



Spatial and temporal dynamics of dissolved nutrients and factors affecting water quality of Chilika lagoon

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Abstract

Water quality of Chilika lagoon was assessed for pre- and post-monsoon seasons. A marked spatial and temporal variability in the water quality was observed in this study. Principal component analysis (PCA) reveals the influence of salinity, anthropogenic factors, as well as vegetation on the water quality. The higher concentration of nitrate (NO_3^-) and phosphate (PO_4^{3-}) in certain pockets of the lagoon water was due to the prevalence of agricultural, municipal, and domestic waste. A positive correlation between PO_4^{3-} and DSI indicates their terrigenous input from freshwater influx. Cyclone *Phailin* had profound impact on several water quality parameters. pH, dissolved oxygen (DO), and dissolved inorganic carbon (DIC) are governed largely by the presence of macrophytes. The impact of severe cyclone *Phailin* can be assessed from the very low salinity values persisting in the lagoon even 2.5 months after the cyclone hit Odisha coast. Some toxic heavy metals like Copper (Cu), Lead (Pb), Nickel (Ni), Cobalt (Co), Manganese (Mn), and Iron (Fe) exceeded the Environmental Protection Agency (EPA) standards at many locations in both the seasons. Non-conservative behavior of nutrients indicates well mixed nature of lagoon which is also indicative of good primary productivity. Northern sector (NS) of the lagoon is susceptible to eutrophication being riverine influenced region. Southern sector has more stable ion chemistry as a result of least freshwater discharge, constant supply of saline water, and lesser water renewal.

Keywords Chilika lagoon · Dissolved nutrients · *Phailin* · Macrophytes · Non-conservative behavior

Introduction

Coastal lagoons are shallow water bodies exhibiting high variability in their physical, chemical, and biological characters. They tend to be unstable environments and the short- and long-term variations that occur in these ecosystems are large in comparison to other saline environments. They receive abundant nutrients from freshwater and support plentiful form of life due to large salinity gradient (Clark et al. 2006; Beltrame et al. 2009). The hydrodynamics of a lagoon is governed by the circulation and mixing of freshwater inputs via river discharge and inflow of saline waters through tidal flows (Lara and Dittmar 1999). Lagoons usually exhibit estuarine characteristics and are regions of high primary

productivity (Sylaios and Theocharis 2002; Panigrahi et al. 2009). Salinity is an important factor, which is having direct and indirect control over the nutrient availability and their transformations in the saline aquatic environments. Tropical coastal lagoons are under huge anthropogenic pressures, but have been studied to a lesser extent when compared to temperate lagoons (Balasubramanian et al. 2004; Burford et al. 2008).

In Chilika lagoon, changes in land use pattern and agricultural practices in the catchment basin and adjoining areas has led to addition of enormous amount of nitrogen and phosphorous as residual fertilizers. The discharge of fresh water into the lagoon is quite high during monsoon and post-monsoon while it is negligible or absent during other periods (Mohanty and Panda 2009). The present study focuses on distribution of major nutrients: nitrogen, phosphorus, and dissolved silica besides other water quality parameters since these nutrients play key role in maintaining the trophic state of the lagoon, phytoplankton abundance, growth and metabolism which form the major link in food webs (Satpathy et al. 2010a, b).

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Study area

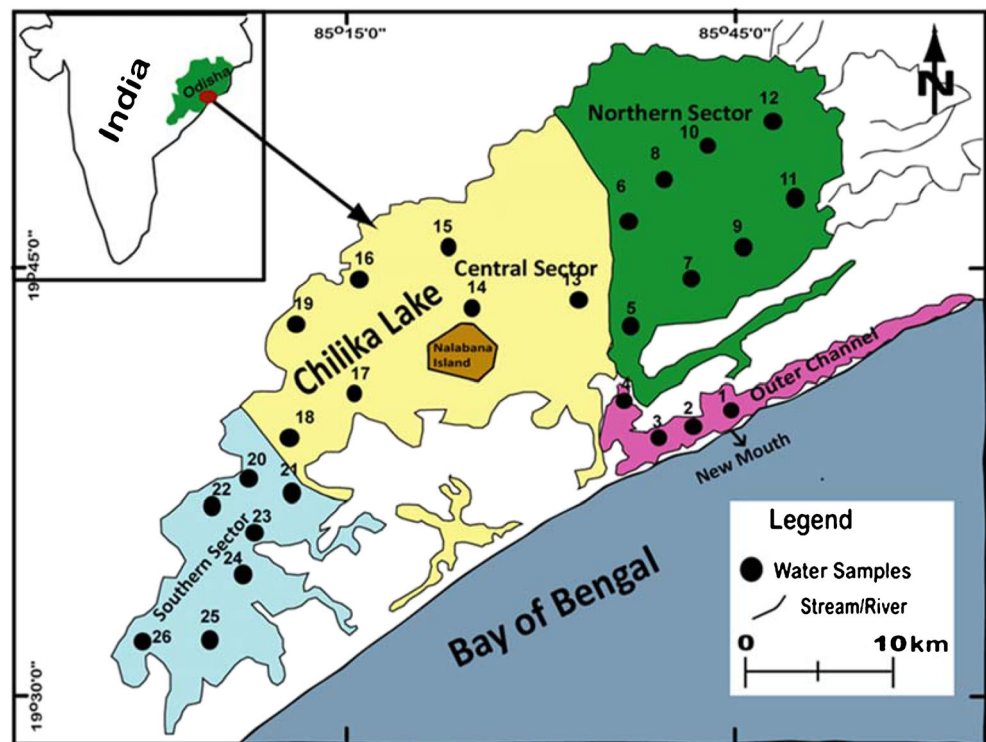
Chilika Lake is the largest tropical lagoon of Asia spread between latitude $19^{\circ} 28' - 19^{\circ} 54' \text{ N}$ and longitude $85^{\circ} 05' - 85^{\circ} 38' \text{ E}$. It is a semi-enclosed, coastal lagoon on the east coast of India in the state of Odisha. Chilika was designated wetland of international importance under Ramsar convention in 1981. It is a biodiversity hotspot and supports many rare, endangered, and vulnerable species besides harboring 1 million birds (Sahu et al. 2014). The lagoon is about 65 km long and varies in breadth from 18 km in north to 5 km in south (Fig. 1). Present studies have estimated the lagoon area to be nearly 704 km^2 during summer which spreads to 1020 km^2 in monsoon (Gupta et al. 2008). The water depth in the lagoon varies from 0.9 to 2.6 m in the dry season and from 1.8 to 3.7 m in the rainy season. The lagoon is situated on the southern part of the Mahanadi delta-complex. Chilika basin is largely formed by silicate minerals like quartz and feldspar (Zachmann et al. 2009). The lagoon is cut off from the Bay of Bengal by a continuous sandy barrier-spit measuring 60 km in length and 150 m in breadth (Khandelwal et al. 2008). The lagoon is connected to the Bay of Bengal in the east. The barrier spit separates the lagoon from the Bay of Bengal and provides an inlet at its northeast extremity which remains open due to continuous flushing action brought by waves and currents. Changes in the position, shape, and breadth of inlet has occurred from time to time depending on the interplay of available energy from land and sea and also due to the silt brought by the tributaries of Mahanadi Daya and Bhargavi

ivers. At present, the lagoon is connected with the Bay of Bengal near Satapada (Sipakuda) by means of an artificial opening made in September 2000.

The main rock types in the Chilika basin are khondalites, charnockites, quartzites, sandstones, conglomerate, and red clays which at places are covered by laterite and alluvium. Physiographically, the region is distinguished into rocky hills at places, rolling plain with lateritic shelves, and terraces in upper reaches of the drainage area. Sandstones, grit, and conglomerates are found in the eastern part of the lagoon (Rai 1985). The rolling plain is characterized by the lateritic residual and transported alluvial soil and deltaic plain is characterized by alluvial soil which is sandy and coarse in texture. Lateritic gravels and ferruginous concretions are common in alluvial soil. Chilika lagoon is part of the Mahanadi delta which has several dead, defunct, and abandoned river channels. These palaeochannels are important sites for palaeobotany, reserves of many important ores, and preserve sedimentary records useful to understand the palaeoclimate conditions (Khandelwal et al. 2008; Misra and Jena 2015).

The catchment area of the lagoon has a tropical climate with an average rainfall of 1238 mm. The local weather condition is mostly controlled by the southwest (SW) and northeast (NE) monsoons and the lagoon experiences the SW monsoon between July and September and the NE monsoon between November and December. December to February is winter which is followed by summer from March to June. The lagoon has several hydrological influences; the most important are its connection to the bay of Bengal in the east and

Fig. 1 Study area and sampling points



freshwater flow in the north due to the joining of tributaries of Mahanadi river. Many rivers and rivulets join the lagoon through its western catchment. Almost 52 small rivers and streams join the lagoon. The main tributaries of Mahanadi (such as Bhargavi, Daya, and Makara) account for almost 61% ($850 \text{ m}^3 \text{ s}^{-1}$) of the total freshwater.

Materials and methods

A total of 26 surface water samples were collected from 4 hydro-ecological (based on the different sectors of the lagoon during pre and post-monsoon seasons (Fig. 1). The lagoon is virtually divided into four sectors based on the hydrological influence, salinity, vegetation, and connection with the sea. The pre-monsoon sampling was conducted in the 1st week of June 2013 and post-monsoon sampling was conducted in January 2014. The post-monsoon sampling was done 2.5 months after the landfall of very severe cyclone *Phailin*. The water samples were collected in 500 ml clean propylene bottles. The sampling was done on a boat. The surface sample was collected by filling the plastic bottles with water from upper few centimeters. Cleaning of all the plastic bottles was carried out by soaking in 5% nitric acid ($\text{HNO}_3 \text{ v/v}$) for 24 h and then rinsing with doubled-distilled water (DDW). After collection, the water samples were poisoned with HgCl_2 for nutrients and dissolved inorganic carbon (DIC) analysis. Another set of samples were collected in 100 ml bottles for dissolved metals analysis. The water samples were filtered through $0.45 \mu\text{m}$ nylon filters and acidified below $\text{pH} < 2$ by addition of concentrated HNO_3 . The samples were transferred to the laboratory in the boxes and stored at 4°C until analysis. All the analysis was completed within 15 days of sampling. In every analysis, appropriate blanks were run as controls. pH, salinity, and EC in the water samples were analyzed on the field with portable multiparameter kit after calibrating with respective buffers for pH and EC. The parameters like DO, DIC, DOC, NO_3^- , NO_2^- , PO_4^{3-} , H_4SiO_4 , SO_4^{2-} , Cl^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were analyzed by standards procedure for surface water.

- The dissolved oxygen (DO) was measured by Wrinkler's method
- HCO_3^- by titrimetric method
- Dissolved organic carbon (DOC) was analyzed by TOC analyzer (Shimadzu TOC -5000 analysers)
- Nitrite (NO_2^-) by indophenol method
- Nitrate (NO_3^-) by cadmium reduction method and phosphate (PO_4^{3-}) by ascorbic acid method
- H_4SiO_4 (dissolved silica) molybdo-silicate method
- SO_4^{2-} by turbidimetric method
- Sodium and potassium (Na^+ and K^+) by Flame photometer (Elico Flame Photometer, CL-378)

- The heavy metals were analyzed on atomic absorption spectrophotometer (Thermoscientific M series)

Results and discussion

The four regions remained significantly different from one another with respect to many parameters. The salinity variation was significantly different in the two seasons. With respect to different sectors, also salinity varied within the lagoon. Sample numbers 1–4 were collected from the outer channel region, 5–12 from northern sector, 13–19 from the central sector, and 20–26 from southern sector. The values of various parameters have been presented in Table 1.

pH

The lagoon water is alkaline in nature. The mean pH value in the pre-monsoon season was 8.1 (7.5–8.6), whereas it was 8.6 (7.4–10.2) in the post-monsoon period. The spatial distribution of pH was more uniform in pre-monsoon as compared to post-monsoon season (Fig. 2). The highest pH values are observed in the southern sector in pre-monsoon period. High pH values in southern sector are because of greater photosynthetic activity by algae and phytoplankton which remove dissolved CO_2 from the surface water and shift the equilibrium toward alkaline (Henneman and Petrucio 2011; Jayakumar et al. 2013). Lowest pH values were observed in the northern sector, due to large freshwater input from the distributaries of Mahanadi river. The average value of pH was higher in the post-monsoon season when compared to the pre-monsoon because of the utilization of CO_2 by the photosynthetic activity of the macrophytic flora, thus shifting the equilibrium towards alkaline (Das et al. 2008). The lowering of salinity in the post-monsoon season gave rise to thick mats of higher plants like *Potamogeton pectinatus*, *Najas foveolata*, *Hydrilla*, and many other weeds. The rates of primary production allows a large amount of withdrawals of CO_2 and HCO_3^- resulting in a large rise in pH values, at times > 10 . In the post-monsoon season, we observe a small patch of water with very high pH of the order 10.2 in the northern sector which is due to a large number of macrophytes with high photosynthetic activity in this region (Fig. 2).

