



# Spatio-temporal variation of major ion chemistry and nutrient stoichiometry in a tropical monsoonal estuary: insight into biogeochemical processes

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## Abstract

Major ions and nutrient chemistry of surface water from the Devi river estuary, eastern India has been studied in order to understand the governing biogeochemical processes. Concentration of Na, K, Ca, Mg, Cl, SO<sub>4</sub> and PO<sub>4</sub> increases toward higher salinity; however, NO<sub>3</sub> and dissolved silica (DSi) decreases from upper to lower estuary. All major ions, except NO<sub>3</sub> and DSi, show the highest and lowest concentration in summer and monsoon season, respectively. Increased surface runoff has resulted in the highest concentration of NO<sub>3</sub> and DSi in the monsoon period. The Na, Cl, SO<sub>4</sub>, NO<sub>3</sub> and PO<sub>4</sub> ions show conservative mixing behavior in the estuary throughout the year. Non-conservative behavior of DSi is attributed to the combined process of mineral weathering and biological removal by diatoms. Enrichment and depletion of Ca and Mg in the estuary is owed to carbonate mineral precipitation and dissolution processes. Decreasing carbonate saturation indices (SI) with reducing pH accompanied by lowering of DO% suggests the influence of organic matter degradation on the carbonate precipitation and/or dissolution potential. Nutrient stoichiometric ratios—NO<sub>3</sub>:PO<sub>4</sub>, DSi:PO<sub>4</sub> and DSi:NO<sub>3</sub>—are found to vary spatially and seasonally as a result of differences in geochemical processes prevailing in the fresh- and marine-water environment. A prominent PO<sub>4</sub> limitation is observed in the upper estuary during summer and winter. However, this limitation reduces toward the lower estuary owing to precipitation of Fe-sulfide under the influence of higher salinity. In contrast, the influx of PO<sub>4</sub>-limited freshwater into the estuary controls the nutrient stoichiometric ratios in the monsoon season. The spatial variation of chlorophyll concentration in the estuary is in accordance to the nutrient stoichiometric ratios. Thus, this study emphasizes on the role of unique biogeochemical processes in controlling the spatial and seasonal distribution of major ions and nutrient stoichiometry in a tropical estuarine system.

**Keywords** Major ions · Nutrient limitation · Saturation index · Mixing behavior · Surface water · Devi estuary

## Introduction

Composition of major ions and nutrients in surface water of estuary provides important insight into different biogeochemical processes (Bianchi 2007; Shulkin et al. 2018). Estuaries represent a major fluvio-marine environment where biogeochemical characteristic is quite distinct from fresh river water and saline ocean water (Pritchard 1952). Therefore, dissolved constituents carried by river undergo major biogeochemical modification in the estuary (Zhang

et al. 2020). Mineral precipitation and dissolution play a significant role in the exchange of ionic species between the dissolved and solid phase, which governs the water chemistry (Stumm and Morgan 2012). The extent of precipitation and dissolution of minerals is primarily controlled by physicochemical parameters such as pH, salinity, dissolved oxygen (DO) and redox condition, which are highly variable in estuarine system.

Estuaries receive a large quantity of nutrients such as NO<sub>3</sub>, PO<sub>4</sub> and dissolved silica (DSi) through fluvial inputs (Yin et al. 2004). Addition and/or removal of nutrients has pronounced effect on the phytoplankton and coastal ecology (Domingues et al. 2011). Differences in water discharge influence the distribution of physicochemical parameters, nutrients and subsequently the primary productivity in tropical monsoonal estuaries (Mourão et al. 2020). Although

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fresh- and marine-water dominated systems are usually found to be limited by  $\text{PO}_4$  and  $\text{NO}_3$ , respectively (Blomqvist et al. 2004), various studies have recently reported contrasting observation (Sterner 2008; Karthik et al. 2020). These deviations in nutrient limitation have been attributed to several mechanisms that vary both spatially and temporally (Das et al. 2017). Moreover, in the last few decades, inputs of nutrients by anthropogenic activities have increased significantly which in turn severely altered the nutrient stoichiometry of estuaries (Liu et al. 2009; Shulkin et al. 2018). Hence, it is important to assess the fate of nutrients in estuarine systems in order to understand their ecology.

Globally, intensive research has been carried out to assess the major ion chemistry and nutrient dynamics in estuaries and coastal water bodies (Ramanathan et al. 1993; Patra et al. 2012; Wang et al. 2009; Zhang et al. 2020). Most of these studies are focused toward the behavior of ionic species under the influence of estuarine mixing processes. Some studies have highlighted the importance of biological activities along with physico-chemical processes in governing the behavior of major ions and nutrients (Hamilton et al. 2006; Mora et al. 2017; Tishchenko et al. 2018). Furthermore, studies conducted in Indian estuaries have mainly focused on a few selected major ions and/or nutrients; however, their seasonal behavior has rarely been studied and discussed (Borole et al. 1979; Gopal et al. 2018; Muthusamy et al. 2021). Thus, this paper aims to evaluate the spatial and seasonal distribution of major ions along with nutrient stoichiometry in the Devi river estuary, east coast of India.

## Study area

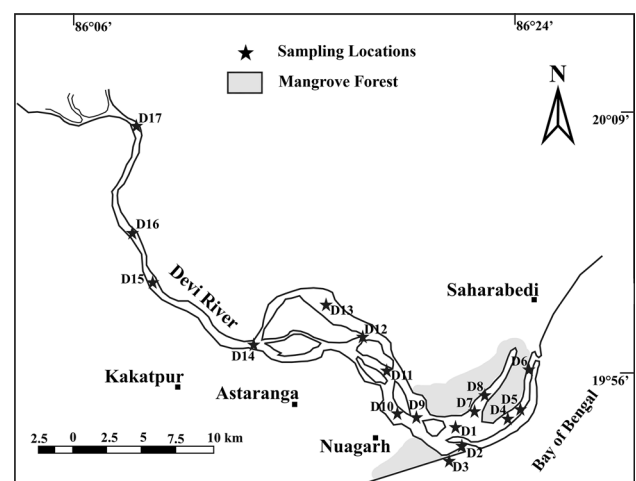
The Devi river estuary, situated in the east coast of India, is formed by the principal distributary of the Mahanadi, which is the third largest peninsular river in India. The Devi river traverses through Cuttack, a highly populated city of Odisha, and receives large amounts of untreated urban and industrial wastes (Pradhan et al. 2009; Chandramouli and General 2011). This river discharges approximately 36% of the total water discharge of the Mahanadi river into the Bay of Bengal near Nuagarh, Odisha (Mishra and Subhalaxmi 2018). The estuary is surrounded by dense mangrove forests and stretches a longitudinal distance of nearly 40 km, roughly covering an area of 34 sq. km. Water depth in the estuary varies between 9 to 14 m. This semi-diurnal, micro-meso tidal estuary is partially-mixed in terms of depth wise mixing of saline- and fresh-water (Mishra et al. 2011; Sundaray et al. 2011; Akhtar et al. 2021). Swell waves of height ranging from 1 to 3 m dominate the coast of the estuary (Kumar and Bhattacharya 2004).

