (b) DSi:DIN (μmol/l) ratios for the Brahmaputra River (excluding tributary).

5. Conclusion

A descriptive analysis of the Brahmaputra River water revealed that most of the water quality are suitable for useful purposes like irrigation. The DO is used as an indicator of healthy environment of an aquatic system. DO was depleted at a few midstream and downstream sites which also contained higher nutrient concentration, indicating the influence of untreated sewage or partially treated sewage, organic discharges, and anoxic discharges. The high TOC concentration in all mainstream sites substantiates the above findings. Population density graphs show that densely populated regions have higher concentrations of NO_3^-, indicating anthropogenic inputs. However population density is not related to sites having higher PO_4^{3-} concentration, indicating inputs from point sources present near the mainstream river such as ammonia-urea fertilizer manufacturing industries. The sewage treatment capacity of Assam State is 1.37 MLD in contrast to sewage generation of 703 MLD. This suggests 701.63 MLD of untreated sewage discharged to water bodies is responsible for deteriorating water quality. Therefore establishment of more sewage treatment plants will greatly reduce the pollution levels. Rainfall has significant impact on nutrient concentration; at sites with low rainfall higher nutrient concentration were observed, due to displacement of nutrients through surface runoff during rainfall events. The comparative table suggests that tropical/subtropical and temperate rivers usually have higher NO_3^- and PO_4^{3-} concentrations due to human intervention. Cluster analysis suggests probable source material and process related to nutrient release in the Brahmaputra River. Thus water quality of the Brahmaputra River is indicating the potential threat imposed by the unmonitored release of both organic and inorganic pollutants into the streams. Unregulated release of these pollutants may not show up localized impact but pose serious impacts on mega scale. Therefore not only seasonal but temporal monitoring is necessary to determine the impacts.

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