Time series monitoring of water quality and microalgal diversity in a tropical bay under intense anthropogenic interference (SW coast of Bay of Bengal, India)

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Abstract:

In the recent decades, material fluxes to the coastal waters from various land based anthropogenic activities have significantly been enhanced around the globe which can considerably impact the coastal water quality and ecosystem health. Hence, there is a critical need to understand the links between anthropogenic activities in watersheds and its health. Kakinada Bay is situated at the SW part of Bay of Bengal, near to the second largest mangrove cover in India with several fertilizer industries along its bank and could be highly vulnerable to different types of pollutants. However, virtually, no data is available so far reporting its physicochemical status and microalgal diversity at this bay. In order to fill this gap, we conducted three time series observations at a fixed station during January, December and June 2012, at this bay measuring more than 15 physical, chemical and biological parameters in every 3 hour over a period of 36 hours in both surface (0m) and subsurface (4.5m) waters. Our results clearly depict a strong seasonality between three sampling months, however, any abnormal values of nutrients, biological oxygen demand or dissolved oxygen level was not observed. A Skeletonema costatum bloom was observed in December which was probably influenced by low saline, high turbid and high Si input through the river discharge. Otherwise, smaller diatoms like Thalassiosira decipiens, Thalassiothrix frauenfeldii, Thalassionema nitzschioides dominated the bay. It is likely that the material loading can be high at the point sources due to intense anthropogenic activities, however, gets diluted with biological, chemical and physical processes in the offshore waters.

Key words: Kakinada Bay, Bay of Bengal, nutrient loading, N:Si ratios, diatom, *Skeletonema costatum*, PHC, TSM, phytoplankton bloom.

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Introduction:

In the recent decades, anthropogenic activities in and around the coastal areas are increasing in an alarming rate and are indeed detrimental for the aquatic ecosystems (Diaz and Rosenberg 2008). Various amounts and types of material (organic/inorganic, dissolved/ particulate) input into the coastal systems from land based anthropogenic activities have significantly been enhanced around the globe due principally to the production of food and energy to support the over growing population. This may often lead to "eutrophication" or enrichment of nutrients in the coastal waters (Seitzinger et al. 2010). Excess anthropogenic nutrients (nitrogen, phosphate and silicate in particular) input to the coastal areas have been increased to the magnitude of many folds over the last three - four decades (Conley et al. 2000; Conley et al. 2009). Enhancement in inorganic nitrogen input to the coastal waters can lead to increased phytoplankton biomass, changes in species composition, the possible proliferation of harmful algae and even hypoxia (Officer and Ryther 1980; Smayda 1990). This has resulted in the changes in structure and function of coastal ecosystems especially of shallow coastal areas where phytoplankton blooms were correlated with fluctuations in river discharge pattern, nutrient dynamics and light availability, water column stratification and grazing pressure by zooplankton (Seitzinger et al. 2010). Thus Coastal marine environmental health is an issue of major concern all over the world (Elmgren and Larsson 1997; Rabalais and Nixon 2002; Smith et al. 1999) and hence, there is a critical need to understand the links between anthropogenic activities in watersheds, nutrient inputs to the coastal systems, and its health.

However, phytoplankton shows immediate response to alterations in environmental conditions (Reynolds 1984; Stolte et al. 1994) and hence has been considered as an excellent bio-indicator to assess natural and seasonal changes in the coastal ecosystems (Harris 1986, Rimet & Bouchez 2012). Compared to the open ocean, coastal areas show wide array of changes in both physicochemical parameters and in phytoplankton assemblages (Cloern 1996; Carter et al. 2005). Smith (1996) combined and analysed data set from 92 coastal zone ecosystems from all over the globe and revealed that Chla (indicator of phytoplankton biomass) was always correlated with total nitrogen and phosphorus loading in to the system. Usually, diatoms dominate the phytoplankton community in the coastal areas due to the presence of sufficient silicate; however, other groups like green algae and dinoflagellate and others can also be present depending on the environmental conditions (Leterme et al. 2006). Coastal phytoplankton contributes to a significant part of global carbon production and hence any alternation in the coastal systems may lead to change in the global carbon cycle. Moreover, the prey-predator relationship in the food chain and commercial fish population are tightly linked to the type and size of phytoplankton that dominate a particular ecosystem. Thus far, any modification in these patterns may significantly alter the entire food chain and finally the fish population, which has direct socioeconomic impact and this has already been observed globally.