The Devi estuary is characterized by a tropical climate with average air temperature ranging from 14 °C to 38 °C.

This tropical estuary receives 70% of its rainfall from southwest monsoon occurring during the months from June to October. The estuary hosts a rich biodiversity consisting of various species of fishes, crabs, shrimps and a diverse range of mangrove trees (Pramanik 2019). It also serves as a sporadic nesting ground for the endangered Olive Ridley turtles (Mohanty et al. 2008). Several species of diatoms and dinoflagellates has been reported in the offshore water of Devi river estuary (Baliarsingh et al. 2016). Pradhan et al. (2009) assessed the coastal water quality off Devi estuary and found that dissolved  $\text{PO}_4$  and DSi were derived from natural sources whereas anthropogenic activities controlled the concentration of nitrogenous species.

## Methodology

Systematic sampling was conducted in the Devi river estuary during May-2018 (summer), September-2018 (monsoon) and February-2019 (winter). Surface water samples were collected in triplicates from mid-channel at 17 different locations covering the entire estuary (Fig. 1). The collected water samples were filtered in-situ using 0.45  $\mu\text{m}$  cellulose nitrate membrane, split into two aliquots and stored in pre-washed LDPE bottles. Ultrapure  $\text{HNO}_3$  was added dropwise to acidify one of the aliquots to bring  $\text{pH} < 2$  for the analysis of cations whereas the non-acidified fraction was stored for the measurement of Cl,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{PO}_4$  and dissolved silica (DSi) concentrations. The fractions were refrigerated until further analysis. All the analyses were performed thrice within a week of sampling, and reported the mean value. Concentration of Na and K were measured by flame photometric method using Microprocessor Flame Photometer-1382. Atomic Absorption Spectrophotometry (Perkin



**Fig. 1** Sampling sites of surface water in the Devi river estuary, eastern India

Elmer, Analyst 200) was used to determine Ca and Mg concentrations. Ion selective electrode (Thermo Scientific Orion 5 star) was used for the analysis of Cl. Concentrations of SO<sub>4</sub> was determined by turbidimetric method. The concentration of NO<sub>3</sub>, PO<sub>4</sub> and DSi was determined following colorimetric method (Grasshoff et al. 1999). The accuracy and precision of the analysis was found to be ± 10%. The saturation index of dolomite (SI<sub>Dol</sub>) was evaluated using PHREEQC software.

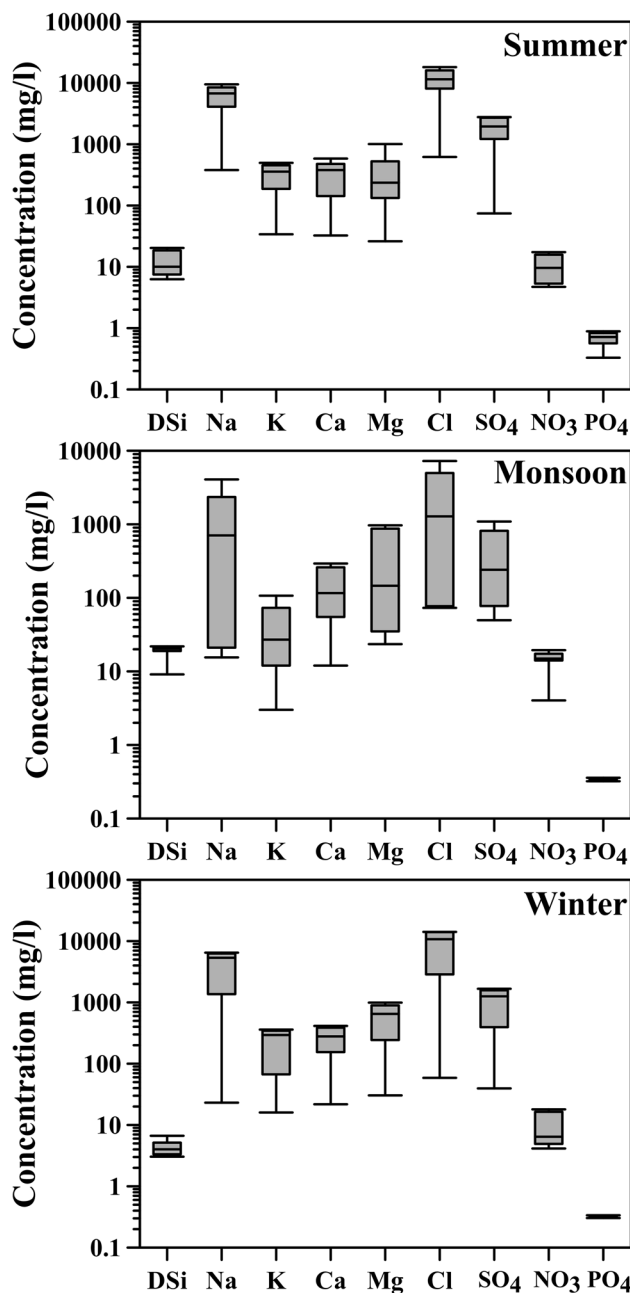
## Results and discussion

### Major ion chemistry

Major ion concentrations in the surface water of Devi River estuary are given in Table 1. Sodium was the most dominant cation having a concentration of 3593 ± 3105 mg/l during the study period (Fig. 2; Table 1). Concentration of Mg ranged from 26 to 1006 mg/l, 24 to 967 mg/l and 30 to 992 mg/l during summer, monsoon and winter seasons, respectively. Potassium was the least abundant cation, and varied between 34 and 497 mg/l during summer, 3 and 107 mg/l in monsoon, and 16 and 360 mg/l in the winter period. The dissolved Ca concentration in the estuary ranged from 12 to 584 mg/l. Chloride was the most abundant anion in the estuarine water with a concentration of 7107 ± 6504 mg/l. The PO<sub>4</sub> concentration was found be the lowest, and varied between 0.30 and 0.89 mg/l. Thus, the major ion concentrations in the surface water are in the order of: Cl > Na > SO<sub>4</sub> > Mg > Ca > K > NO<sub>3</sub>, DSi > PO<sub>4</sub>. The observed concentrations are well within

**Table 1** Concentration of major ions in the surface water of Devi River estuary (Unit: mg/l)

	Summer	Monsoon	Winter
Na	5927.65 ± 3063.17 (379.00–9495.00)	1056.34 ± 1235.65 (15.50–4063.00)	3796.08 ± 2561.71 (23.10–6478.00)
K	298.12 ± 159.63 (34.00–497.00)	37.33 ± 31.91 (3.00–107.00)	220.41 ± 136.69 (16.00–360.00)
Ca	316.78 ± 186.23 (32.40–584.00)	156.59 ± 108.87 (12.00–293.00)	250.98 ± 131.67 (21.80–412.70)
Mg	352.55 ± 288.39 (26.10–1006.00)	296.16 ± 359.86 (23.50–967.00)	543.79 ± 344.31 (30.40–991.70)
Cl	10,964.88 ± 5747.30 (619.00–18,123.00)	2075.14 ± 2367.06 (73.00–7240.00)	8281.06 ± 5635.36 (58.70–14124.00)
SO <sub>4</sub>	1829.96 ± 953.76 (74.27–2774.00)	358.55 ± 344.50 (49.61–1090.81)	949.63 ± 599.28 (39.52–1669.1)
NO <sub>3</sub>	9.61 ± 4.78 (4.71–17.38)	13.93 ± 4.60 (4.03–19.43)	9.78 ± 5.46 (4.13–17.98)
PO <sub>4</sub>	0.67 ± 0.21 (0.33–0.89)	0.33 ± 0.01 (0.32–0.36)	0.32 ± 0.01 (0.30–0.34)
SiO <sub>2</sub>	11.81 ± 5.12 (6.29–20.32)	18.31 ± 4.55 (9.10–21.64)	4.16 ± 1.10 (3.04–5.96)



**Fig. 2** Seasonal variation in the concentration of major ions in Devi river estuary

the range obtained in other global estuaries (Cohen et al. 1999; Patra et al. 2012; Zhang et al. 2020).