Salinity

Salinity is one of the most important factors which determine the concentration of other nutrients in a brackish water system. The mean salinity value in pre-monsoon season was 21.44 PSU (1.3–32.8), whereas the post-monsoon mean value was 4.40 PSU (0.2–13.8). Spatial distribution of salinity showed more stratification during the pre-monsoon season as compared to the post-monsoon season (Fig. 3). The salinity value

Table 1 Physiochemical properties of water samples of Chilika lagoon during pre-monsoon and post-monsoon seasons

Sample	pH		EC ($\mu\text{S}/\text{Cm}$)		Sal (PSU)		DIC (mg/l)		DOC (mg/l)		DO (mg/l)		NO_2^- (mg/l)		NO_3^- (mg/l)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
1	8.1	8.2	51,400	22,800	32.8	13.8	203.6	143.47	4.94	4.41	2.84	3.21	0.00	0.00	0.7	0.8
2	8.1	8.3	50,000	12,110	32.3	7.0	167.6	147.74	3.87	4.05	5.45	6.07	0.00	0.00	0.5	3.9
3	8.0	8.2	50,100	11,800	32	6.8	191.2	155.87	5.25	4.32	4.21	4.74	0.01	0.00	3.2	6.3
4	8.1	7.4	50,500	7380	32.4	4.1	163.6	135.36	5.94	4.14	2.34	2.3	0.04	0.00	0.9	1.8
5	8.1	8.3	50,400	6490	32.3	3.5	159.5	111.90	6.12	4.87	4.45	3.86	0.04	0.00	0.3	0.8
6	7.8	10.2	47,300	7980	30.1	1.5	132.0	131.21	7.39	4.31	6.65	6.98	0.04	0.02	0.2	2.5
7	7.8	8.5	46,600	3120	29.7	0.6	155.9	136.00	5.54	4.82	6.75	7.43	0.04	0.06	0.5	6.5
8	7.9	9.4	34,200	1286	21	0.4	171.8	155.34	7.65	5.21	7.23	9.31	0.04	0.07	0.7	3.1
9	7.7	9.9	31,300	1198	15	0.4	148.0	143.27	4.58	6.047	7.64	9.79	0.05	0.09	0.8	2.3
10	8.7	9.3	3970	932	2.1	0.2	136.0	103.60	6.09	6.801	9.65	11.97	0.06	0.09	0.9	8.3
11	7.8	9.8	4200	871	2.1	0.2	160.0	131.27	7.21	7.753	11.34	10.87	0.07	0.32	0.9	2.3
12	7.7	8.6	2720	2800	1.3	1.3	196.0	131.87	7.89	5.62	12.86	11.21	0.07	0.42	3.4	6.7
13	8.0	7.9	49,900	7980	32.8	4.4	151.8	131.87	6.98	4.35	3.45	4.38	0.08	0.50	4.7	9.3
14	8.1	8.0	42,700	7534	26.7	4.3	171.3	135.60	5.25	4.13	6.43	8.26	0.09	0.60	2.4	7.5
15	8.3	8.0	35,000	7470	21.4	4.1	159.5	135.93	5.29	4.44	12.85	12.54	0.23	0.64	1.2	3.4
16	8.6	8.7	26,500	7060	16.1	3.9	183.3	107.47	5.87	4.244	11.63	11.34	0.32	0.74	1.0	4.8
17	8.3	8.2	37,600	8270	23.3	4.6	183.5	159.80	4.23	4.79	7.98	7.86	0.48	0.77	0.6	5.3
18	8.2	8.0	37,200	8160	23	4.6	171.8	151.74	4.91	3.973	8.54	7.65	0.65	0.99	2.6	7.6
19	7.5	8.9	37,300	7970	23	4.4	188.0	123.67	5.04	7.748	13.43	17.39	0.73	1.12	3.7	8.2
20	8.2	9.0	36,000	8900	22.7	5.4	155.9	135.80	4.83	4.83	10.54	11.21	0.80	1.20	2.3	5.3
21	8.3	8.2	33,300	8940	20.6	5.0	179.6	155.80	5.56	9.72	7.32	8.93	0.84	1.30	2.2	5.6
22	8.3	8.4	31,400	8700	19.1	4.9	199.2	155.80	4.41	9.754	4.32	5.34	0.86	1.30	2.5	6.4
23	8.3	8.0	35,800	10,080	17.5	5.7	167.7	163.60	5.12	7.627	5.21	3.3	0.87	1.50	4.4	8.8
24	8.3	8.2	28,700	10,620	17.1	6.1	175.7	167.67	6.51	8.56	4.65	4.53	0.99	1.50	1.4	2.4
25	8.3	8.6	31,500	10,080	19.1	5.7	183.5	163.80	5.65	5.15	4.43	3.21	1.20	2.21	7.5	9.6
26	8.3	9.3	33,300	10,760	20.6	6.2	179.6	158.68	4.37	8.436	7.64	8.96	1.67	2.35	5.8	7.8
Min	7.5	7.4	2720	871	1.3	0.2	132.0	103.60	3.87	3.97	2.34	2.30	0.00	0.00	0.2	0.8
Max	8.7	10.2	51,400	22,800	32.8	13.8	203.6	167.67	7.89	9.75	13.43	17.39	1.67	2.35	7.5	9.6
Ave	8.1	8.6	34,750.4	8034.36	21.44	4.40	170.4	140.91	5.65	5.85	7.34	7.94	0.43	0.72	2.2	5.3
Std dev	0.27	0.68	13,718	4476.80	9.14	2.86	17.9	17.11	1.07	1.83	3.18	3.59	0.45	0.69	1.8	2.7
Sample	PO_4^{3-} (mg/l)		DSi (mg/l)		SO_4^{2-} (mg/l)		Cl^- (mg/l)		Na^+ (mg/l)		K^+ (mg/l)		Ca^{2+} (mg/l)		Mg^{2+} (mg/l)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
1	0.050	0.035	0.60	5.45	138	170	20,450	9000	11,190	4850	430	136.3	1000	528	5080	2064
2	0.010	0.065	0.60	7.83	160	166	21,200	4560	10,900	2900	420	77.9	962.5	212	5437.5	1248
3	0.010	0.031	0.30	7.12	65	242	20,400	4550	10,830	2540	460	75.7	800	196	3960	900
4	0.000	0.049	0.80	7.98	164	174	22,200	3000	11,150	1330	400	60	912.5	160	3527.5	704
5	0.030	0.009	0.70	8.27	159	172	20,600	2550	11,900	1210	420	43.2	987.5	128	4012.5	540
6	0.000	0.011	1.80	2.51	166	47	18,900	3200	9940	270	186	5.1	987.5	52	4934.5	164
7	0.010	0.033	2.60	8.19	184	117	19,200	4150	10,450	560	390	22.1	837.5	76	5402	332
8	0.020	0.062	4.00	2.51	101	47	15,550	2300	7130	213	260	5.5	637.5	44	4934.5	168
9	0.010	0.024	6.70	0.99	110	15	9600	2550	5730	191	96	4.6	637.5	56	2547.5	128
10	0.080	0.069	8.70	4.30	48	13	1700	500	680	153	10	4.5	23.75	52	448.25	92
11	0.090	0.039	8.20	2.38	168	15	1550	660	720	140	20	2.7	32.5	68	83.5	120
12	0.090	0.042	10.30	1.00	177	97	1200	1960	590	733	10	20.8	22.5	80	148.5	256
13	0.080	0.038	9.10	8.55	161	162	21,100	3200	11,520	1680	420	54.4	900	144	3940	676
14	0.090	0.040	1.50	7.73	154	174	17,960	3200	9220	1750	400	53.9	812.5	132	2867.5	696
15	0.000	0.092	0.90	9.34	151	174	14,000	2900	7240	1630	260	51	600	132	2320	628
16	0.010	0.040	1.10	9.46	167	166	10,400	3150	5180	1340	180	50	450	136	3590	712

Table 1 (continued)

17	0.010	0.015	1.80	7.81	145	158	16,400	3350	8779	1860	520	56.1	750	164	3650	684
18	0.010	0.036	1.60	7.95	141	176	14,600	2800	8300	1550	290	54.9	750	136	3090	688
19	0.080	0.043	1.80	4.91	156	173	14,800	3200	8130	1720	330	51.5	725	132	3595	648
20	0.020	0.021	2.30	8.09	154	160.1	16,800	3400	7670	1890	280	56.1	600	140	5080	760
21	0.010	0.088	2.80	8.79	155	174	13,100	3800	6850	1700	194	60.2	550	174	4650	764
22	0.020	0.044	3.20	8.51	149	172.7	12,980	3650	5270	1710	260	59.3	537.5	160	3622.5	764
23	0.010	0.011	2.40	8.17	169	170.8	11,000	3700	6380	2100	210	67	537.5	172	4462.5	860
24	0.030	0.035	2.90	8.62	165	164.5	12,200	4100	6360	2060	240	69.3	512.5	220	1987.5	892
25	0.020	0.032	3.20	8.77	183	169.9	12,090	3950	6120	1950	180	67.2	525	172	3035	836
26	0.010	0.028	2.80	7.18	155	168.3	13,100	4200	6380	2090	194	69.2	550	212	4650	780
Min	0.0	0.01	0.3	0.99	48	13	1200	500	590	140	10	2.7	22.5	44	83.5	92
Max	0.09	0.09	10.3	9.46	184	242	22,200	9000	11,900	4850	520	136.3	1000	528	5437.5	2064
Ave	0.03	0.04	3.33	6.53	146	139.0	14,160	3467	7396	1611	271	50.63	630.8	159	3449.2	688
Std Dev	0.03	0.02	2.9	2.6	32.1	59.9	5874.2	1492.9	3195.4	1002.4	140.26	29.52	275.9	92	1498.3	403

in pre-monsoon period was similar to the previous studies in this lagoon (Nayak and Behera 2004; Panigrahi et al. 2007; Rajawat et al. 2007; Panigrahi et al. 2009; Muduli et al. 2012); however, the salinity values in the post-monsoon period were lower than previous studies (Panigrahi et al. 2007; Panigrahi et al. 2009). The higher and comparatively stable salinity values observed in the southern sector during the pre-monsoon could be a result of the input of saline water from Rushikulya estuary through the enclosed Palur canal throughout the year which maintains an even salinity value (Muduli et al. 2012). Another reason for higher and stable salinity values in the southern sector could be less freshwater discharge in this region. Moderate salinity values observed in the central sector during pre-monsoon is due to good circulation and mixing of both marine and freshwater in this region. This region is well mixed due to the freshwater discharge from small rivulets and streams joining the western catchment of the lagoon and entry of the seawater from the inlets present in the outer channel region.

Spatial distribution of salinity during the post-monsoon depicts very low values in the entire lagoon. During post-monsoon, salinity decreases abruptly over the entire lagoon. The heavy rainfall brought by the southwest and northeast monsoon causes the addition of huge amounts of freshwater into the lagoon which causes substantial dilution lowering down the salinity values considerably (Rajawat et al. 2007). Very low values for salinity ranging from 0.2 to 13.8 PSU in the entire lagoon during the post-monsoon period could also be a result of the large influx of freshwater during the very severe cyclone *Phailin* which occurred in October 2013. The heavy downpour of about 738 mm during the cyclone may have further lowered the salinity in the post-monsoon season (Sahoo et al. 2014).