Organic carbon concentration (both terrestrial sources and in situ phytoplankton production) can largely control several physical, biological and chemical characters of the water bodies (Kirk 1994) including oxygen consumption by heterotrophic microbial activities leading to a hypoxic condition and high biological oxygen

demand (BOD). The BOD test is one commonly used method to quantify the consumption of oxygen in the water column from the decay of organic matter and nitrification of ammonia (Sullivan et al. 2010). BOD has been widely used as an indicator for the amount of organic pollutants in most aquatic systems, especially a good indicator for biodegradable organic compounds (Hur and Kong 2008). Thus BOD can be used as a proxy for organic carbon loading in the aquatic ecosystems (APHA, 2005) and a close coupling has been observed between DOC loading and BOD concentrations in different aquatic systems (Kwak et al. 2013; Reader et al. 2014). Worldwide, there are numerous cases reporting increasing BOD concentrations either due to increasing organic carbon pollution or due to extensive algal blooms induced by eutrophication in the coastal waters.

With increasing population worldwide, the usage of petroleum (provides 40% of world's energy) and its contaminants have been increased several times in the coastal environments (Tahir et al. 1997; Saramun and Wattayakorn, 2000; Wattayakorn., 2012) and can have severe damaging effects on its biota (Mackay and Hodgkinson 1996; Hylland 2006; Venkatachalapathy et al. 2012). PHC are the primary constituents of oil, gasoline, diesel, and a variety of solvents and some are highly toxic (aromatic hydrocarbons, poly-nuclear aromatic hydrocarbons, gasoline additives and combustion emissions from fuels). Pollution of the coastal and marine areas by PHC occurs mainly through land based discharges, marine operations and atmospheric and natural inputs (Laws 2000). A significant part of PHC can come from land run off, urban drainage, municipal waste, oil tanker operation, shipping, boating, atmospheric deposition and docking activities from the urban areas. PHC is a viscous mixture of thousands of organic compounds mainly consisting carbon and hydrogen. In general, they are long chain hydrophobic organic compounds and are highly insoluble, hence persistent in the water column. Possible fates of hydrocarbons released into the environment include volatilization, photooxidation, chemical oxidation, bioaccumulation, and adsorption on soil particles, leaching, and microbial degradation (Cerniglia 1992; Harayama et al. 1999). Increasing input of PHC in the coastal waters can adversely impact phytoplankton communities and can also enhance BOD values during aerobic degradation process. There are plenty examples showing acute toxicity of PHC on phytoplankton communities in tropical waters in both experimental exposure (Nayar et al., 2005; Sushma et al. 2008) as well as during natural oil spill events (Jaiswar et al., 2013). Hence, PHC contamination in the coastal waters is a growing concern globally (Mackay and Hodgkinson 1996) and essential to monitor for those areas that are vulnerable to oil pollution.

Although, nutrient input to the coastal waters is increasing globally, the South Asian countries were found to be the highest contributor of inorganic nitrogen and phosphorus input into the coastal waters (Seitzinger 2010). India is one of the fastest growing countries in the world with second largest population and hence the coastal waters of India could be extremely vulnerable to anthropogenically induced eutrophication. Coastal waters of the Bay of Bengal are highly dynamic with low surface salinity due to the immense freshwater inputs through excessive precipitation over evaporation and river discharge (McCreary et al. 2003). Thus, this large freshwater influx causes considerable seasonal variability with varying sediment load and nutrient input to the nearby coastal waters. The present study was carried out in the coastal waters of Kakinada Bay, south

east coast of India, offering an opportunity to analyze the effects of local hydrology and other allochthonous activities on phytoplankton community structure during three different times of the year. Although hydrography of this region was well reported, there was little or no attention paid towards monitoring the temporal and seasonal variability among phytoplankton communities with respect to the environmental alterations induced by river discharge, urban and industrial runoff from nearby areas. However, a lag in extensive observations along the south west coast of India in general and from the Kakinada Bay waters in particular has motivated to carry out the present investigation.