### Spatial and seasonal distribution

All major ion concentration, except NO<sub>3</sub> and DSi, are found to increase toward the mouth of the estuary, and showed significant positive correlations with salinity in all seasons (Figs. 3, 4, 5; Table S1). Similar behavior of these ions has been reported in other estuaries (Ramanathan et al. 1993;

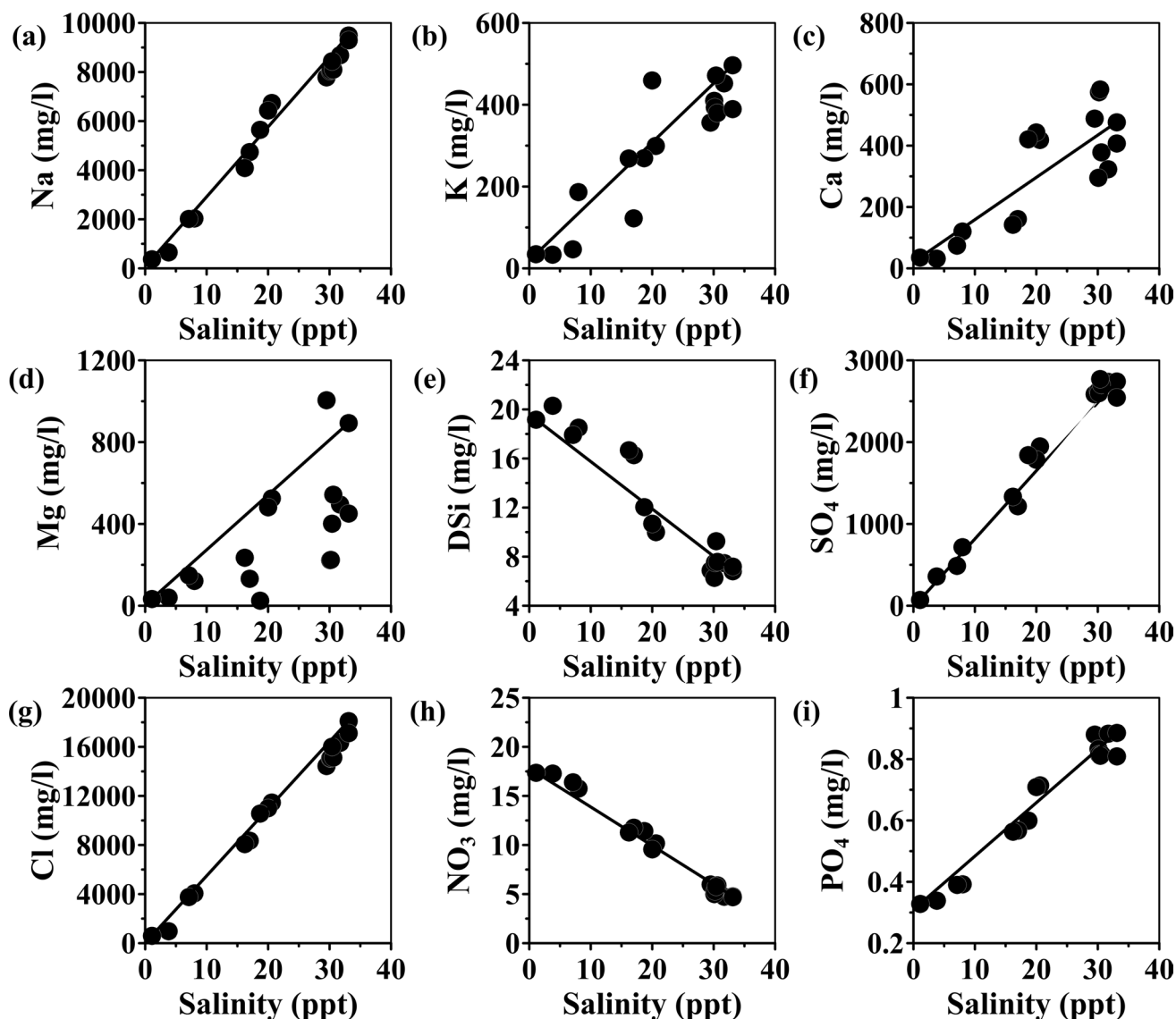


Fig. 3 Spatial distribution of major ions during summer season

Kumar et al. 2015; Wang et al. 2009). Concentration of  $\text{NO}_3$  and DSi decreases from upper to lower estuary. This is due to the fluvial inputs of  $\text{NO}_3$  and DSi to the estuary. Domestic sewage, manure and agricultural fertilizers contribute largely to the  $\text{NO}_3$  concentration in rivers (Chen et al. 2021). However, primary producers and microbial denitrification rapidly utilize this  $\text{NO}_3$  in the ocean water (Singh and Ramesh 2011; Bartoli et al. 2021). This causes lower  $\text{NO}_3$  concentration toward the mouth of the estuary. The DSi in rivers and coastal waters are mainly derived by weathering and erosion of continental crust (Tréguer and De La Rocha 2013). Biological uptake of DSi by diatoms removes a significant part of this riverine DSi, which results in a decrease in its flux to the ocean (Tréguer et al. 1995). Hence, ocean water generally has 10–15 times lower concentration of DSi

as compared to river water (Bien et al. 1958). Thus, the mixing of these two water masses results in a strong negative correlation between DSi and salinity in the estuary. Similar decrease in concentration of  $\text{NO}_3$  and DSi with increasing salinity have been observed in various other studies (Padmavathi and Satyanarayana 1999; Fatema et al. 2015; Sanders and Laanbroek 2018).