Dissolved inorganic carbon

Dissolved inorganic carbon (DIC) mean value during the pre-monsoon period was 170.4 mg/l (132–203.6 mg/l). The average

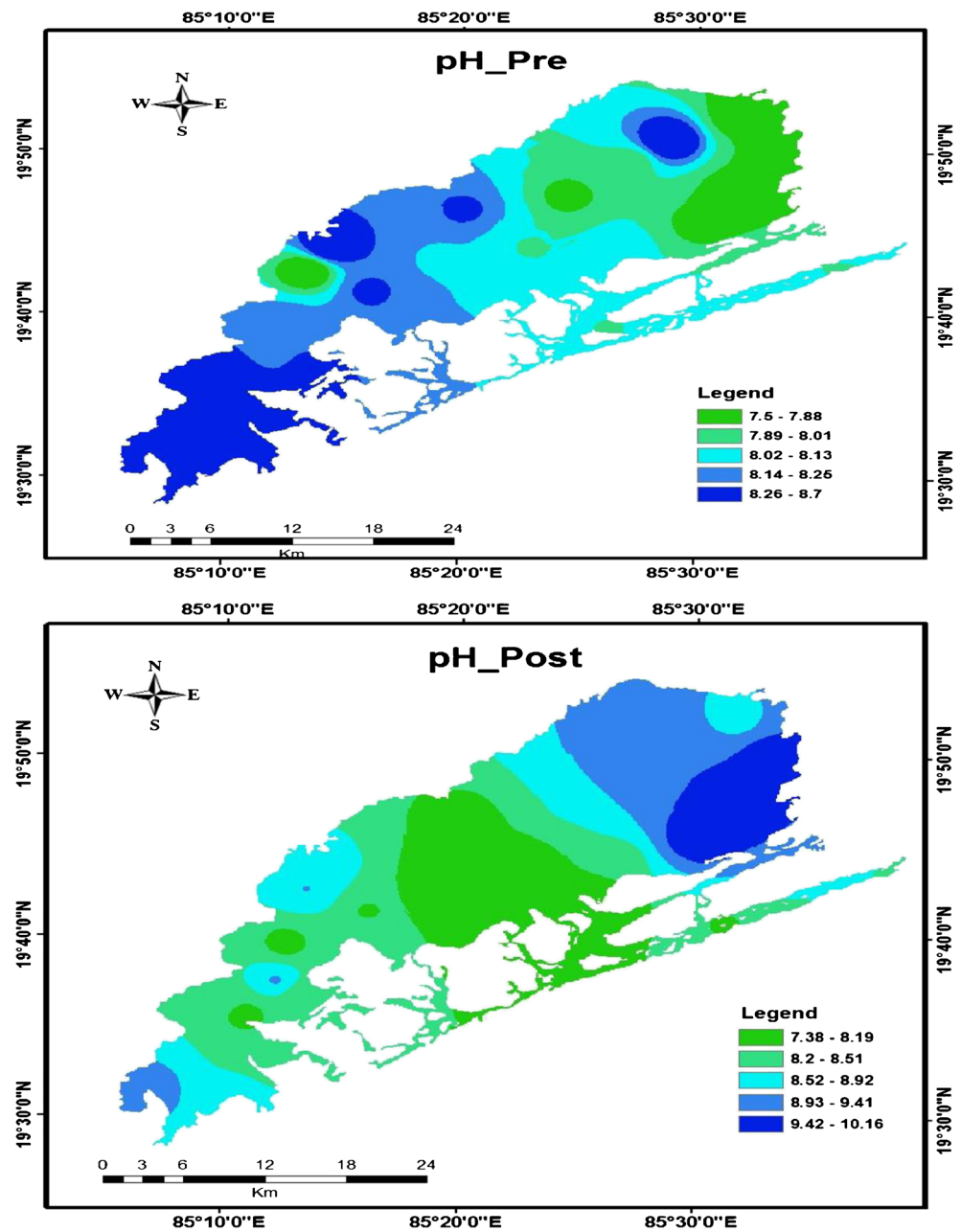
value of DIC during post-monsoon was 140.91 mg/l (103.6–167.7 mg/l). In aquatic systems, DIC concentration is governed by chemical, physical, and biological processes. Spatial and temporal variation of DIC could be related to the catchment area characteristics and variability in hydrology. The spatial and temporal variability of DIC is mostly due to the weathering of the bed rock in the drainage basin; however, biological activity also has a large influence in controlling the DIC values in Chilika lagoon (Gupta et al. 2008). Exchange of CO₂ with atmosphere, pH, salinity, carbonates, respiration, and photosynthesis are some of the factors that govern DIC concentration in a water body. Photosynthetic uptake of CO₂ and precipitation of calcareous material lowers DIC (Muduli et al. 2013).

The spatial distribution values of DIC for both the seasons have been presented in Fig. 4. DIC shows a higher average value in pre-monsoon season when compared to the post-monsoon season. The higher DIC during the summer may be due to its lesser assimilation by the biological systems. Moderate to high values of DIC has been observed in most parts of southern sector and some parts of central sector during the pre-monsoon season as these regions do not have higher plants which make use of dissolved carbon for photosynthesis. Lower values of DIC observed in the post-monsoon season could be a result of primary production and bacterial respiration of carbon which causes variations in DIC concentration (Muduli et al. 2012; Kanuri et al. 2013).

Dissolved organic carbon

The mean dissolved organic carbon (DOC) value in the pre-monsoon period was 5.65 mg/l (3.87–7.89 mg/l). The mean DOC value for post-monsoon period was 5.85 mg/l (3.97–9.75 mg/l). The chief sources of organic carbon to these environments are allochthonous materials exported from the land through rivers and autochthonous production of organic matter by algae through photosynthesis and intertidal vegetation (Kanuri et al. 2013). The combination of primary production of plant matter and decomposition rates controls the amount of

Fig. 2 Spatial distribution of pH in pre- and post-monsoon seasons

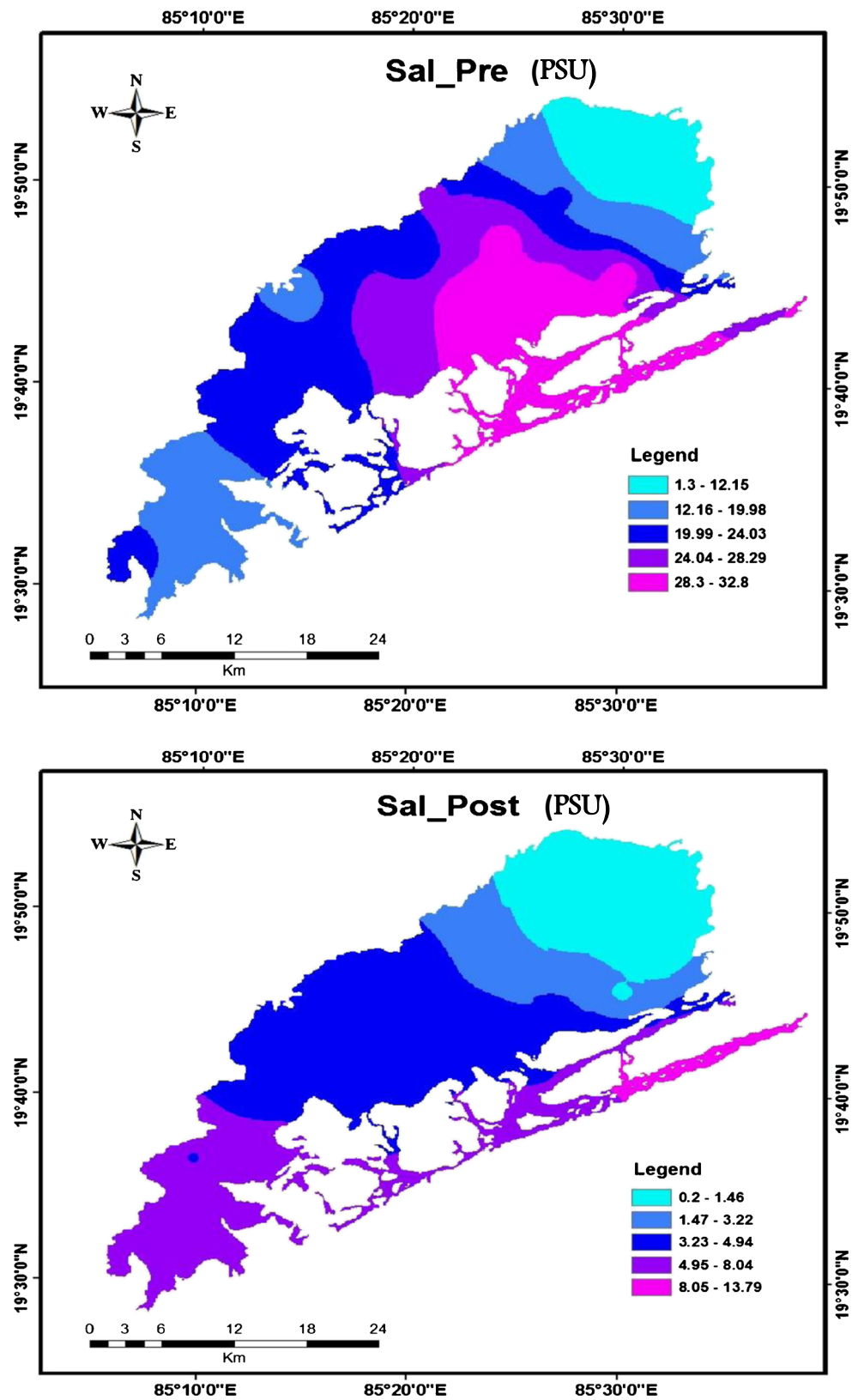


DOC in water. Spatial distribution of DOC has been presented in (Fig. 5). The lower DOC values observed in pre-monsoon season when compared to the post-monsoon season may be a result of DOC being converted to CO_2 (Kanuri et al. 2013). Slightly higher DOC during the post-monsoon period can be attributed to heavy downpour and freshwater influence on the entire lagoon which has contributed to the carbon from terrestrial sources. DOC fluxes from sediments are also an important carbon source in many estuaries and benthic remobilization is expected to be an internal source of DOC in shallow systems (Clark et al. 2006). Rivers draining into Chilika carry higher DOC concentration, thus Chilika has appreciable DOC load (Gupta et al. 2008).

Dissolved oxygen

The mean dissolved oxygen (DO) value for pre-monsoon season was 7.34 mg/l (2.34–13.43 mg/l) and 7.94 mg/l for post-monsoon (2.30–17.39 mg/l). The spatial distribution of DO shows higher values in the northern sector during pre-monsoon when compared to the other sectors except near the Balugaon town in the central sector (Fig. 6). Northern sector is dominated by a large number of freshwater macrophytes which engage in active photosynthesis. Oxygen is released as a by-product of photosynthesis. Therefore, northern sector remains well oxygenated. Higher DO concentration near the Balugaon region could be a result of high

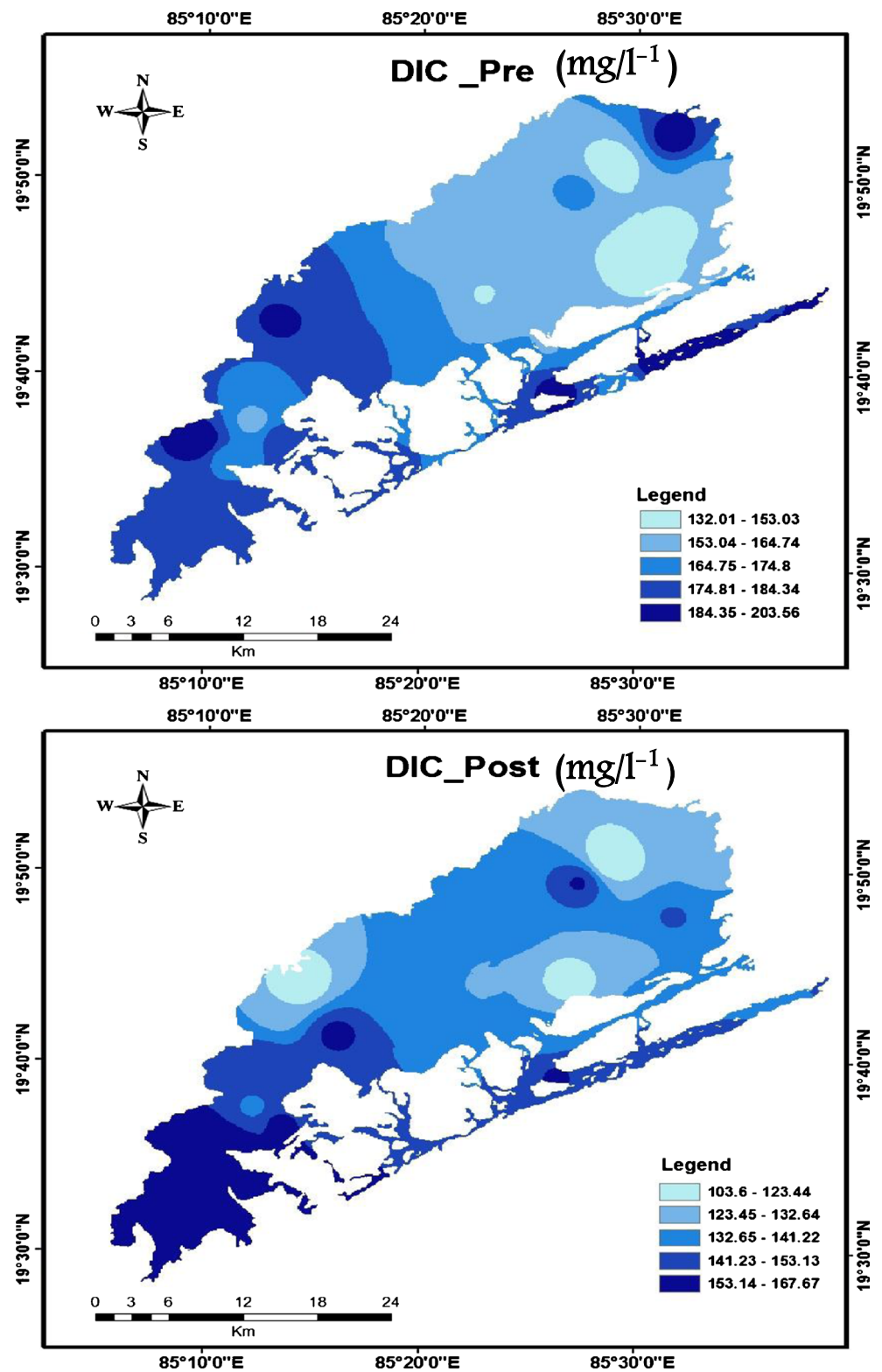
Fig. 3 Spatial distribution of salinity in pre- and post-monsoon seasons



concentrations of nutrients like NO_3^+ and PO_4^{3+} entering the lagoon from Balugaon township which gives rise thick algal

mat. Presence of plants leads to photosynthetic activity and release of oxygen (Bose et al. 2012).