1. Study area:

Kakinada bay, situated in the south western part of Bay of Bengal, is a shallow marginal bay and a part of the Kakinada-Godavari estuarine area (16°41′ -16°53′ N and 82°14′ - 82°21′ E). One of the branches of the river Godavari, called Goutami-Godavari meets the Bay of Bengal at south of this point. On its southern part a mangrove swamp, Coringa mangrove, Indian's second largest mangrove system is situated and a natural sand bar runs from the mangrove area towards the northern side almost 11km along the coast. This area is under heavy anthropogenic activities due to extensive agricultural practices, proximity of several fertilizer industries, aquaculture farms, port activities and contiguity of the Kakinada city. Kakinada is part of the proposed Special Economic Zone called 'Petroleum, Chemical and Petrochemical Investment Region (PCPIR) and it is also nicknamed as 'Fertilizer City' because of several fertilizer industries in close vicinity. Many channels and creeks from the Coringa mangrove system are connected to this bay and deliver significant amount of organic and inorganic materials in to the bay along with huge amount of city sewage through the Kakinada canal. In the view of the importance and scarcity of reports from this coastal bay (Fig. 1), time series observations were carried out to monitor the physicochemical parameters and phytoplankton bloom dynamics over 36 hours time scale in the months of January (Jan), June and December (Dec) in 2012 at this bay. Almost 15 parameters including salinity, water temperature, pH, total alkalinity, dissolved oxygen (DO), biological oxygen demand (BOD), dissolved inorganic phosphate (DIP), dissolved inorganic silicate (Si) and dissolved inorganic nitrogen (DIN), petroleum hydrocarbon (PHC) and phytoplankton community structure over 36 hours time period (in every 3 hours) were measured.

2. Materials and Methods:

2.1. Physicochemical parameters:

Water samples were collected from both surface and subsurface (average depth 4.3m) using a pre cleaned 5L Niskin water sampler for the estimation of chemical and biological parameters. Salinity was measured by using a portable Conductivity-Temperature-Depth profiler (CTD; SBE-19 plus, Sea Bird Electronics, USA) at the bay location, Kakinada. For nutrient analysis 500ml of water samples were collected in acid cleaned plastic containers (from Tarsion, India) and were preserved with mercuric chloride in order to restrict the consumption/release of inorganic nutrients (NO₃+NO₂, NO₂, NH₄⁺, PO₄⁻³ and SiO₄⁻) and kept closed till analysis. Dissolved inorganic nutrients were analyzed following standard spectrophotometric methods

(Grasshoff et al. 1992). Samples were pH and alkalinity were collected in pre-acid cleaned glass bottles and samples were filled without any head space and were also fixed with mercuric chloride solution. Bottles were tightly closed to avoid any change. pH and total alkalinity was analysed using a 794 Basic Titrino from Metrohm, following Dickson (2003). For measuring total suspended matter (TSM) about 300ml of water sample was filtered through a pre weighed 0.45um polycarbonate filter (Millipore), dried at 40°C and reweighed to quantify TSM (mg L⁻¹). For estimating dissolved oxygen, glass bottles of 125ml capacity were filled to overflowing from Niskin water sampler with the help of pre cleaned Teflon sampling tube. To these water samples Winkler's A and Winkler's B solution were added and mixed very well uniformly for all bottles and kept aide till the precipitate settled down to one third of the bottle. Sulphuric acid with 1:1 concentration was added to dissolve the brown precipitate and Winkler titration was performed against diluted solution of sodium thiosulphate for the determination of dissolved oxygen.

Oxygen % of saturation was calculated using the expected DO concentrations at a given temperature and salinity as: (Observed DO)*100/ (Expected DO). Expected DO values were calculated using the formula of Weiss (1970) including salinity and temperature corrections.

For the estimation of Biological oxygen demand (BOD), water samples were incubated for 5 days at 25°C in a BOD incubator and then estimated by the above mentioned Winkler's titration method. The final values were deducted from the initial values and were divided by the number of days to get oxygen consumption per day at that temperature. Petroleum hydro carbons (PHC) determined spectroflourometrically (following the methodology of IOC- UNESCO manual, 1984) after extracting an aliquot of water sample from 1litre of sample collected with n-hexane. The samples were analyzed for Petroleum hydrocarbons using a Varian make Cary Eclipse Spectrofluorometer. The fluorescence of the samples was measured at 310nm excitation and at 364nm emission wavelength respectively. Blank were treated identically using crude oil extract (Merck) as a standard reference to test precision, accuracy and solvent purity in the analytical procedure and the units were expressed in terms of $\mu g L^{-1}$. All the respective 36 hours time series data were taken as average of the values and reported along with their respective standard deviations. The monthly mean values of rainfall and river discharge were calculated and obtained from the Irrigation Department, Dowleswaram, Andhra Pradesh.