Seasonally, significantly higher concentration of Na, K, Ca, Cl,  $\text{SO}_4$  and  $\text{PO}_4$  have been observed during summer period in comparison to winter while the lowest concentrations are found in monsoon season (Fig. 2). Low water discharge during the dry seasons (summer and winter) leads to greater residence time. This causes the dissolved ionic species to be retained within the estuary (John et al. 2020). Also, higher temperatures in summer results in the increased rates

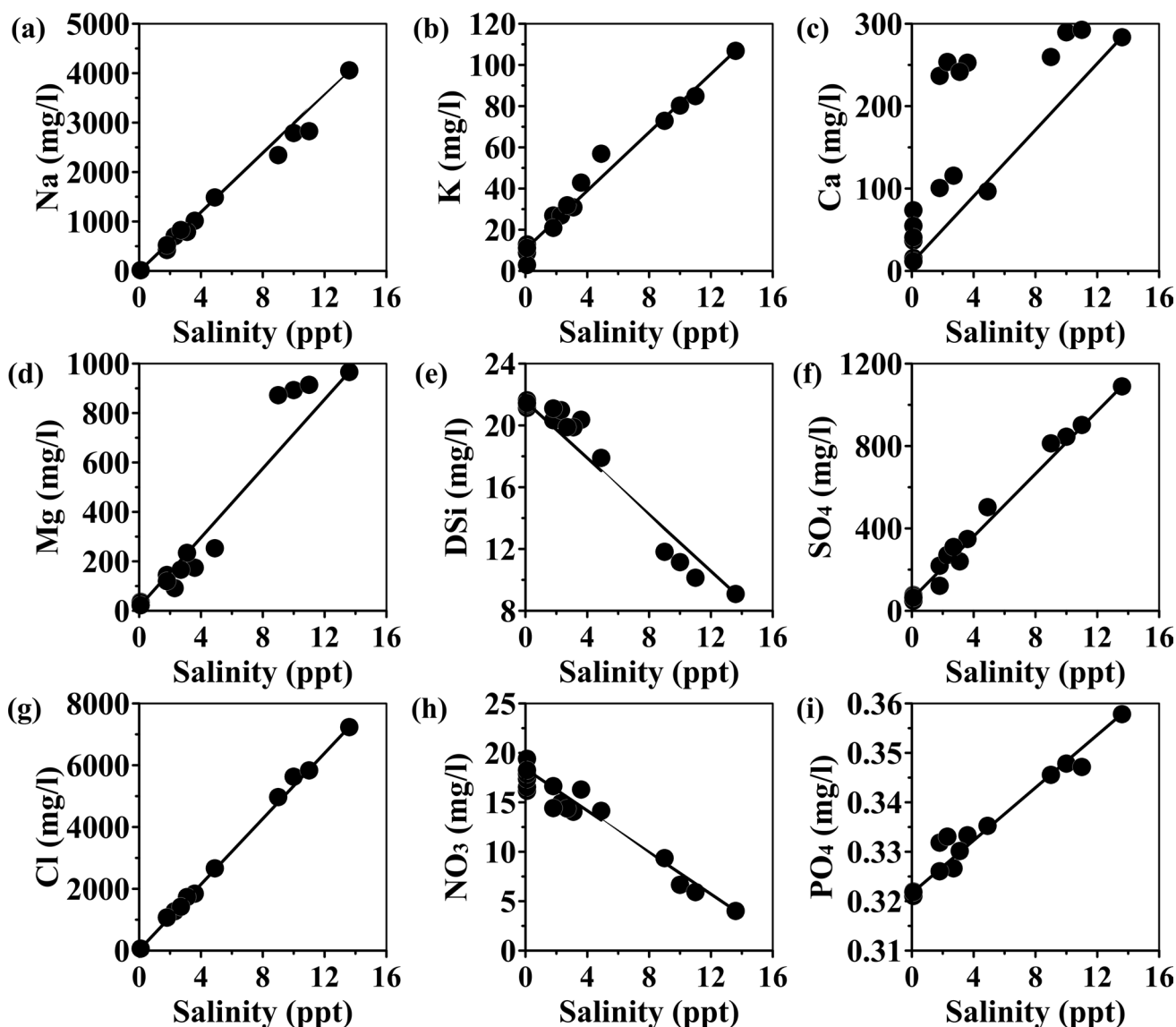


Fig. 4 Spatial distribution of major ions during monsoon season

of evaporation over precipitation (Montagna et al. 2018). Thus, the combined influence of lower freshwater input and higher evaporation rates have led to peak concentration of these ions in surface water during summer. On the other hand, increased precipitation and high freshwater discharge during monsoon season has a diluting effect on these major ions and causes a reduction in ionic concentration during monsoon (Sumner and Belaine 2005). However, the concentrations of  $\text{NO}_3$  and DSi are found to be relatively lower in the dry periods in comparison to the wet period. Greater particle supply via increased erosion rates mostly occur during monsoon period (Mangalaa et al. 2017). This increases the greater availability of silicate minerals for dissolution, which releases DSi into the water column (Asano et al. 2003; Sospedra et al. 2018). Significantly, higher terrestrial runoff

during monsoon have led to increased nitrate concentrations (Hershey et al. 2021). Such pattern in seasonal variation of major ion chemistry has been observed in other estuaries (Sarin et al. 1985; Jordan et al. 1991; Padmavathi and Satyanarayana 1999).

**Saturation indices of minerals**

The saturation index (SI) is a theoretical indicator for understanding the dissolution and/or precipitation potential of a mineral in an aqueous system. It is estimated using the ionic activity potential (IAP) and solubility product ( $K_{sp}$ ) following Eq. 1. When  $SI < 0$ , the solution is considered to be under-saturated with respect to the mineral, and leading to its dissolution. However, when  $SI > 0$ , the solution is