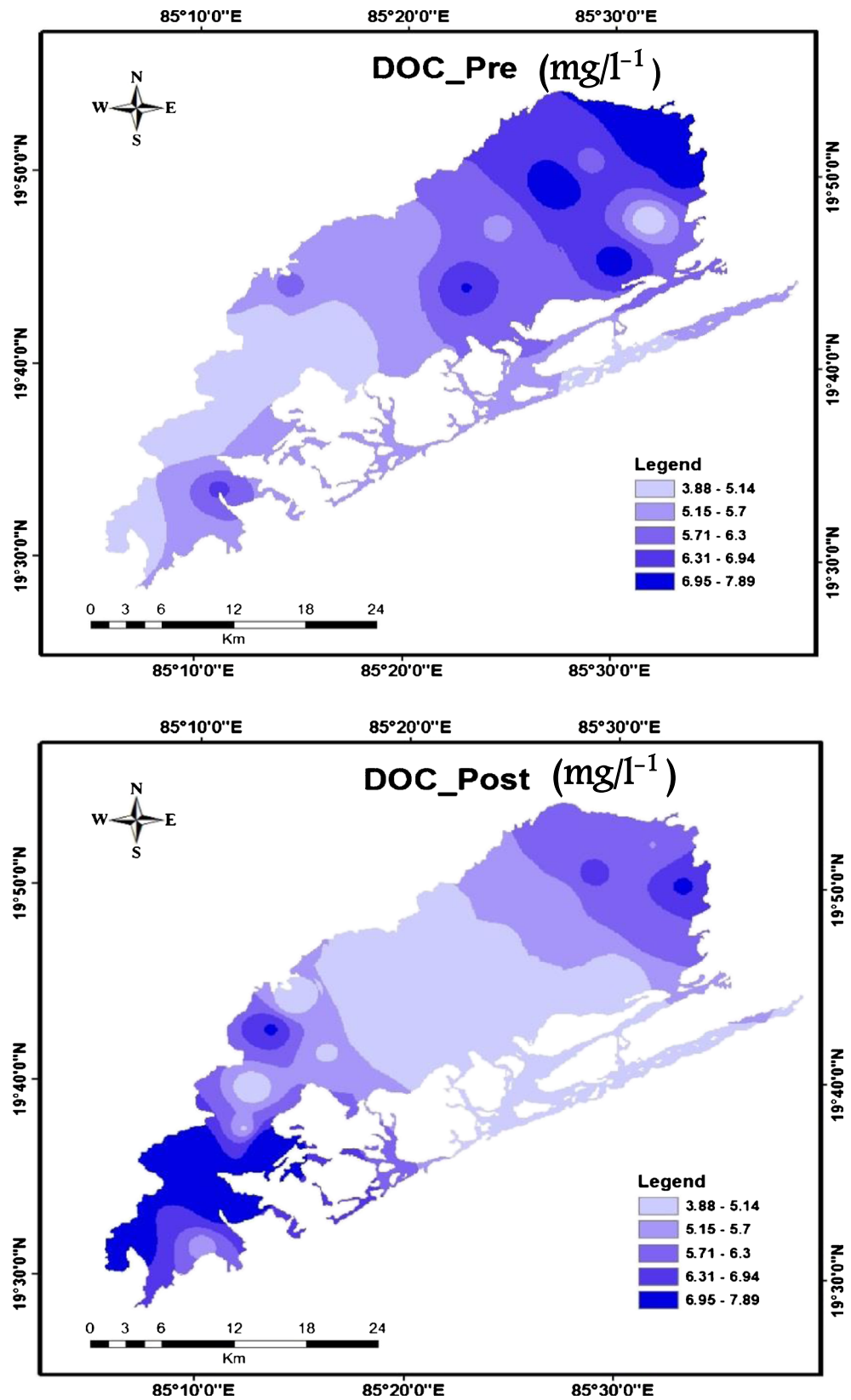
Fig. 4 Spatial distribution of DIC in pre- and post-monsoon seasons



In the post-monsoon season also a similar pattern is observed in DO values in the entire lagoon (Fig. 6). Slightly higher DO values in the post-monsoon season could be a result of the photosynthetic activity of micro

and macrophytes along with DO-rich freshwater reaching the system due to the large amount of precipitation which occurred due to *Phailin* (Srichandan et al. 2015a, b). Greater values of DO in the post-monsoon

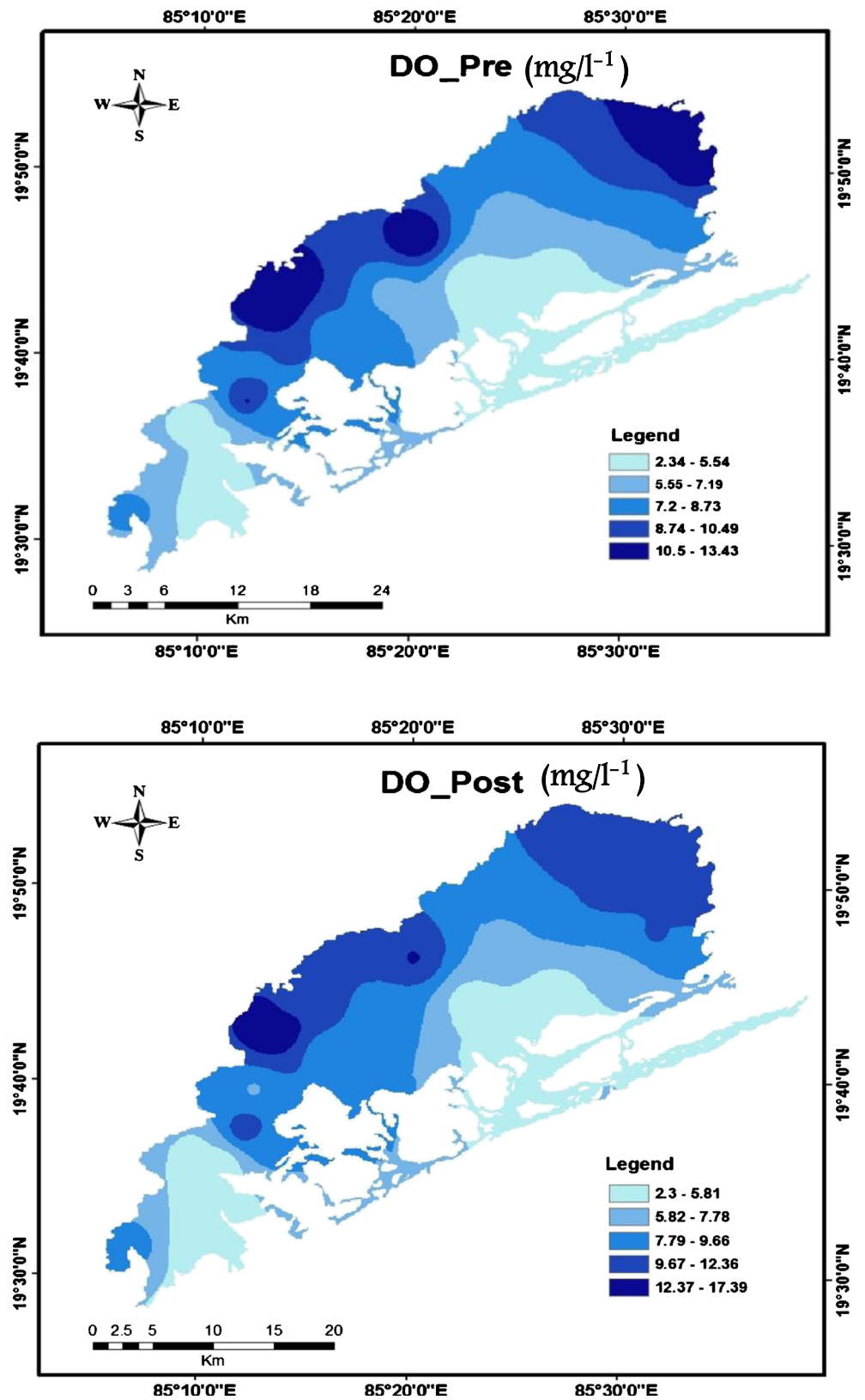
Fig. 5 Spatial distribution of DOC in pre- and post-monsoon seasons



season could also be a result of wind-induced enhanced vertical mixing due to *Phailin* and lower water

temperature which holds more DO (Fawzy et al. 2012; Barik et al. 2017).

Fig. 6 Spatial distribution of DO in pre- and post-monsoon seasons



Nitrite

Mean value for nitrite (NO_2^-) was 0.43 mg/l (0–1.67 mg/l) and 0.72 mg/l (0–2.34 mg/l) for pre and post-monsoon seasons, respectively. NO_2^- is the intermediate oxidation state between ammonia and nitrate; therefore, it can appear as an intermediate transient species by the oxidation of ammonia or by the reduction of nitrate. NO_2^- being an unstable species does not remain as such and it gets readily reduced to NO_3^- . The higher average values of NO_2^- were observed during post-monsoon season. Higher values ranging from 0.3 to 1.32 mg/l are observed in the southern sector during the pre-monsoon season, whereas values ranging from 0.7 to 2.2 mg/l of NO_2^- are observed in few patches in a post-monsoon season. NO_2^- is added into the system due to the phytoplankton excretion, oxidation of ammonia, and reduction of nitrate and by recycling of nitrogen and bacterial decomposition of planktonic debris (Prabu et al. 2008; Satpathy et al. 2010a, b).

The spatial distribution of NO_2^- has been shown in (Fig. 7). A gradual increase in NO_2^- concentration is observed moving toward south from the northern part of the lagoon. This may be due to higher NO_3^- concentration in a southern sector which gets converted to NO_2^- . We observe very low NO_2^- in northern sector in spite of higher NO_3^- . This may be due to rapid assimilation of NO_3^- by a large number of submerged and floating macrophytes. In post-monsoon season, a very variable trend is observed in the spatial distribution of NO_2^- . Low concentration is observed in both northern and southern sectors. This could be due to rapid conversion of NO_2^- to NO_3^- and its assimilation by the intrinsic vegetation.

Nitrate

Mean value for nitrate (NO_3^-) was 2.2 mg/l (0.2–7.5 mg/l) for pre-monsoon, whereas average value for NO_3^- in the post-monsoon season was 5.3 mg/l (0.8–9.6 mg/l). Nitrate in aquatic environments is mainly derived from terrestrial runoff. Concentration and rate of supply of nitrate are related to land use practices in drainage basin, since NO_3^- moves easily through soils and is rapidly lost from land through natural drainage systems. NO_3^- is the most stable form of inorganic nitrogen in well-oxygenated waters. Variations in nitrate are predominantly due to biologically activated reactions (Satpathy et al. 2010a, b). It is added through nitrogenous fertilizers, industrial effluents, human and animal wastes through the biochemical activity of nitrifying bacteria, such as nitrosomonas and nitrobacter (Raju et al. 2009).