2.2. Identification and Quantification of phytoplankton species:

For an assessment of generic composition and cell counts of phytoplankton, 1l water sample was collected from surface waters and were fixed with Lugol's iodine (1%; w/v). Samples were stored in dark at low temperature and a settling and siphoning procedure was followed to concentrate samples from 1l of water sample to 25 ml (Utermohl 1958). One ml of concentrated samples were then examined microscopically (OLYMPUS BX 53) in a Sedgewick- Rafter plankton counting chamber at 400X magnification.

Phytoplankton enumeration was done following the manuals of Desikachary (1987) and Hasle et al (1997). Total phytoplankton abundance was calculated in terms of number of phytoplankton cells observed in 1L of water sample and is also expressed in terms of relative percentage for each phytoplankton genera identified.

As far as possible, the phytoplankton groups were identified to species level, but in some taxonomic groups, identification is confined to genera.

Phytoplankton diversity index (H') or Shannon-weaver diversity index was calculated according to the following formula: H' = $-\ln(n/N)x \ln(n/N)$ where n = individual no. of species in a community and N = total no. of individual in that community.

3. Results:

3.1. Physicochemical parameters:

Indian climate is significantly influenced by its summer monsoon, hence, river discharge and rainfall patterns have large impacts on physicochemical characters of the coastal waters. Here the annual rainfall and river discharge data for the year 2012 has been given in Fig. 2 which clearly indicates that from January onwards there is almost no rain and nil river discharge was observed till May. However rainfall started only in the late June and our sampling was done before monsoon hit the coast. Hence it was the peak of premonsoon which is usually characterized by hot and dry period. Rainfall and river discharge both increased to their highest values during August-September and started to decline again and reached to a zero value in the month of December. Although, rainfall ceased in December, river discharge did not, however significantly reduced. The impact of freshwater input was well seen in all physicochemical parameters. In table 1 the minimum, maximum and average values of all physicochemical parameters are given for three sampling periods (Jan, June and December 2012). Fig. 3 represents diurnal variability of temperature, salinity, pH, alkalinity and total suspended matter (TSM) during three time series observations. It must be noted that during Jan and June sampling was done over 36 hours time period from 7am to next day 7pm and it started only by 1pm in Dec due to some technical problems. All figures have been drawn according to this timing.

Water temperature (Fig. 3a) showed sharp difference between Jan, June and Dec. The highest temperature was noticed in June with an average value of 28.88±0.65°C at the surface and 28.51±0.63°C in the subsurface. The average temperature of surface (25.8°C) and subsurface (25.7°C) waters in Jan and Dec were almost the same. During these times temperature inversion was noticed during the night times where subsurface water temperature was higher than that of the surface waters. In December, this difference was quite significant relative to Jan. Diel variation in water temperature was very much prominent in Dec. In June no such effects were observed. Like temperature, salinity values revealed a similar trend with maximum values detected in June and minimum during Dec (Fig. 3b). Average salinity value in June was 34.3±0.34 and 34.45±0.45 in surface and subsurface, respectively. In Jan salinity values ranged between 28.1 -28.91 in surface and 28.16 -28.95 in subsurface, respectively. In Dec, salinity was minimum with an average value of 27.82±0.56 in surface and 27.94±0.44 in subsurface. Average pH values during Jan were quite low both in surface (8.08±0.03) and subsurface (8.08±0.04), however varied significantly over the 36 hours cycles (Fig. 3c) influenced by both day/night and tidal cycle. In June the average pH values increased to 8.13±0.06 in surface and 8.12±0.05 in the subsurface waters. The maximum observed pH was 8.23 in the surface waters during this

time. In December, there were further enhancements in pH values in both surface (8.16±0.03) and subsurface (8.16±0.04) waters and the maximum detected pH was 8.26. Total alkalinity was lowest during December with an average value of $2106\pm42.67\mu\text{molL}^{-1}$ in the surface and $2107\pm28.4\mu\text{mol L}^{-1}$ in the subsurface waters. However, in June noticeably higher values of total alkalinity (Fig. 3d) were observed within the range from 2329 to $2472\mu\text{molL}^{-1}$ in the surface and 2299 to $2390\mu\text{molL}^{-1}$ in the subsurface waters. These higher values were in consistent with higher salinity values at the same time (Fig. 3b). In January, total alkalinity values were moderate with an average values 2158 ± 7.8 and 2166 ± 21.4 μmolL^{-1} for subsurface and surface waters, respectively. Total alkalinity values revealed a significant positive relation with salinity ($R^2=0.917$, R=74, R=74,