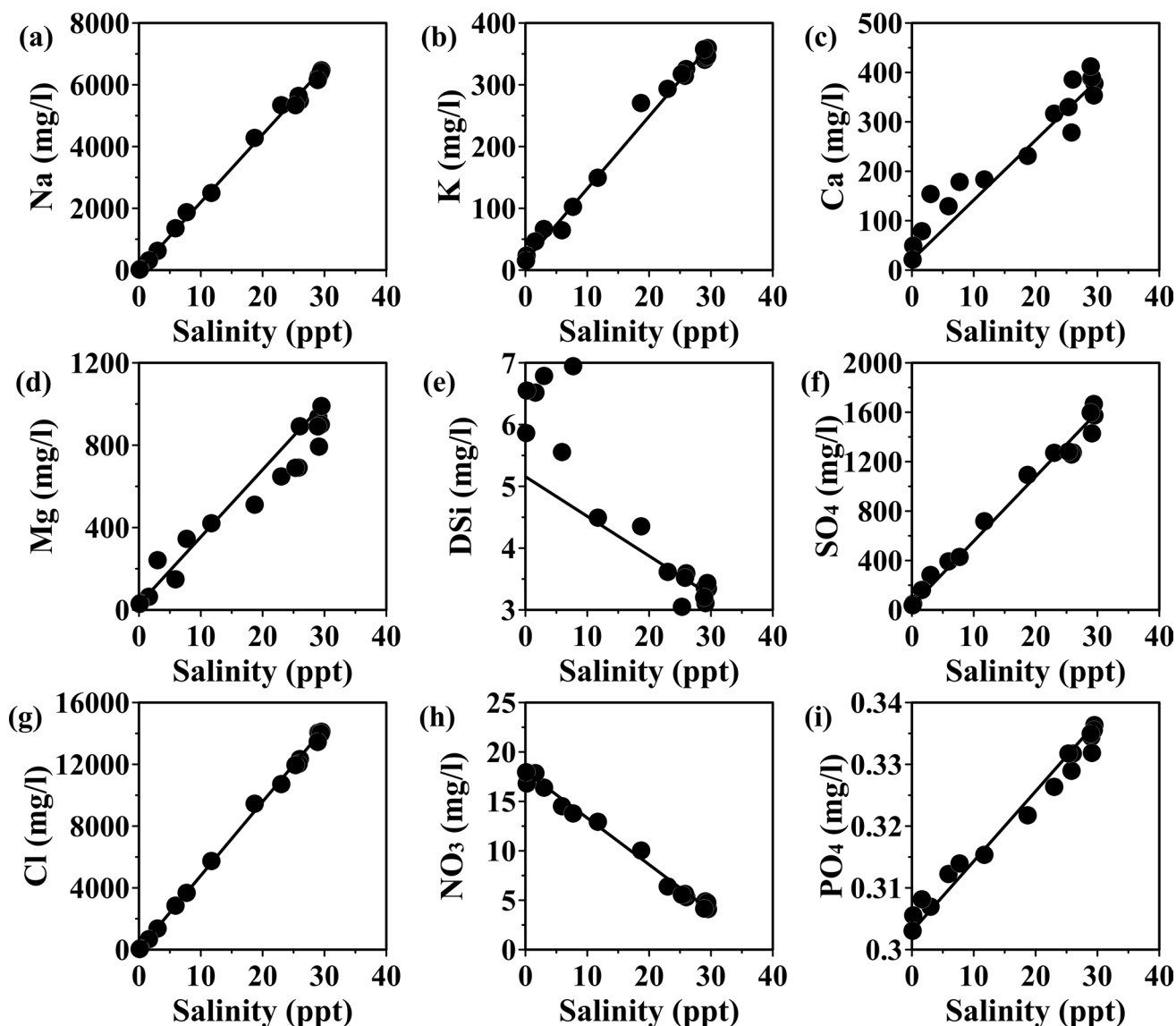


Fig. 5 Spatial distribution of major ions during winter season

oversaturated with respect to the particular mineral, and its precipitation is expected. An aqueous solution with  $SI=0$  will promote neither dissolution or precipitation as the solution is considered to be in equilibrium.

$$SI = \log \frac{IAP}{K_{SP}} \quad (1)$$

The saturation index of calcite ( $SI_{Cal}$ ) and aragonite ( $SI_{Arag}$ ) ranges from  $-1.73$  to  $0.98$  and  $-1.87$  to  $0.83$  respectively, and having the highest SI during summer and lowest in winter in the Devi estuary (Akhtar et al. 2021). The  $SI_{Dol}$  varies between  $-2.84$  and  $2.68$  and is also found to be have the highest value in summer and lowest during monsoon. Spatially, increase in the  $SI_{Cal}$ ,  $SI_{Arag}$  and  $SI_{Dol}$  are

observed toward the mouth of estuary during summer and winter (Fig. 6). Similar distribution of SI along the salinity gradient has been reported in several other estuaries (Jiang et al. 2010; Wit et al. 2018; Li et al. 2020). Significant positive correlation between pH and SI values is found in the estuary (Table S1). Dependency of SI on pH of water is well reported by various authors (Abril et al. 2003; Li et al. 2020). An increase in pH toward the mouth of estuary is evident from its positive correlation with salinity (Table S1). River water is generally characterized by low pH due to the production of carbonic acid via organic matter decomposition (Wang et al. 2011; Hossain and Marshall 2014). Thus, lowering of pH in the upper estuary may have resulted in a decrease in SI values. Additionally, strong positive correlation between dissolved oxygen saturation (DO%) and

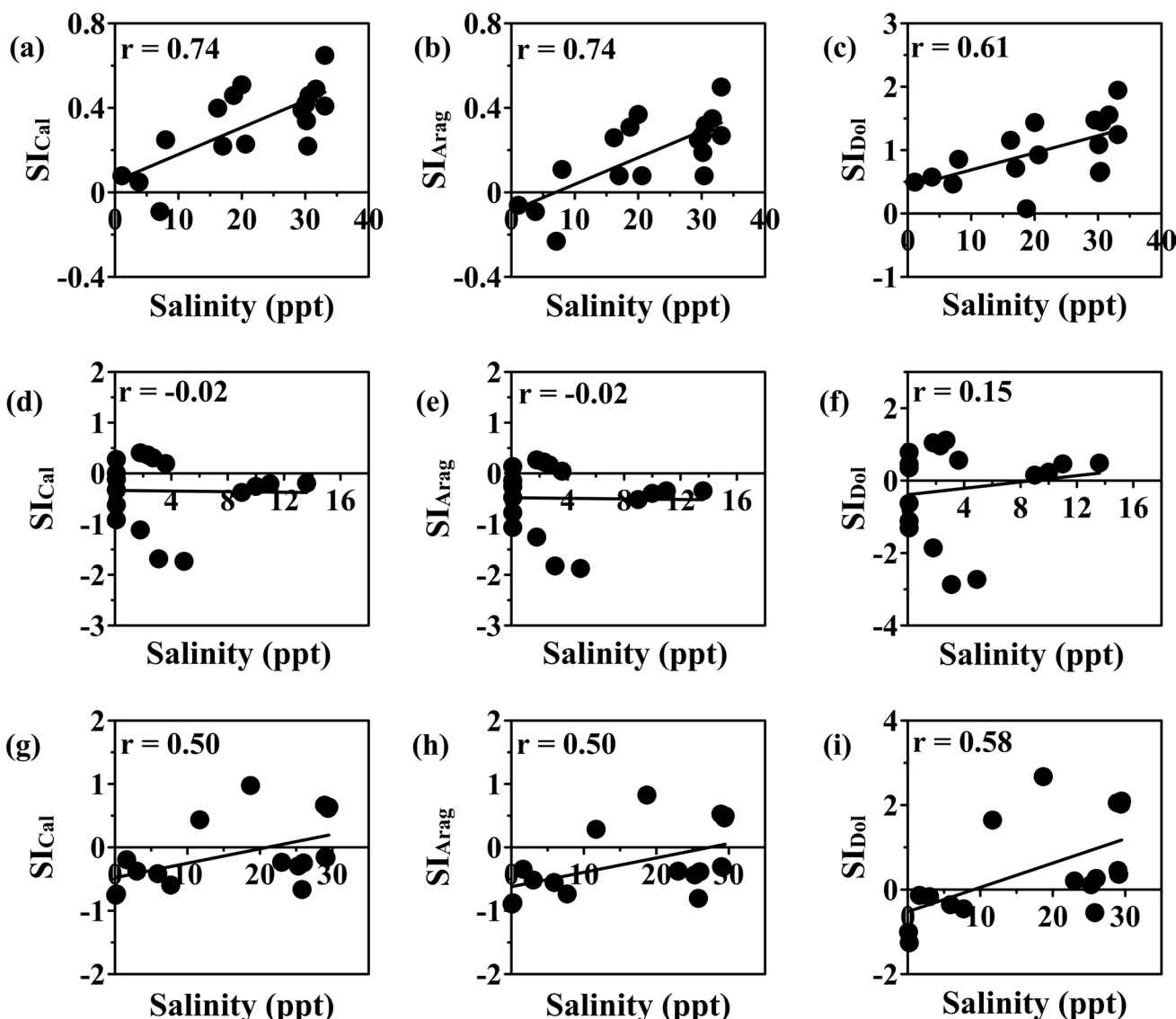


Fig. 6 Spatial variation of  $SI_{Cal}$ ,  $SI_{Arag}$  and  $SI_{Dol}$  during summer (a–c), monsoon (d–f) and winter (g–i)