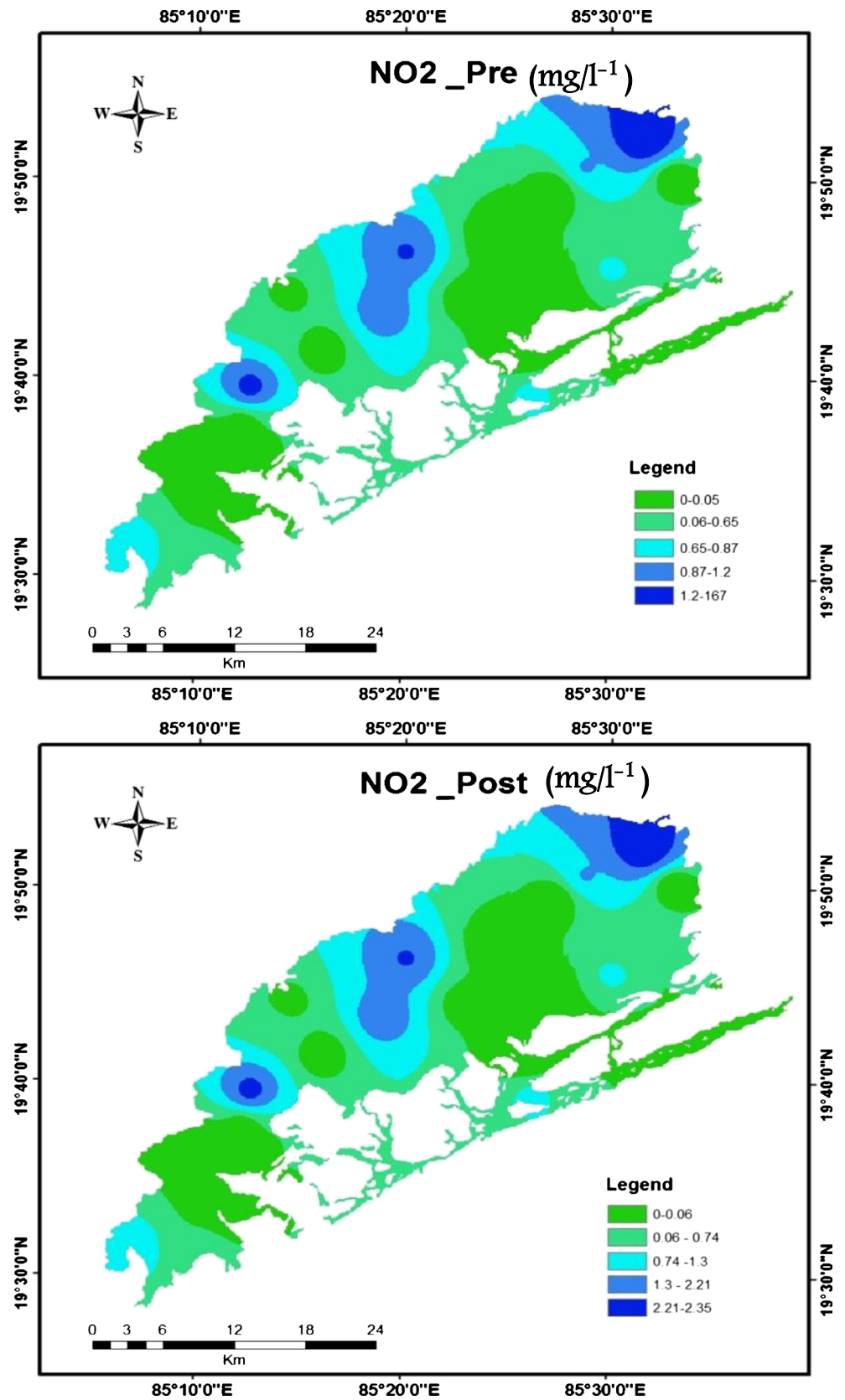
The spatial distribution of NO_3^- has been presented in Fig. 8. In the pre-monsoon season, highest NO_3^- values are observed in the southern sector. Small patches having higher NO_3^- concentration are also observed in northern and central sectors (Fig. 8). These patches may be witnessing NO_3^- inputs due to agricultural runoff, untreated sewage discharge, aquaculture ponds, and other

household wastes being directly dumped into the lagoon water. Organic nitrogen present in domestic sewage is bound to carbon-containing compounds as proteins (R-NH_2). Decomposition of organic nitrogen in the sewage soil by a variety of microorganisms slowly transforms the organic nitrogen to ammonia (NH_3) by a process called “mineralization” (Raju et al. 2009). Further during nitrification process, ammonia gets converted to NO_2^- first and then NO_3^- . NO_2^- is unstable therefore its gets oxidized to NO_3^- . Nitrate is quite soluble in water and being stable does not get adsorbed to soil particles as well. The majority of agricultural fertilizers contain nitrogen in the forms of ammonium and nitrate, often as ammonium nitrate (NH_4NO_3), which could be the prime source of nitrogen species in the coastal water (Newton and Mudge 2005). High NO_3^- concentration in the post-monsoon season may be due to large amount of nitrate brought about from the agricultural fields by the large freshwater flow into the lagoon. One of major reasons for high nitrates in certain pockets during post-monsoon may be due to aquaculture ponds and domestic wastes directly released into the water by the fishing villages around the lagoon. Moreover, in winter, the rates of nitrification and denitrification become slow which may have led to NO_3^- accumulation at some places in the lagoon (Zhang et al. 2014). Higher nitrate concentration in post-monsoon season may also be due to release of NO_3^- by the death and decay of macroflora. A patch of high NO_3^- is observed near the Kalijai temple during post-monsoon (Fig. 8). Low water levels and large amount of waste dumped by the visitors to the temple could be the possible reason for high NO_3^- values in this region. Moderately higher values of NO_3^- observed in the post-monsoon is a consequence of heavy freshwater discharge during the cyclone *Phailin* carrying agricultural runoff into the lagoon.

Phosphate

The mean value of phosphate (PO_4^{3-}) was 0.03 mg/l (0.0–0.09 mg/l) in the pre-monsoon season and 0.04 mg/l (0.01–0.09 mg/l) in the post-monsoon. Phosphate is one of the major nutrients responsible for biological production in the aquatic ecosystems. PO_4^{3-} is also the limiting nutrient in most of the aquatic ecosystems. Phosphate is mainly derived from agricultural runoff and domestic sewage, part of it is also derived from weathering of P bearing minerals as apatite and fluoroapatite (Nazneen and Raju 2017). Domestic sewage is a major source of ammonium and phosphate. Phosphate is also added through fertilizers which contain di-ammonium phosphate (Chauhan and Ramanathan 2008). Low phosphate concentration may be due to its rapid assimilation by the micro and macrophytic vegetation in the lagoon or due to its adsorption on the surface of sediments. Other reasons for PO_4^{3-} removal from the water column is its microbial incorporation. The spatial distribution of PO_4^{3-} shows a higher value in some parts of the northern sector and in small patches in the central sector during pre-monsoon (Fig. 9). This is also the place where a large number of birds

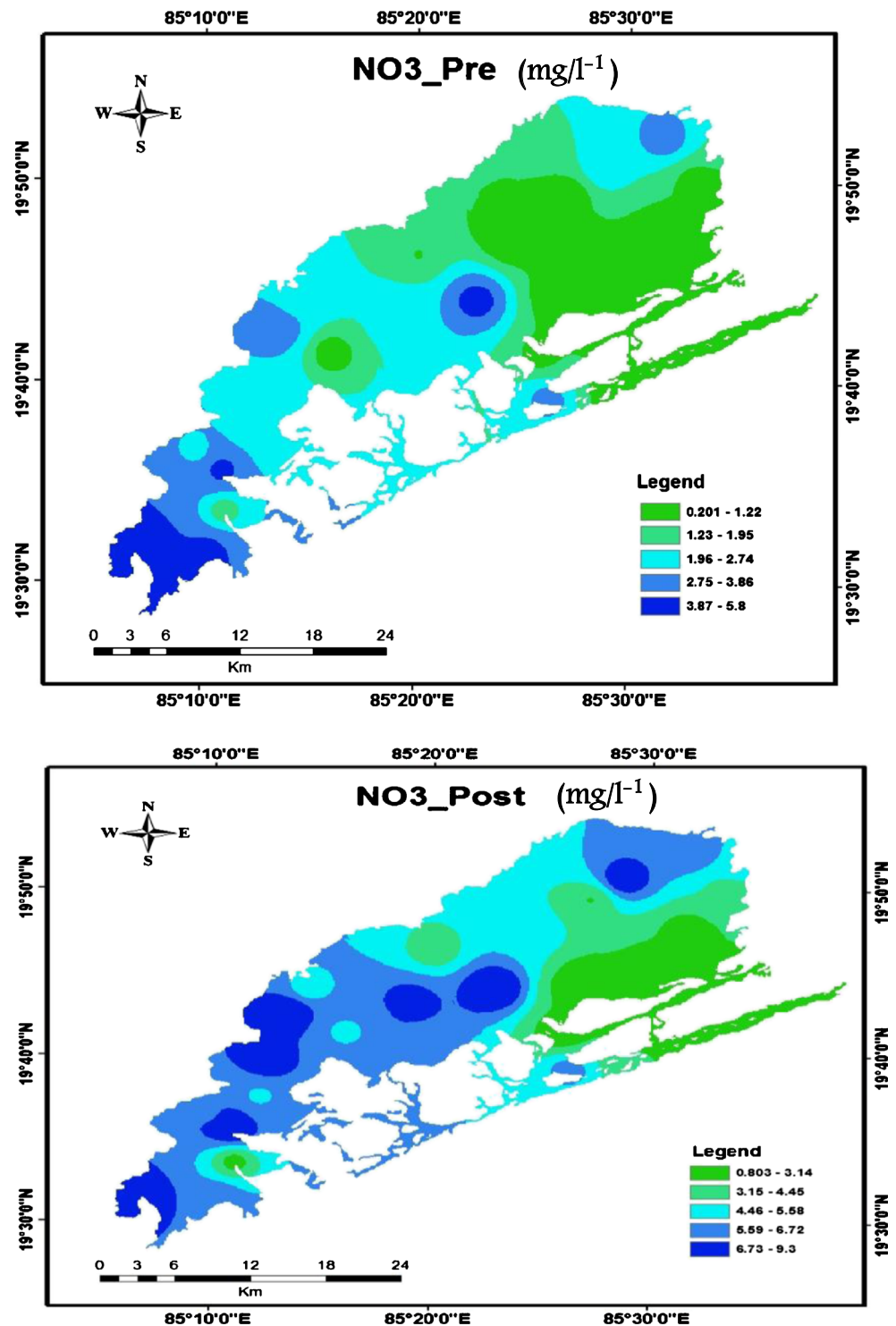
Fig. 7 Spatial distribution of NO_2^- in pre- and post-monsoon seasons



assemble. The release of phosphate from guano of birds is also responsible for the higher concentration of PO_4^{3-} near

Nalabana island in the central sector of the lagoon. The congregation of birds adds 33.8 t of nitrogen and 10.5 t of phosphorous

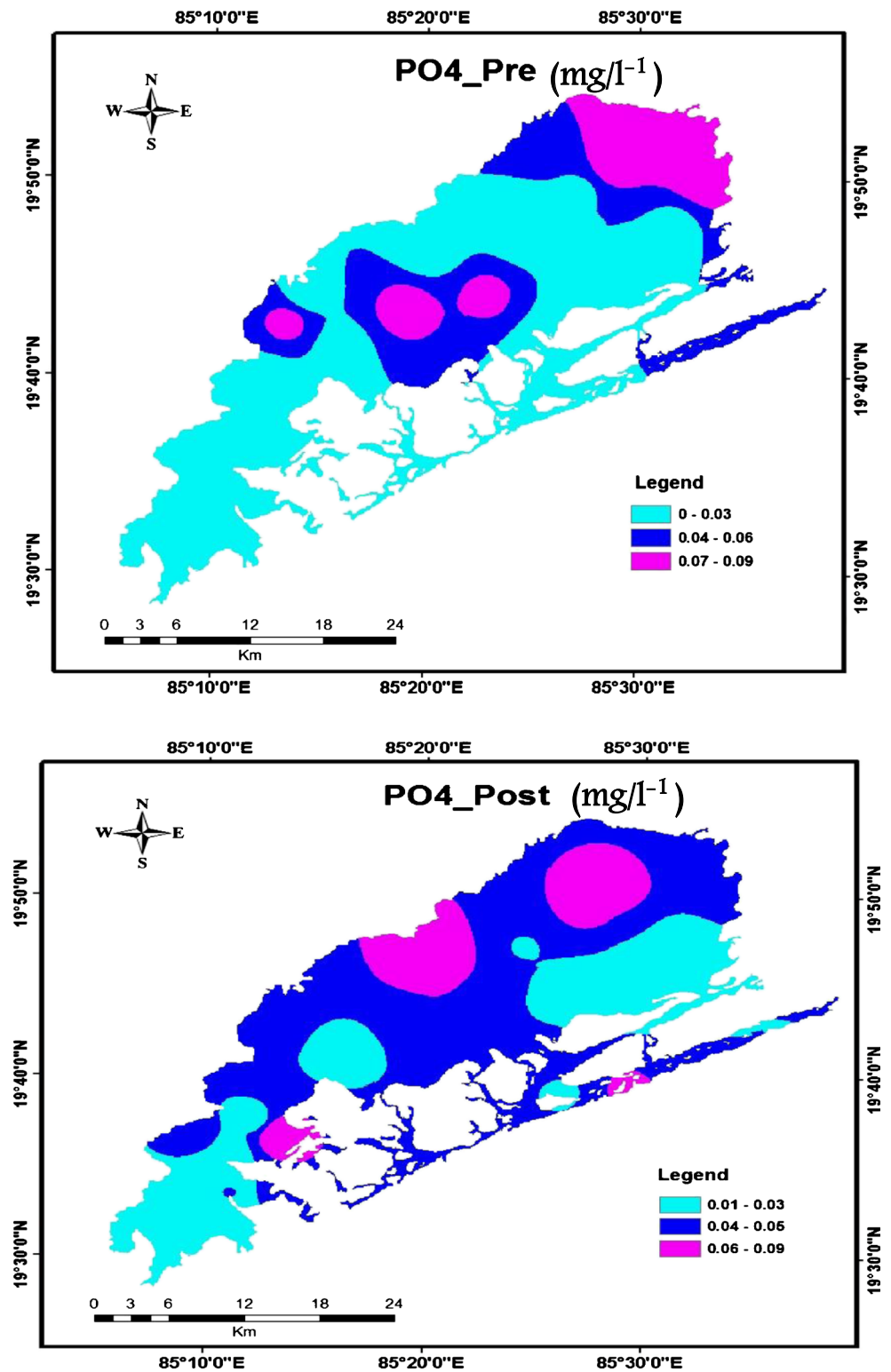
Fig. 8 Spatial distribution of NO_3^- in pre- and post-monsoon seasons



(in the form of guano) to the lagoon which helps in high biomass production of macrophytes and lucrative fisheries in Chilika (Wetlands International Report 2011). Highest PO_4^{3-} concentrations ranging from 0.07 to 0.09 mg/l observed in the inner portion of the lagoon during pre-monsoon season might have been primarily influenced by external sources as well as contributions from sediment fluxes (Silva et al. 2013; Barik

et al. 2017). There could be a result of PO_4^{3-} addition from the river runoff in the northern and western boundaries of the lagoon. During post-monsoon, moderately higher values ranging from 0.04 to 0.06 mg/l prevails in most parts of the lagoon. The values observed in both the seasons are comparable to the values observed in previous studies (Panigrahi et al. 2007, 2009).