The observed variability in total suspended matter (TSM) has been depicted in Fig. 3e which clearly indicates two peaks during January and December. Subsurface waters showed higher TSM concentrations relative to the surface waters in all three sampling times. The range of TSM values in January were 35-71mg L⁻¹ in surface and 37 -106 mg L⁻¹ in the subsurface, respectively. In December the average value in the surface water was 58.55±8.6 mg L⁻¹, whereas, the value observed in January in the surface waters was 48.5±10.84 mg L⁻¹. During June the minimum values of TSM were 30 mg L⁻¹ (surface) and 39 mg L⁻¹ (subsurface) and the maximum values were almost double of it.

Dissolved oxygen values during the three sampling periods have been presented in Fig. 4a. Surface waters have always been detected with higher DO concentrations relative to the subsurface. A clear diel variation was noticed for all three sampling times. Distinct peaks of DO values were observed during the day time which was followed by a drop down during the night times. In Jan and Dec higher values of DO were recorded relative to the values noticed in June. DO values revealed a significant linear negative correlation with salinity (Table 2). Minimum DO values were noticed in June (4.89 mg L⁻¹ in subsurface and 5.2 mg L⁻¹ in surface), however, the average values were 5.7±0.32 mg L⁻¹ in surface and 5.52±0.37 mg L⁻¹ in the subsurface waters. In Jan the average DO concentration was almost 17% higher in the surface and 13% higher in the subsurface waters than the values observed in June. In December 10% and 19% enhanced DO values were observed in the surface and subsurface relative to the average values noticed in June. Average oxygen % of saturation (Table 1) was <100% in all seasons, however, the highest values were observed in Jan (97.73±6%) which was almost 9% reduced in June. in December again the % of was enhanced.

Biological oxygen demand (BOD) values revealed a reverse trend (Fig. 4b) showing its higher values in June (1.4±0.5mgL⁻¹in subsurface and 1.02±0.57mgL⁻¹ in surface) and significantly lower values in Jan and Dec with high fluctuations on day/night cycle. BOD values decreased more than twice in Dec both in surface and subsurface waters (Table 1). In Jan, BOD values were slightly lower than the values observed in June. BOD values did not reveal any definite correlation with oxygen % of saturation during this study.

The concentrations of PHC were highest during June (Fig. 4c) and on average higher values were associated with surface waters. Variability in PHC concentrations was very high on diel cycle. In June the average

highest value observed in subsurface water was $15.8\pm8.6~\mu g L^{-1}$ which was 1.83 times reduced in the surface waters. Conversely, in Jan PHC concentrations were higher in surface $(7.52\pm4.41\mu g L^{-1})$ waters relative to the subsurface $(4.93\pm3.88\mu g L^{-1})$. A similar trend was also observed in Dec $(6.48\pm2.62~\mu g L^{-1})$ in surface and $4.19\pm2.49~\mu g L^{-1}$ in subsurface waters). PHC and BOD values revealed a significant linear positive correlation (Table 2) indicating a direct relation between these two parameters. PHC concentrations also revealed a linear positive correlation with salinity ($R^2=0.245$, n=74, p<0.05).