SI of calcite ( $r = 0.69–0.83$ ), aragonite ( $r = 0.69–0.83$ ) and dolomite ( $r = 0.65–0.86$ ) are observed in the study area (Table S1). The influence of heterotrophic processes such as organic matter degradation on DO% has been previously reported in the Devi estuary (Akhtar et al. 2021). During decomposition of organic matter, a decrease in DO% is accompanied by a reduction in pH which further leads to the lowering of SI. Hence, a coupling between carbonate saturation state in the estuarine water and the process of organic matter degradation is inferred. Similar coupled behavior has been reported in several other estuaries (Abril et al. 2003; Guo et al. 2021). Increase in pH toward the mouth of the estuary is due to the buffering effect of seawater, which causes higher SI in the water. Both SI and pH show unsystematic spatial variation in the monsoon season.

### Mixing behavior

Distribution of dissolved ions in estuaries is primarily governed by the mixing of two largely different water masses, i.e., fresh riverine water and saline seawater (Telesh and Khlebovich 2010). Hence, concentration of these dissolved constituents tends to fall on a straight line which is referred to as the theoretical dilution line (TDL) when plotted against the salinity. However, various biogeochemical processes are responsible for the removal or addition of the ionic constituents within the estuary that causes deviation of ionic concentrations from the TDL (Liss 1976). Based on this concept, the mixing behavior of major ions in the Devi River estuary has been evaluated and subsequently their percentage of addition or removal (PA/PR) were calculated using

Eqs. 2–4. The PA/PR of the major ions in Devi estuary are given in Table 2.

$$N_{\text{mix}} = f_r \times N_r + (1 - f_r) \times N_o \quad (2)$$

$$f_r = (S_o - S_{\text{mix}}) / (S_o - S_r) \quad (3)$$

$$\text{PA/PR} = 100[(N_m / N_{\text{mix}}) - 1] \quad (4)$$

where,  $N_{\text{mix}}$  and  $N_m$  are the theoretical and measured concentration of constituents at a particular salinity while  $N_r$  and  $N_o$  are the concentration of ion in river- and sea-water, respectively. The  $S_{\text{mix}}$ ,  $S_r$  and  $S_o$  are the salinity in the sample, river- and sea-water respectively whereas  $f_r$  is the mixing ratio of fresh- and saline-water in the estuary.

The concentration of Na and Cl are mostly plotted along the TDL, which indicates their conservative behavior throughout the studied period (Figs. 3, 4, 5; Table 2). Behavior of Na and Cl is considered to remain conservative in both seawater and estuarine water, as they generally do not take part in biochemical processes (Borole et al. 1979; Mora et al. 2017). Apart from Na and Cl, the distributions of  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{PO}_4$  in the estuary are also mostly conservative in the estuary. Hence, it can be inferred that distribution of  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{PO}_4$  are mostly hydro-dynamically controlled by the mixing of fresh- and saline-water rather than any biogeochemical process. Conservative behavior of these major ions has been reported in several estuaries worldwide (Balls 1992; Patra et al. 2012). The DSi shows enrichment in the upper reaches of the estuary and gets depleted toward the mouth of the estuary. Intense weathering due to land use and/or land cover changes has been reported to increase the DSi concentrations in rivers (Hartmann et al. 2011). This may have led to the excess DSi concentrations in the upper estuary. However, as discussed in “Spatial and seasonal distribution” Section, incorporation of silica in the frustules of marine diatoms present in coastal water acts as a sink for the DSi supplied by fluvial input. The presence of centric diatoms in the estuarine sediment is confirmed in the SEM

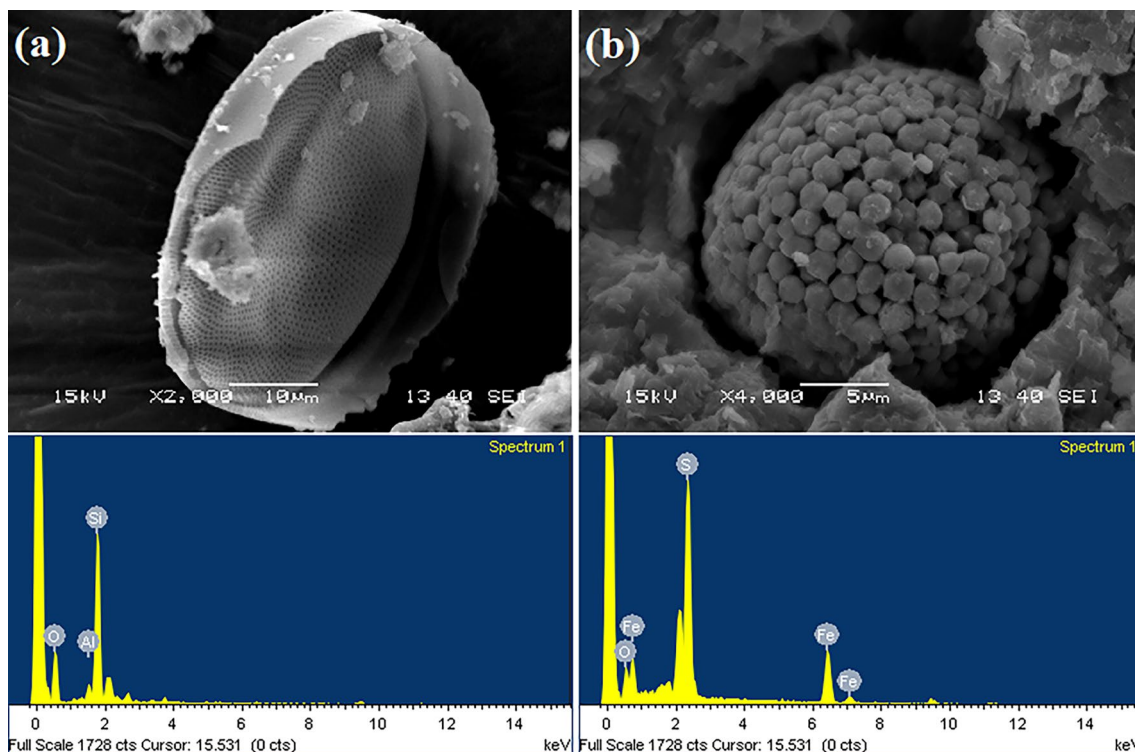
microphotograph and EDX spectra (Fig. 7a). Hence, biogenic removal occurring near the mouth of estuary can explain the depletion of DSi. This contrasting behavior of DSi between the upper and lower estuary is more prominent during the dry seasons (Figs. 3, 5). This is due to less supply of DSi to the coast because of decreased water flow. However, during monsoon, increased water discharge leads to continuous supply of DSi to the mouth of estuary. This compensates the removal of DSi by diatom uptake and causes less deviation from the TDL. Such non-conservative behavior of DSi in estuaries has been widely reported (Bell 1994; Amann et al. 2014; Akshitha et al. 2021).