Fig. 9 Spatial distribution of PO_4^{3-} in pre- and post-monsoon seasons



Dissolved silica

The mean concentration of dissolved silica (DSi) was 3.33 mg/l (0.3–10.3 mg/l) in pre-monsoon and 6.53 mg/l (0.99–9.46 mg/l) in post-monsoon seasons respectively. The spatiotemporal variations of DSi in coastal water is influenced

by several factors, including the proportional physical mixing of seawater with fresh water (Purushothaman and Venugopalan 1972), adsorption of reactive silicate into sedimentary particles, chemical interaction with clay minerals (Gouda and Panigrahy 1992), co-precipitation with humic compounds, and iron and biological removal by

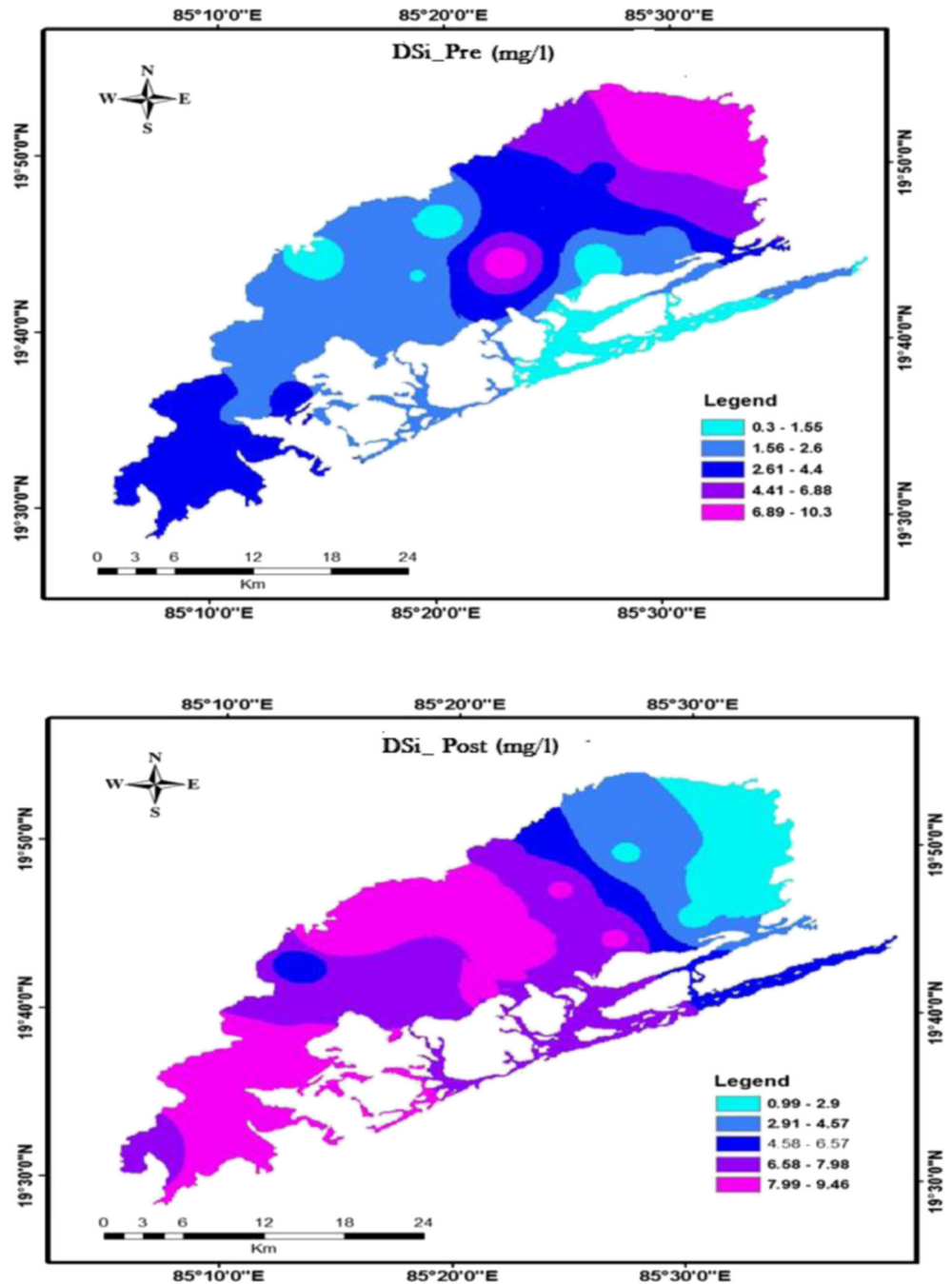
phytoplankton, especially by diatoms and silicoflagellates (Beucher et al. 2004). The DSi values are lower in the pre-monsoon or summer season; this could be a result of silicate assimilation by the diatoms (Silva et al. 2013). Increased concentration of DSi has been observed in the post-monsoon period over the entire lagoon as compared to pre-monsoon period (Fig. 10). This could be due to increased river discharge after heavy rainfall during tropical cyclone *Phailin* (Sahoo et al. 2014; Barik et al. 2017). The elevated value of DSi in post-monsoon season is because of freshwater intrusion in the entire lagoon which carries higher DSi load. Another reason

for the higher concentration of DSi during the post-monsoon season could be a result of death and decay of diatoms due to low salinity values prevailing in the lagoon. The death of diatoms causes subsequent release of biogenic silica locked up into their frustule into the water column.

Chloride

In the pre-monsoon season, mean value of cchloride (Cl^-) was 14,160 mg/l (1200–22,200 mg/l), whereas it was 3467 mg/l (500–9000 mg/l) in the post-monsoon season.

Fig. 10 Spatial distribution of DSi in pre- and post-monsoon season



Chloride is the most dominant anion in the seawater. NaCl is the major salt present in the seawater. Therefore, Cl^- exhibits a similar spatial variation like salinity in both the seasons. In the pre-monsoon season, highest concentration of Cl^- is observed in the outer channel region (Table 1), followed by central and southern sectors. The presence of Cl^- is largely due to saltwater intrusion; however, evaporate dissolution could also be one of the prominent sources (Raju et al. 2016). The Cl^- values are lowest in the northern sector which has major river discharge, and least salinity values. The Cl^- values remain quite low in the post-monsoon season when compared to the pre-monsoon season. Chilika receives a large amount of precipitation due to the southwest and northeast monsoons which brings down the salinity to lower values in the subsequent months. The salinity remains very low during the December and January months. In October 2013, cyclone *Phailin* hit the east coast of India which brought down heavy discharge which further lowered the salinity values in Chilika. Therefore in the post-monsoon season, the highest Cl^- of 9000 mg/l value is observed only in the outer channel region near the inlet to Bay of Bengal (Table 1). Southern sector has slightly higher Cl^- values due to lesser discharge of freshwater in this sector when compared to others. Southern sector is also connected to the sea by Palur canal and has a constant supply of saline water. Another pathway of saltwater intrusion is due to its connection to Rambha Bay through Rushikulya estuary (Ray 2011).

Sodium and potassium

A similar trend like salinity is observed for sodium and potassium (Na^+ and K^+) in both the seasons as sea water is the major contributor of these ions. Na^+ had a mean value of 7396 mg/l (590–11,900 mg/l) in the pre-monsoon. The post-monsoon mean value for Na^+ was 1611 mg/l (140–4850 mg/l). Mean value of K^+ in the pre-monsoon season was 271 mg/l (10–520 mg/l) and 50.6 mg/l (2.7–136.3 mg/l). Both the cations have a similar distribution like salinity as these ions are the major constituents of seawater. The mean value of Na^+ was higher in pre-monsoon season owing to higher salinity values. The other sources of Na^+ and K^+ could also be due to weathering, erosion, and agricultural drainage in the catchment area which adds these ions into the lagoon (Raju et al. 2012). Clay minerals like illite are also a source of K^+ in aquatic bodies. Khandelwal et al. (2008) have mentioned that the southern sector remains relatively undisturbed because of much slower water renewal, and hence brackish water conditions prevail in this zone even during monsoons. This region also has greatest depth, least freshwater discharge, and constant supply of saline

water through Palur canal (Muduli et al. 2012). The more stable ion chemistry in the southern sector is reminiscence of geological past of the Chilika basin and can be attributed to several palaeochannels in this region (Misra and Jena 2015).

Calcium and magnesium

Mean calcium (Ca^{2+}) was 630.8 mg/l (22.5–1000 mg/l) in pre-monsoon and 159 mg/l (44–528 mg/l) in the post-monsoon season respectively. Average value of magnesium (Mg^{2+}) was 3449.2 mg/l (83.5–5437.5 mg/l) in pre-monsoon and 688 mg/l (92–2064 mg/l) in post monsoon season respectively. Seawater is the major contributor of these cations in Chilika lagoon. Though freshwater has a considerable amount of Ca^{2+} and Mg^{2+} ions, but in Chilika the dominant source of these ions is sea water.

Conservative and non-conservative behavior of nutrients along the salinity gradient

In the estuarine system, the nutrients behave either conservatively or non-conservatively depending on their chemistry, seasonal and biological influence, and several other factors (Liu et al. 2011). An element is conservative if its ratio to salinity is constant. If a material moves through the estuarine system in direct proportion to its relative abundance in relation to some non-reactive material like salinity, then this material is said to be “conservative” with respect to salinity. This implies that the system exerts no control on the fate of the material throughout its passage through the system. If the material moves disproportionately relative to a conservative tracer, it is said to be “non-conservative” with respect to the tracer. Materials, which are non-conservative, are of biogeochemical and ecological interest. Conservative elements have very low chemical reactivity in the ocean and marine systems and their distributions in the ocean interior are determined only by currents and mixing. Nutrients like carbon, phosphorus, and nitrogen are non-conservative in the coastal environment and are essential for the biological productivity of the system. All the nutrients (NO_3^- , PO_4^{3-} , DSi) showed a nonlinear behavior with salinity in both the seasons (Fig. 11a) which marks mixing in the lagoon. On the other hand, all major cations like Na^+ , K^+ , Ca^{2+} , and Mg^{2+} show a strong positive correlation with salinity. The anions like Cl^- , SO_4^{2-} is used by sulphate reducing bacteria to form HS^- or H_2S yet we do not observe a nonlinear behavior for these anions, which is due to their high abundance in comparison to their utilization.