3.2. Dissolved inorganic nutrients:

Dissolved inorganic nitrogen (DIN) concentrations have been presented in Fig. 4d. In Jan, DIN concentrations varied from 8.14 to 11.31µmolL⁻¹ in the surface and 9.8 to 12.3µmolL⁻¹ in the subsurface waters. The highest DIN concentrations were observed during June with an average value of 14.6±2.2µmolL⁻¹ in the subsurface and 12.79±0.94µmolL⁻¹ in the surface waters. In December, DIN values were significantly lower relative to June and Jan. The average values of DIN in the subsurface waters were almost half the values noticed in June. The variability of individual DIN components, NO₃-1, NO₂-1 and NH₄⁺ have not been presented in figures, however their minimum, maximum and average values have been presented in Table 1. NO₃-1 concentrations were the highest among these three DIN species and were significantly low in Dec (1.53 -6.45µmolL⁻¹ in the subsurface and 2.87 -8.14 μmolL⁻¹ in the surface waters). In June the range of values of NO₃⁻¹ in surface water was 9.18 -11.97 µgL⁻¹ and in subsurface waters NO₃⁻¹ varied from 8.99 -16.1µmolL⁻¹. NO₂⁻¹ values were always < 2 µmolL⁻¹ in all sampling periods. The highest NO₂⁻¹ values were observed in Jan in the subsurface water (1.77μmolL⁻¹). The average values in surface (0.71±0.18μmolL⁻¹) and subsurface (1.14±0.42μmolL⁻¹) waters were also higher during this time. In June these values were slightly reduced and the minimum concentrations were noticed in Dec with an average value of 0.33±0.16 µmolL⁻¹ in the surface and $0.46\pm0.18\mu\text{molL}^{-1}$ in subsurface waters. The concentrations of NH₄⁺ were < 2 μ molL⁻¹ in Jan with an average value of 1.22±0.48µmolL⁻¹ in the subsurface and 0.79±0.3µmolL⁻¹ in the surface waters. Slightly higher values of NH₄⁺ were observed in June and the highest concentrations were noticed in Jan (2.21±0.8μmolL⁻¹ in surface and 1.74±0.49µmolL⁻¹ in the subsurface waters) (Table 1).

The variability of dissolved inorganic phosphate (DIP) concentrations (Fig. 4e; Table 1) revealed that the highest concentrations were noticed in Jan with significantly higher values in subsurface (1.71±0.82μmolL⁻¹) relative to the surface (1.18±0.6μmolL⁻¹). In June the average concentrations of DIP in the surface and subsurface waters were 1.35±0.27μmolL⁻¹ and 1.58±0.36μmolL⁻¹, respectively. In Dec the average DIP values reduced to almost half of the values observed in June in both surface and subsurface waters. Dissolved silicate (Si) values varied significantly between Jan, June and Dec (Fig. 5a; Table 1). Si concentrations were < 15μmolL⁻¹ in Jan and Jun, however were significantly higher in Dec. In Jan, the average Si concentrations varied from 6.38 -12.45μmolL⁻¹ and 7.74 -13.02μmolL⁻¹ in the surface and subsurface waters, respectively. The lowest values of Si were recorded in June, both in surface (5.54±2.19μmolL⁻¹) and subsurface (6.37±2.7μmolL⁻¹) waters.

DIN and DIP concentrations show a clear day night variation. During the day time and mid of the day, DIN and DIP concentrations clearly depleted and increased again during the night time. The ratios of DIN to DIP (N:P) is a significant indicator of trophic status in any aquatic systems. During this study, the average N:P ratios remained below 16:1 most of the times (Fig. 5b) except few occasions in Jan and Dec. Distinct diel variation in N:P ratios were observed during all sampling times. Similarly Si to DIN ratios (Si:N) values were close to 1:1 during Jan with slight variability and well below 1 in June (0.45±0.23 in surface and 0.44±0.21 in subsurface waters) and almost 5 times higher in Dec (Fig. 5c).

3.3. Phytoplankton biomass, cell count, diversity and community composition:

Chlorophyll a (Chla) concentrations during Jan, June and Dec is presented in Fig. 5d and Table 1. The highest concentrations of Chla were detected in Dec, whereas, the lowest values were noticed in June. The average Chla values in Jan were 1.25±0.53 μgL⁻¹ and 1.16±0.41 μgL⁻¹ in the subsurface and surface waters, respectively. In June Chla concentrations were significantly low (0.51±0.27μgL⁻¹ in surface and 0.89±0.31μgL⁻¹ subsurface waters) and again increased to its maximum value in Dec. High variability was observed in Chla concentrations during Dec in both surface (0.14-5.2μg L⁻¹) and subsurface (0.98-4.92μgL⁻¹) waters. However, the average values were higher (2.47±1.21μgL⁻¹) in the surface waters relative to the subsurface (1.9±1.31μgL⁻¹).

Chla values revealed a negative polynomial correlation with DIN (Table 2) and was statistically significant (R^2 =0.242, n =74, p < 0.05). However, Si values revealed a significant positive exponential relation with Chla values (R^2 =0.696, n =74, p < 0.001) (Table 2) indicating strong correlation of chlorophyll biomass with Si concentrations in the ambient waters. A highly significant linear positive correlation (R^2 =0.999, n =3, p < 0.001) was observed while considering the average values of Si:N and Chla from three sampling months. This indicates that Si:N ratios have strong impact on phytoplankton growth in this bay.