Behavior of Ca and Mg along the salinity gradient shows marked variation in different seasons. During summer, negative deviation of Ca (PA/PR =  $-3.03 \pm 34.05$ ) and Mg (PA/PR =  $-38.45 \pm 32.31$ ) from the dilution line is observed (Fig. 3; Table 2). This depletion is caused due to the removal of Ca and Mg from water column as a result of precipitation of carbonates such as calcite, aragonite and dolomite. Precipitation has been found to be an important ongoing process in the estuary during the summer season (Fig. 6). Depletion in the concentration of K ( $-10.00 \pm 28.92$ ) relative to the TDL indicates its removal from water. This is possibly due to incorporation of K in the crystal lattices of carbonates (calcite and aragonite) (White 1977; Ishikawa and Ichikuni 1984). Positive correlations of K with calcite and aragonite further supports this inference (Table S1). However, K mostly shows conservative behavior during monsoon and winter. The monsoon period is characterized by significant non-conservative behavior of Ca in the estuary though Mg shows mostly conservative behavior in this season with slight enrichment at higher salinity. The enrichment of Ca and Mg coincides with the negative saturation indices during monsoon indicates that carbonates dissolution contributes the excess Ca and Mg ions in the surface water. However, the significant enrichment of Ca during this period cannot be explained by the dissolution of carbonate minerals solely. Hence, other factors such as groundwater discharge may have contributed to the enrichment of Ca in this period. Increase in groundwater

**Table 2** Percentage addition and removal (PA/PR) of dissolved ions in the estuary

	SiO <sub>2</sub>	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	NO <sub>3</sub>	PO <sub>4</sub>
Summer									
Average	1.94	-4.86	-10.00	-3.03	-38.45	-7.59	4.45	-0.03	-2.45
SD	13.49	12.06	28.92	34.05	32.31	12.51	9.84	7.23	6.13
Monsoon									
Average	0.60	-6.26	-5.86	167.63	9.62	3.52	4.55	-3.23	0.11
SD	6.51	8.63	27.79	164.93	31.85	4.00	16.53	7.88	0.68
Winter									
Average	1.88	0.17	6.09	30.13	-2.46	-0.91	7.15	0.20	-0.07
SD	10.07	4.74	16.87	52.03	28.12	3.46	15.79	7.89	0.66





**Fig. 7** SEM microphotograph and EDX spectra of centric diatom (a) and framboidal pyrite (b) in sediment of Devi estuary

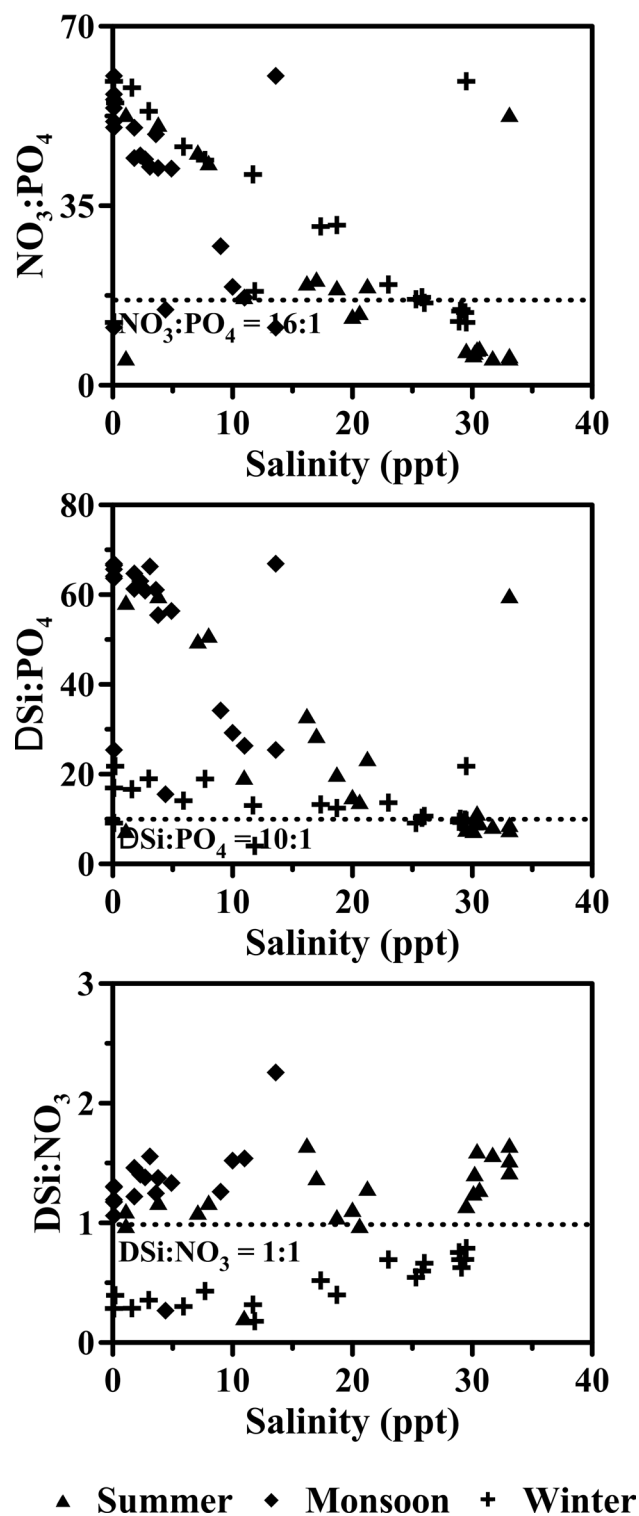
input into estuaries have been reported during the monsoon period (Rahaman and Singh 2012; Selvam et al. 2021). Lagomasino et al. (2015) also observed excess Ca in the Sian Ka'an Biosphere Reserves estuary due to the combined effects of dissolution of carbonates and influx of Ca-rich groundwater into the estuary. Slight enrichment and depletion of Ca and Mg are observed in the upper and lower estuary, respectively in the winter period. Therefore, during winter, the SI shows mostly negative values in the upper estuary, and positive values in the lower estuary (Fig. 6). Dissolution and/or precipitation of carbonates have been reported to influence the non-conservative behavior of Ca and Mg in estuaries (Ramanathan et al. 1993; Jarvie et al. 2000; Patra et al. 2012).

### Nutrient stoichiometry

Nutrient availability and their stoichiometry in estuarine water play an important role in modulating the phytoplankton growth, biomass and species composition (Kilham 1990; Domingues et al. 2011). Spatial and temporal availability of nutrient can be changed drastically in estuary due to mixing of fresh river water and saline ocean water. In natural water, the stoichiometric ratio between the nitrate and phosphate ( $\text{NO}_3:\text{PO}_4$ ) is found to have a constant value of 16:1, which is referred to as the Redfield ratio (Redfield 1958). Brzezinski (1985) further observed that DSi also acts as an important

nutrient and exhibits constant ratios with phosphate and nitrate, i.e.  $\text{DSi}:\text{PO}_4 = 10:1$  and  $\text{DSi}:\text{NO}_3 = 1:1$ . The availability of  $\text{NO}_3$ ,  $\text{PO}_4$  and DSi in these stoichiometric ratios are considered to be optimal for the growth of phytoplankton (Figler et al. 2021). The constancy of these nutrient ratios is maintained by the continuous biogeochemical cycling of nutrients into and out of their bioavailable forms. Limitation or non-availability of a particular nutrient has profound effect on the phytoplankton growth and their assemblage. Therefore, these ratios are important for assessing the condition of phytoplankton growth. Further, any perturbation in these ratios can be used to determine the nutrient limitation in localized areas (von Oheimb et al. 2010).