The input of terrigenous materials from agricultural runoff is responsible for the higher concentration of nutrients like NO_3^- and PO_4^{3-} . The nonlinear behavior of nutrients with salinity indicates their non-conservative

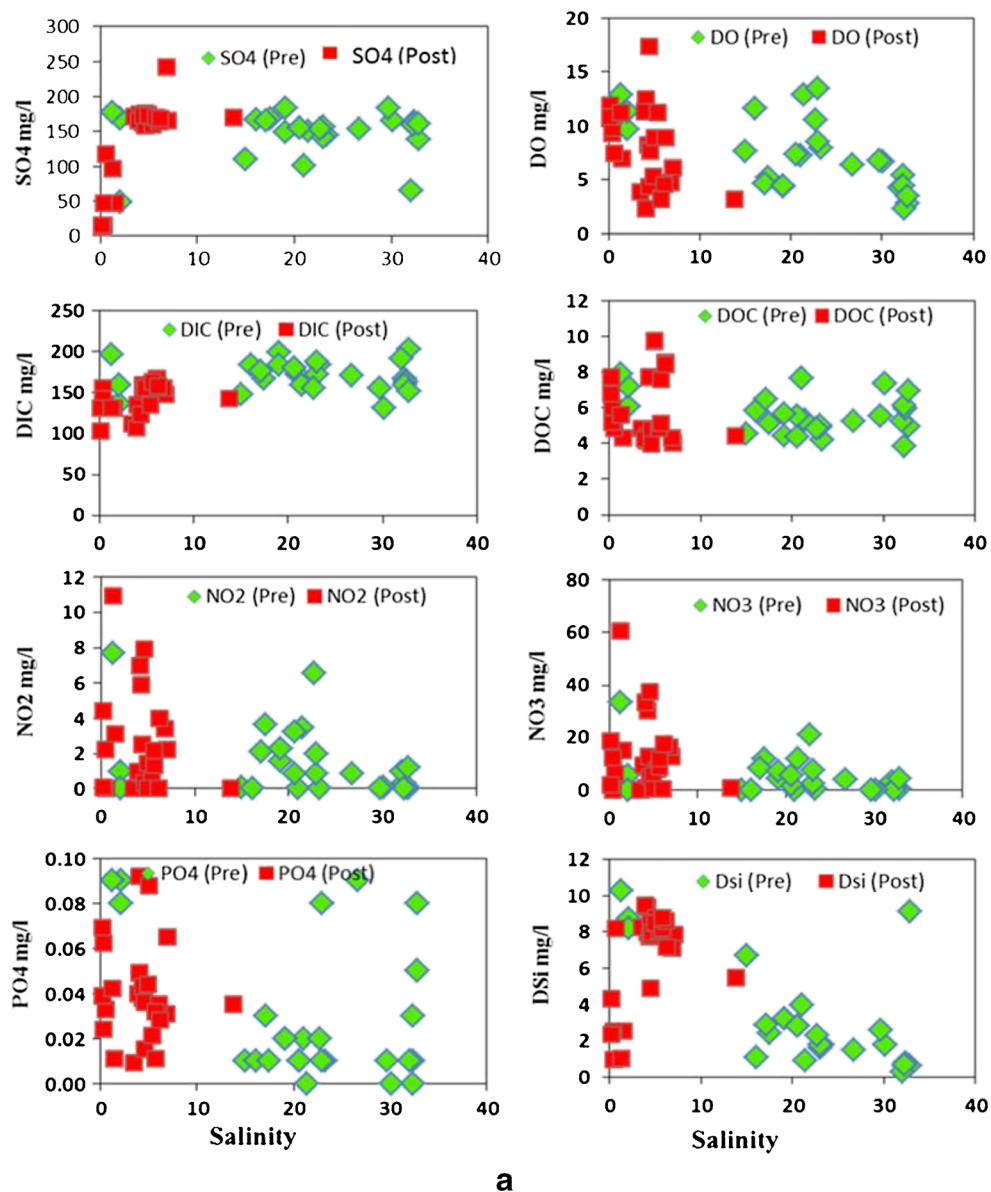


Fig. 11 **a** Spatial distributions of nutrients as a function of salinity. **b** Spatial distributions of EC and other ions as a function of salinity

behavior. This kind of non-linear behavior points toward a good amount of mixing in the lagoon beside biological uptake (Wang et al. 2014). The other parameters like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- do not show much scatter (Fig. 11b). We observe a strong linearity in these parameters with salinity. These ions are governed by the seawater intrusion into the lake. Freshwater is not a major source of these ions; therefore, they behave in a conservative manner. In the present study, NO_3^- shows a non-conservative behavior but it shows a conservative behavior in Delaware estuary, whereas a non-conservative behavior for NO_3^- has been observed in Godavari estuary due to removal at lower salinity zone by the uptake from phytoplanktons and addition in high salinity zone due to remineralization (Padmavathi and Satyanarayana 1999).

Correlation analysis

A bivariate correlation analysis is applied to describe the relationship between the two geochemical parameters. A correlation value above 0.5 between two parameters is considered good, whereas a correlation value around 1 (either positive or negative) between two parameters renders them very high relative relationship. The correlation between various parameters has been presented in during the pre and post-monsoon seasons have been presented in Tables 2 and 3.

In pre-monsoon season, a strong positive correlation between salinity (Sal), EC, Cl^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} indicates that seawater is the major source of these ions. The correlation value of salinity denotes a moderate negative correlation with DO and DSI. Dissolved oxygen decreases with

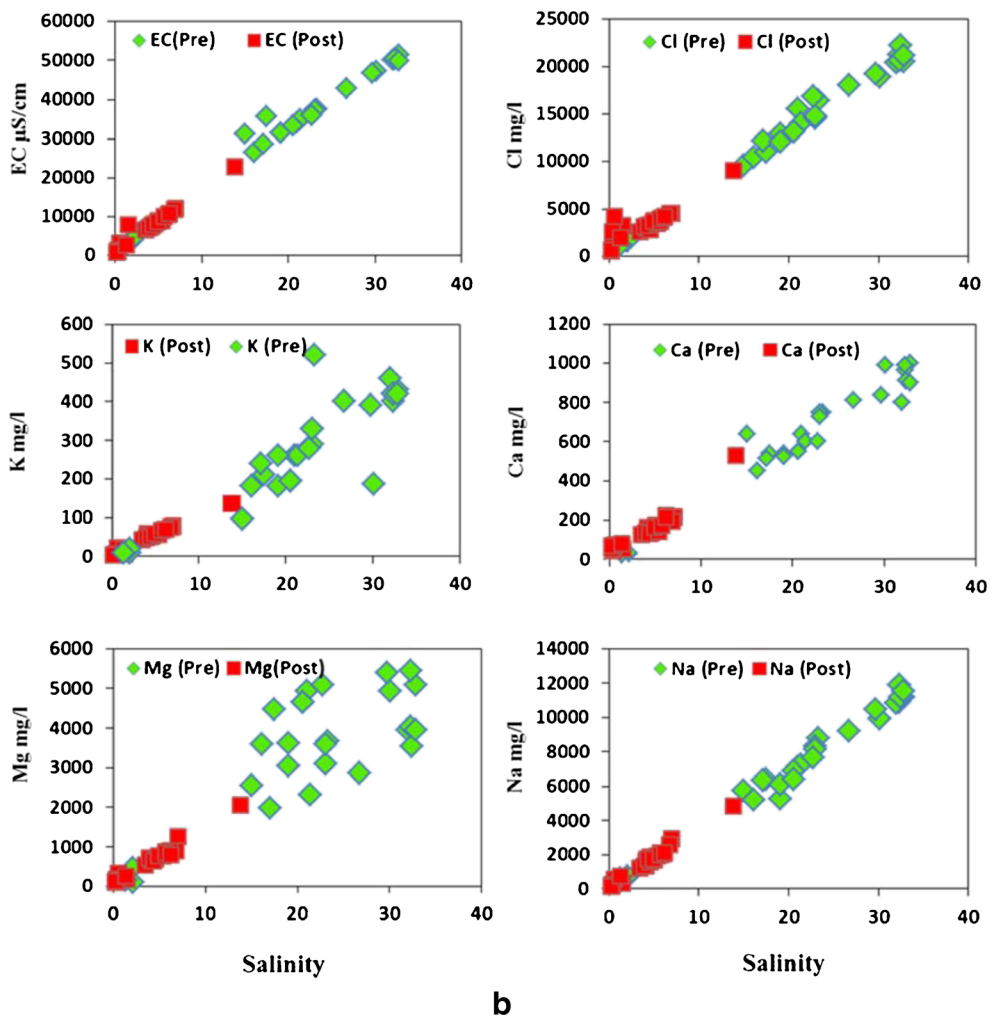


Fig. 11 (continued)

Table 2 Correlation analysis for pre-monsoon

	pH	EC	Sal	DIC	DOC	DO	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ³⁻	DSi	SO ₄ ²⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
pH	1															
EC	-0.13	1														
Sal	-0.13	<i>0.99</i>	1													
DIC	0.03	-0.01	0.01	1												
DOC	-0.28	-0.35	-0.31	-0.25	1											
DO	-0.13	-0.62	-0.61	-0.06	0.13	1										
NO ₂ ⁻	-0.01	-0.37	-0.38	0.18	0.07	0.40	1									
NO ₃ ⁻	-0.07	-0.44	-0.43	0.18	0.20	0.43	<i>0.97</i>	1								
PO ₄ ³⁻	-0.26	-0.45	-0.40	0.05	0.39	0.27	0.18	0.29	1							
DSi	-0.19	<i>-0.69</i>	<i>-0.68</i>	-0.24	0.53	0.27	0.27	0.36	<i>0.62</i>	1						
SO ₄ ²⁻	-0.17	0.12	0.12	0.12	0.07	0.02	0.21	0.19	-0.05	-0.13	1					
Cl ⁻	-0.12	<i>0.98</i>	<i>0.99</i>	0.01	-0.30	<i>-0.60</i>	-0.36	-0.41	-0.41	<i>-0.68</i>	0.11	1				
Na ⁺	-0.16	<i>0.99</i>	<i>0.99</i>	-0.02	-0.29	<i>-0.59</i>	-0.39	-0.43	-0.38	<i>-0.66</i>	0.12	<i>0.98</i>	1			
K ⁺	-0.05	<i>0.86</i>	<i>0.88</i>	0.22	-0.41	<i>-0.51</i>	-0.34	-0.36	-0.24	<i>-0.64</i>	0.05	<i>0.89</i>	<i>0.89</i>	1		
Ca ²⁺	-0.20	<i>0.98</i>	<i>0.97</i>	-0.04	-0.32	<i>-0.58</i>	-0.44	-0.48	-0.41	<i>-0.67</i>	0.13	<i>0.96</i>	<i>0.98</i>	<i>0.83</i>	1	
Mg ²⁺	-0.03	<i>0.80</i>	<i>0.79</i>	0.06	-0.38	-0.44	-0.23	-0.35	-0.57	<i>-0.64</i>	0.15	<i>0.79</i>	<i>0.75</i>	<i>0.62</i>	<i>0.77</i>	1

The values in italics indicate strong positive or negative correlation between the parameters

Table 3 Correlation analysis for post-monsoon

	pH	EC	Sal	DIC	DOC	DO	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ³⁻	DSi	SO ₄ ²⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
pH	1																
EC	-0.45	1															
Sal	-0.52	0.98	1														
DIC	-0.20	0.37	0.38	1													
DOC	0.21	-0.09	-0.05	0.29	1												
DO	0.38	-0.47	-0.44	-0.41	0.15	1											
NO ₂ ⁻	-0.03	-0.16	-0.16	-0.11	-0.18	0.29	1										
NO ₃ ⁻	-0.04	-0.18	-0.18	-0.13	-0.24	0.30	0.98	1									
PO ₄ ³⁻	-0.18	-0.13	-0.07	-0.08	0.15	0.36	0.23	0.17	1								
DSi	-0.72	0.44	0.48	0.20	-0.05	-0.33	-0.23	-0.23	0.09	1							
SO ₄ ²⁻	-0.78	0.68	0.72	0.32	-0.10	-0.35	-0.02	-0.01	-0.03	0.80	1						
Cl ⁻	-0.36	0.90	0.88	0.40	-0.12	-0.47	-0.26	-0.25	-0.14	0.32	0.55	1					
Na ⁺	-0.55	0.96	0.99	0.37	-0.09	-0.41	-0.13	-0.14	-0.03	0.47	0.73	0.87	1				
K ⁺	-0.65	0.94	0.98	0.39	-0.05	-0.46	-0.15	-0.17	-0.03	0.59	0.81	0.85	0.98	1			
Ca ²⁺	-0.45	0.93	0.95	0.32	-0.02	-0.44	-0.21	-0.23	-0.04	0.33	0.55	0.90	0.94	0.93	1		
Mg ²⁺	-0.56	0.95	0.98	0.34	-0.10	-0.43	-0.20	-0.21	-0.01	0.49	0.69	0.89	0.99	0.98	0.96	1	

The values in italics indicate strong positive or negative correlation between the parameters

salinity because high salinity waters are low in DO. Negative relation indicates that DSi is mainly brought by the freshwater since tropical rivers have high DSi concentration (Li et al. 2014). A strong positive correlation between NO₂⁻ and NO₃⁻ is because NO₂⁻ being unstable is converted to NO₃⁻ in aquatic systems. A positive correlation between PO₄³⁻ and DSi indicates their terrigenous source. The probable sources of PO₄³⁻ could be fertilizer residue from the agricultural field. Studies have indicated SiO₂ reaching water bodies from the agricultural field along with other nutrients. DSi has a negative correlation with Cl⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺ which shows its freshwater source, as the other ions are predominantly from the seawater. Different sources of PO₄³⁻ (freshwater) and Mg²⁺ (seawater) could be a reason for the negative correlation between PO₄³⁻ and Mg. Salinity and EC are positively related to Cl⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺. All these ions are present in major quantity in seawater. This relation is also an indication of seawater dominance in the lagoon. The geochemical studies on Chilika reveal that Montmorillonite, illite, Kaolinite with Chlorite are present in the sediment sample as major soil is alluvium in Chilika basin. These minerals are also the sources of major ions in Chilika water (Rai 1985).