Phytoplankton cell counts also revealed a similar result (Fig. 5e) and the number of cells per L of water was significantly high in Dec relative to Jan and June. Chla and phytoplankton cell counts were significantly correlated with each other (R^2 =0.521, n =74, p < 0.001). The average cell count in Jan was 9088±4986 cells L^{-1} in surface waters and varied between 2250 -20250 cells L^{-1} . In June cell counts were significantly low where the average value reduced to half than that of Jan and cell counts varied between 1540 -12000 cells L^{-1} . In Dec, phytoplankton cell abundance drastically enhanced to a range from 29,000 -2,34,000 cells L^{-1} and the average value was 99,339±63607 cells L^{-1} . Phytoplankton cell numbers also revealed significant exponential positive correlation with Si concentrations (Table 2) (R^2 =0.571, n =74, p < 0.001).

Total 24 genera of phytoplankton were identified and out of them 21 were diatoms with 3 dinoflagellates. There were also more than 6 unidentified diatom and 3 dinoflagellate species found during this study. Diversity index (H') was calculated for all these three sampling periods (Fig. 6; Table 1) and the highest values of H' was observed in Jan (1.36±0.35) with high variability (0.85 -2.07). Total 13 identified diatom genera along with some identified and non-identified dinoflagellates were noticed in Jan. In June, total

identified diatom genera were 14; however, only one dinoflagellate was identified along with few unknown species. H' values reduced to 1.22±0.26 and varied within the range from 0.84 -1.60. The lowest values of H' was recorded in Dec (0.83±0.29) with a variation from 0.26 -1.25. In all sampling periods, H' values varied noticeably over the diel cycle. Although, the total identified diatom genera was more or less equal (14), the dominance of a chain forming centric diatom was very high in this month.

Phytoplankton community composition and relative % of different phytoplankton (Fig. 7; Table 3) varied considerably during these three sampling periods. In January the community was mostly dominated by Thalassiosira decipiens (39.83%) and Thalassionema nitzschioides (22.39%) (Fig. 7a). Besides, Chaetoceros sp. (5.37%), Navicula sp. (3.52%) and Coscinodiscus sp. (2.66) were also present. Different species of dinoflagellate including Protoperidinium sp., Prorocentrum sp. and others constitute almost 11% of the total population during this time. Skeletonema costatum cells were not observed in any of the samples. In June Thalassiosira decipiens cells reduced to 2.15 times and contribute 18.6% to the total relative %. This time the highest abundance was of Thalassionema nitzschioides (21.9%) and Thalassiothrix frauenfeldii (19.3%) (Fig. 7b). The relative % of *Chaetoceros* sp. decreased to 1.7% in June. Dinoflagelate relative % also decreased to 8.2% in June. Coscinodiscus sp. relative % increased to 7.2% in June. In Dec (Fig. 7c) the relative % of Skeletonema costatum increased to 64.77 and dominated the bloom. Large chain forming colonies were abundant in all samples over the diel cycle. Interestingly, the relative % of Thalassionema nitzschioides did not decrease much and remained as 24.5%. Chaetoceros sp. abundance dropped down to 0.29% during this time. Thalassiosira decipiens abundance dropped to 1.8% (Table 3). Dinoflagellate abundance decreased to 0.10% among the total community. Small species like *Navicula* sp. did not show large variation in its relative abundance and varied from 3.52% in Jan to 1.9% in June and 2.64% in Dec.

4. Discussion:

The physicochemical parameters in Jan and Dec indicated a well mixed low saline water column and could be influenced by the NE monsoon wind. From a hydrographic survey conducted along the Indian coast during northeast monsoon (Shetye et al. 1996), the occurrences of low salinity water along the entire Indian east coast as a narrow current flowing southward called East India Coastal Current (EICC) was reported. The author also reported the presence of uniform temperature and salinity in a homogeneous surface layer, on average, 25 m form the vertical profiling. The upper ocean stratification in the northern Bay of Bengal was found to be dominated by salinity rather than temperature (Shetye et al. 1996). Indian summer monsoon impacts the subcontinent with heavy downpour and all coastal areas in India particularly those on the eastern side receive huge amount of freshwater input from the monsoon fed rivers. Bay of Bengal receives more than 70% of the river discharge during the month of June to September (Unger et al. 2003) as a consequence of Southwest monsoon (SWM) (Milliman and Meade 1983) which significantly lowers the salinity at the upper layer of the bay. Due to the proximity of Godavari River, India's second largest river significant amount of materials and freshwater flux enters the Godavari delta region including Kakinada bay. The observed low salinity waster masses in the study area during Dec and Jan, the postmonsoon months, were well consistent with this view.