The  $\text{NO}_3:\text{PO}_4$  ratio ranges from 5.38 to 52.89 in summer followed by 12.27 to 59.32 during winter and 11.26 to 60.36 in monsoon. The highest  $\text{DSi}:\text{PO}_4$  ratio is observed in monsoon season ( $55.45 \pm 15.55$ ) while the lowest in winter ( $13.26 \pm 4.05$ ). Estuarine water is characterized by  $\text{DSi}:\text{PO}_4$  ratio of  $23.56 \pm 19.40$  in the summer period. During summer and winter, high  $\text{NO}_3:\text{PO}_4$  values are observed in upper parts of the estuary whereas most of the middle and lower estuary samples show values closer to that of the Redfield ratio (Fig. 8a). Input from various anthropogenic sources accounts for high  $\text{NO}_3$  content in the upper estuary. However, microbial denitrification in the lower estuary removes  $\text{NO}_3$  from the water column and brings the  $\text{NO}_3:\text{PO}_4$  ratio close to the Redfield value (Lenton and Watson 2000; Howarth and



**Fig. 8** Distribution of nutrient stoichiometric ratios along salinity gradient

Marino 2006). Another explanation for the wide variation in  $\text{NO}_3:\text{PO}_4$  values between upper and lower estuary could be the greater availability of  $\text{PO}_4$  toward estuary mouth (Caraco

et al. 1989; Blomqvist et al. 2004). Under the anoxic conditions prevailing in the lower estuary,  $\text{PO}_4$  bound to  $\text{Fe}^{3+}$  oxide is easily released into the water column due to reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Further, the  $\text{Fe}^{2+}$  precipitates in the form of sulfides in sediments underlying the sulfate rich seawater (Hartzell and Jordan 2012). This prevents the escape of  $\text{Fe}^{2+}$  to the overlying oxic layers and inhibits further complexing with  $\text{PO}_4$ . Framboidal pyrite has been identified in sediments near mouth of the Devi estuary which supports the above geochemical process (Fig. 7b). However, low concentrations of sulfate in the fresh water causes the  $\text{Fe}^{2+}$  to form particulate ferrous compounds with  $\text{PO}_4$ , and thereby reducing the availability of latter (Caraco et al. 1989).

Similar spatial distribution of  $\text{DSi}:\text{PO}_4$  ratio is also observed during summer and winter period. This indicates that productivity is limited by nutrient  $\text{PO}_4$  in the upper estuary during the dry periods (Fig. 8b). Further, the decrease in  $\text{DSi}:\text{PO}_4$  ratio may also be the result of biological uptake of  $\text{DSi}$  near the mouth. Several studies have observed the control of biological uptake on this ratio (Pingree et al. 1977; Ragueneau et al. 2002; Leblanc et al. 2003). An increase in chlorophyll concentration toward the mouth of the estuary during dry period in Devi estuary has also been reported by Akhtar et al. (2021). The availability of nutrients in accordance to the Redfield ratio supports proliferation of primary producers in the lower estuary. Similar  $\text{PO}_4$  limitation in the fresh water dominated low salinity zone have been reported in some of the major estuaries such as Neva estuary (Russia), Pearl river estuary (China) and Chesapeake Bay (US) (Pitkänen and Tamminen 1995; Yin et al. 2004; Hartzell and Jordan 2012). Contrastingly,  $\text{NO}_3:\text{PO}_4$  higher than the Redfield ratio has been observed during monsoon period throughout the estuary. Phosphate limitation has been widely reported in river water (Howarth and Marino 2006). This is attributed to increase in  $\text{NO}_3$  because of higher nitrogen fixation rates and relatively lower availability of  $\text{PO}_4$  due to complexation with Fe-oxides in freshwater systems (Blomqvist et al. 2004). The estuary remains dominated by fresh water in monsoon season due to high river discharge. This leads to the influx of  $\text{PO}_4$ -limited fresh water into the estuary and increases the  $\text{NO}_3:\text{PO}_4$  ratio. Thus,  $\text{PO}_4$  is stoichiometrically the limiting nutrient during the monsoon season. The significantly high values of  $\text{DSi}:\text{PO}_4$  in rainy season also indicate a  $\text{PO}_4$ -limitation in the estuary. This is further supported by the lowest chlorophyll concentration ( $0.35 \pm 0.17 \mu\text{g/l}$ ) in the Devi estuary during the monsoon period (Akhtar et al. 2021).

The  $\text{DSi}:\text{NO}_3$  ratio has primary control over the growth of diatom in estuaries (Egge and Aksnes 1992; Conley et al. 1993; Choudhury and Bhadury 2015). It is found to be  $1.29 \pm 0.21$ ,  $1.37 \pm 0.26$  and  $0.52 \pm 0.18$  in summer, monsoon and winter, respectively. Thus, this ratio is observed to be approximately 1:1 during summer and

monsoon that suggests nutrient availability is favorable for diatom growth. However, low DSi:NO<sub>3</sub> ratios in upper estuary during winter represents DSi-limitation.

## Conclusion

This study aims to evaluate the spatial and seasonal variability of major ions and nutrients in the Devi river estuary in response to several physicochemical parameters. The order of abundance of major ions in the surface water is Cl > Na > SO<sub>4</sub> > Mg > Ca > K > NO<sub>3</sub>, DSi > PO<sub>4</sub>. Although mixing of river- and sea-water primarily controls the distribution of major ions, other processes such as evaporation, dilution by freshwater, fluvial inputs via terrestrial runoff and biological activities also play significant role. Concentration of Na, Cl, SO<sub>4</sub>, NO<sub>3</sub> and PO<sub>4</sub> varies linearly along salinity gradient suggesting their conservative behavior. Weathering processes and biological productivity in the form of diatoms causes deviation of DSi from the TDL. Seasonal differences in the non-conservative behavior of Ca and Mg are found to be consistent with the variations in carbonate saturation indices, and demonstrate the importance of precipitation and dissolution mechanisms in governing the water quality. Saturation indices increase toward the mouth of the estuary in response to increase in pH due to mixing with seawater. Coupling of carbonate precipitation and/or dissolution processes with organic matter degradation is inferred from the relationships between SI, pH and DO% in the estuary. Spatial and seasonal variations in nutrient limitation has been found. Large variation in NO<sub>3</sub>:PO<sub>4</sub> values between upper and lower estuary could be due to the greater availability of PO<sub>4</sub> toward the mouth which is caused by less availability of Fe for sequestering PO<sub>4</sub>. Nutrient stoichiometry is observed to play an important role in the primary productivity of the estuary.

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## Declarations

**Conflict of interest** There is no conflict of interest.

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