In post-monsoon season, a good correlation of EC and salinity with SO₄²⁻, Cl⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺ indicates that these anions and cations are mainly governed by the seawater since these ions are in major quantity in seawater. NO₂⁻ shows a strong positive correlation with NO₃⁻ because NO₂⁻ is an intermediate state of NO₃⁻ in aquatic systems. SO₄²⁻ is strongly correlated with DSi which could be due to SO₄²⁻ and DSi release from the death and decay of the diatoms. DSi also

shows a positive correlation with K⁺ which could be due to the simultaneous release of silica and K⁺ from clay minerals.

Principal component analysis

Principal component analysis (PCA) is a technique for taking high dimensional data and reducing it to more manageable, lower dimensional form without losing significant information. The PCA enables a reduction in data and description of a given multidimensional system by means of a small number of new variables (Loska and Wiechula 2003; Garali et al. 2011). Relevant components are those whose eigenvalue is higher than 1 (Kaiser 1960). The application of varimax rotation of standardized component loadings enables us to obtain a clear system as a result of the maximization of component loadings variance and elimination of less valid components (Chakrapani and Subramanian 1993; Mustapha et al. 2013). In the pre-monsoon season, three factors are formed which show 74% of the total variance. PCA 1 is explained by 47.7% of the variance. PC2 and PC3 show 13% of variance each (Table 4).

Factor 1—this factor accounts for 47.7% of the total variability. Factor 1 shows positive loadings of salinity, EC, Cl⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺. This factor can be explained by the influence of seawater. EC is governed by the concentration of ions in a solution. Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ are the dominant ions in seawater; hence, they show a positive loading with salinity and EC.

Factor 2—current factor shows a positive loading of NO₂⁻, NO₃⁻, and SO₄²⁻. A high positive loading

Table 4 Principal component analysis for pre- monsoon season

	Rotated component matrix		
	Components		
	1	2	3
pH	-0.234	-0.231	-0.715
EC	<i>0.980</i>	-0.083	-0.100
Sal	<i>0.982</i>	-0.079	-0.076
DIC	0.046	0.468	-0.376
DOC	-0.275	-0.059	<i>0.734</i>
DO	-0.586	0.314	0.096
NO ₂ ⁻	-0.350	<i>0.851</i>	0.010
NO ₃ ⁻	-0.399	<i>0.827</i>	0.126
PO ₄ ³⁻	-0.448	0.101	<i>0.631</i>
DSi	-0.665	-0.030	<i>0.569</i>
SO ₄ ²⁻	0.235	<i>0.528</i>	0.192
Cl ⁻	<i>0.978</i>	-0.064	-0.078
Na ⁺	<i>0.982</i>	-0.088	-0.033
K ⁺	<i>0.870</i>	-0.010	-0.157
Ca ²⁺	<i>0.973</i>	-0.125	-0.043
Mg ²⁺	<i>0.796</i>	0.019	-0.287

PCA loading > 0.5 are shown in italics

between NO₂⁻ and NO₃⁻ is an indication of the oxidizing environment which oxidizes unstable nitrite to nitrate. Slightly positive loading of NO₂⁻, NO₃⁻, and SO₄²⁻ could be an indication of their anthropogenic source. Like NO₃⁻, SO₄²⁻ can also be added to the system from agricultural fields (Singh et al. 2015).

Factor 3—this factor depicts high positive loadings of DOC, PO₄³⁻, and DSi. A positive relation between these components suggests their allochthonous source. DOC is mainly transported into estuarine systems by rivers which carry carbon in the dissolved form to the coastal waters (Bouillon and Dehairs 2007., Gupta et al. 2008). Similarly, PO₄³⁻ and DSi are usually brought by the land and river runoff into the lagoon.

In the post-monsoon season, PCA is explained by 90% of the variance. PC 1 shows 42% variance. PC2 is explained by 17% variance. PC3 by 13%, PC4 by 9%, and PC5 by 8% (Table 5).

Factor 1: factor 1 shows strong positive loadings of salinity, EC, SO₄²⁻, Cl⁻, K⁺, Ca²⁺, and Mg²⁺. This is due to influence of marine water which contains very high concentration of these ions.

Factor 2: factor 2 shows strong positive loadings of DSi and SO₄²⁻. This could be the result of terrigenous input of these anions into the system besides release from the death and decay of diatoms and algae.

Factor 3: this factor has positive loadings on NO₂⁻ and NO₃⁻. Since NO₂⁻ is an intermediate state of NO₃⁻, we observe a positive correlation between these two nutrients.

Table 5 Principal component analysis for the post-monsoon season

	Rotated component matrix				
	Components				
	1	2	3	4	5
pH	-0.329	-0.859	-0.105	-0.009	0.050
EC	<i>0.941</i>	0.215	-0.049	-0.149	0.049
Sal	<i>0.948</i>	0.267	-0.048	-0.080	0.075
DIC	0.284	0.169	0.051	-0.328	<i>0.783</i>
DOC	-0.080	-0.144	-0.246	0.329	<i>0.792</i>
DO	-0.310	-0.319	0.174	0.697	-0.131
NO ₂ ⁻	-0.099	-0.031	<i>0.972</i>	0.147	-0.046
NO ₃ ⁻	-0.117	-0.021	<i>0.974</i>	0.102	-0.103
PO ₄ ³⁻	-0.025	0.182	0.132	<i>0.835</i>	0.090
DSi	0.230	<i>0.887</i>	-0.211	0.023	0.022
SO ₄ ²⁻	<i>0.519</i>	<i>0.768</i>	0.075	-0.079	0.064
Cl ⁻	<i>0.909</i>	0.092	-0.124	-0.192	0.042
Na ⁺	<i>0.944</i>	0.289	-0.009	-0.050	0.050
K ⁺	<i>0.892</i>	0.422	-0.044	-0.064	0.087
Ca ²⁺	<i>0.963</i>	0.118	-0.114	-0.049	0.049
Mg ²⁺	<i>0.944</i>	0.291	-0.090	-0.035	0.015

PCA loading > 0.5 are shown in italics

Factor 4: factor 4 shows a positive relationship between DO and PO₄³⁻. This relation can be explained by the deep intrusion of freshwater into the lagoon which brings DO and PO₄³⁻ load to the lagoon. A positive loading of DO and PO₄³⁻ suggests PO₄³⁻ assimilation by the flora and in turn release of DO.

Factor 5: strong positive loadings of DIC and DOC are observed in this factor. The concentrations of both these components are governed by catchment characteristics and aquatic vegetation. There increase or decrease is governed by plant uptake and release.

Heavy metal distribution in water

Heavy metal concentration in Chilika water was analyzed for pre and post-monsoon seasons and compared with standard values of metals for surface water determined by EPA 2009

Table 6 Summary statistics of heavy metals in water samples

Metal	Pre-monsoon (µg/l)			Post-monsoon (µg/l)		
	Min	Max	Mean	Min	Max	Mean
Pb	10	80	50	12	134	63
Cu	10	50	30	ND	ND	ND
Ni	20	67	37	ND	ND	ND
Co	10	50	30	ND	80	20
Fe	65	2790	594	120	11,240	1620
Mn	40	580	140	70	8410	1080

Table 7 Comparison of heavy metal values with EPA standard

Metal	Standard values	% of samples exceeding EPA limits	
		Pre-monsoon	Post-monsoon
Pb	8.1	38	57.7
Cu	3.1	100	–
Ni	8.2	50	–
Co	23.0	34.6	7.7
Fe	1000	19.2	20
Mn	120	85	–

(the United States Environmental Protection Agency). The range and average values of dissolved metals have been presented in Table 6. Some of the heavy metals like Zn, Cd, and Cr were non-detectable in the water in both the seasons, whereas the water samples at many locations exceeded the EPA standard values for other metals like Pb, Cu, Ni, Co, Mn, and Fe (Table 7).

In general, the heavy metal values were higher in the pre-monsoon season. Cu has a value higher than the standard in all the samples during pre-monsoon, whereas 50% and 85% of Ni and Mn respectively have higher values compared to standards (Table 7). There are several sources of Cu in coastal waters including fertilizers from agricultural fields, municipal and industrial wastewater, and antifouling paints used in the boats (Gardham et al. 2015). Copper is acutely toxic causing deleterious affect on primary producers and decomposers, which are crucial players in essential processes such as the nutrient cycling in aquatic ecosystems (Gardham et al. 2015). In the post-monsoon season due to dilution, heavy metals values were lower. However, Pb was detected in more number of samples in the post-monsoon season (Table 7). This could be due to precipitation during monsoon which washes the Pb present in the vehicular dust. The dissolved metal concentration in Chilika waters is higher and can impose a risk to the fishes and other organisms. The presence of Cu, Co, Ni, Fe, and Mn could be an indicator of corrosion-resistant paints used in fishing boats, fertilizers, and pesticides used in the agricultural fields (Singh et al. 2015; Satapathy and Panda 2015; Nazneen et al. 2018). Elevated Fe levels could be due to dissolution of ferruginous minerals and domestic sewage discharges (Raju et al. 2016).

The wetlands are mostly polluted through agricultural runoff and discharge of untreated sewage and other wastes from urban areas (Bassi et al. 2014; Sarkar et al. 2017). Chilika lagoon receives significant anthropogenic input from Daya and Bhargavi rivers which join the lagoon in its northern periphery. Untreated domestic waste from the capital city of Bhubaneswar reaches the lagoon through these rivers. Ghosh et al. 2006 have reported that 550MLD of sewage water reaches Chilika lagoon along with domestic wastes from nearly 150 villages in the catchment basin of Chilika

lagoon. There are also fish processing units and other small scale industries in the Balguon township which add significant waste at the western periphery. Besides this, a large number of fishing boats ply in Chilika which often use low-grade paints and antifouling agents which contain metals like Pb, Cu, and Zn (Barik et al. 2018; Nazneen et al. 2018). The overall elevated concentrations of the metals in the water samples may be attributed to mobilizing factors like oversiltation, intensive use of mechanized boat for transport using low-grade fuels, tourism and fishing, untreated discharges from the fish processing units, and aquaculture which has been highlighted in the recent studies on sediments of Chilika lagoon (Nazneen and Patel 2016; Barik et al. 2018; Nazneen et al. 2018).

Impact of Phailin on water quality of Chilika lagoon

The water quality of Chilika lagoon was significantly affected by the advent of very severe cyclone *Phailin*. The study was undertaken 3 months before and 3 months after the cyclone hit the Odisha Coast. There was drastic change observed in salinity post *Phailin* as the salinity values remained very low. There was a remarkable impact on nutrient biogeochemistry. The NO_3^- and PO_4^{3-} values were higher than the pre-*Phailin* period. DSi values also increased significantly. An increase in DO and pH values was also observed. The pH became more alkaline as a result of enhanced photosynthesis which withdrew CO_2 from the system, thus shifting the pH toward alkaline. The NS showed larger changes in water quality due to maximum addition of freshwater from river discharge; eutrophication was evident with thick mats of macrophytic growth. The advent of *Phailin* lowered down salinity in the entire lagoon which gave rise to changes in other parameters.

Conclusions

A marked spatial and temporal variability is observed in the Chilika lagoon water. The water quality of Chilika lagoon in this study shows the influence of very severe cyclone *Phailin* in particular and lagoon vegetation, increased agriculture, domestic sewage discharge, and fishing in general. The biological activity plays a major role in governing the water quality parameters. Nutrients like NO_3^- , PO_4^{3-} , and DSi show higher values in the post-monsoon season due to heavy freshwater discharge in particular due to very severe cyclone *Phailin* bringing these from terrestrial sources. Higher nutrient concentration observed in the northern sector of the lagoon is leading to heavy macrophytic infestation. PCA revealed a major influence of seawater besides geological factors in both the seasons as can be seen by the values of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . The other parameters like DSi show that freshwater entering the lagoon also has significant influence on the water quality. The non-conservative behavior of nutrients indicates a

good amount of mixing besides biological uptake. Heavy metals like Cu, Pb, Ni, Co, Mn, and Fe exceeded EPA standards at many locations in both the seasons. To control the influx of excess nutrients and heavy metals, the soil from agricultural runoff needs to be reduced. The dumping of untreated domestic waste from the peripheral villages' lagoon has to be checked. Another important aspect is management and treatment of the urban waste from the capital city of Bhubaneswar entering the lagoon from Daya and Bhargavi rivers. The number of boats plying in the lagoon need to be restricted and the fishermen community should be made aware of the perils of heavy metal pollution. Further to reduce the heavy metal concentration, the approach needed to be followed should be holistic catchment area treatment in terms of agricultural management and reduction of silt reaching the lagoon.

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