Salinity, temperature, pH and alkalinity data clearly demonstrated distinct difference between three sampling times. During June, the water balance was negative due to high rate of evaporation and nil freshwater addition which might have resulted in high saline and more alkaline water masses in this bay. Conversely, during Jan and Dec, low salinity and total alkalinity were associated with rainfall and river discharge. The significant linear correlation between salinity and total alkalinity indicates their tight coupling. Total alkalinity variation in the surface oceans are usually controlled by freshwater addition and removal (Millero 1998; Lee et al. 2006; Jiang et al. 2014) and it has been observed that almost 80% variability in total alkalinity can be explained by the variability in freshwater discharge in the subtropical oceans (Millero 1998). Usually high salinity values are associated with higher pH due to increased alkalinity, however in Jan it was consistent, but not in Dec. This could be due to the fact that higher phytoplankton growth drew down CO₂ in the form of dissolved inorganic carbon (DIC) leading to higher pH values. It has often been observed in the marine environment that pCO₂ values decreases in the surface water drastically followed by intense phytoplankton bloom (Codispoti et al. 1982, Murata et al. 2002). The significant negative correlation between DO and salinity values indicates that dissolution of oxygen in the coastal water is directly controlled by salinity. However, biological activities like photosynthesis and respiration also control DO values in the coastal waters over day/night cycle. In June the low DO values could be due to higher salinity of the coastal waters. The observed higher DO values during Jan and Dec could be due to low salinity, nonetheless, in Dec higher phytoplankton photosynthetic rate could also enhance DO values.

PHC values observed during our study revealed a moderate range of values compared to the level found in other Asian countries like Thailand, Malaysia and China, Pakistan, etc. Chouksey et al. (2004) reported PHC values within the range of 2.9 -39.2µg L⁻¹ from off Bassein Mumbai (west coast of India) surface waters which is slightly higher relative to our observed range (0.88 -29.44 µg L⁻¹). Saramun and Wattayakorn (2000) reported PHC values from 0.03 -0.47 µg L⁻¹ from the South China Sea off the western coast of the Philippines and these values were quite low relative to the values observed during the present study. Wattayakorn (2012) presented a review including a series of PHC values from various coastal regions in Thailand and the reported values were always lower than the values noticed in the present study. Conversely, Li et al. (2010) reported a long term (1996 -2005) PHC values from the Bohai Bay, China and the values were highly variable, ranging from 23.7 - 508µgL⁻¹ and were significantly high than the other reported values. Lower PHC values during Jan and Dec were probably due to the dilution impact. Higher PHC values during June were associated with higher salinity and could be because no dilution effect. Higher PHC in the subsurface relative to the surface waters in June could be due to reduced photo-degradation induced by high sunlight. Although microbial community can efficiently degrade PHC in the marine environment, however, sunlight could be responsible for 10-50% of the photochemical degradation of the PHC in the surface waters (Ehrhardt and Patrick 1993; Harayama et al. 1999; Guipeng et al. 2006).

Higher BOD values were associated with higher PHC abundance in June, which could be due to higher bacterial degradation rate influenced by high temperature (Atlas, 1975). Microorganisms are highly efficient

to degrade hydrocarbons in versatile ways (Head et al. 2006) and molecular oxygen is essentially consumed by the microbial community during the initial hydroxylation of the PHC (Cerniglia 1992). Hence, high amount of oxygen is being used during the biodegradation of PHC in the environment and it has been observed that supply of oxygen enhances the speed and rate of biodegradation of PHC (Schaffner and Jeneau 2006). Sharma and Pant (2001) noticed the optimum rate of biodegradation of crude oil in seawater was 30°C and the rate was lower in both greater and lesser than this temperature. During June the highest temperature both in surface and subsurface waters were observed during mid day of June and can potentially accelerate PHC degradation. Amund and Igri (1990) reported that in the tropical estuarine environment, biodegradation of crude oil can take place within 25 -33°C. Naturally PHC degrading aerobic bacterial abundance can be quite high in the coastal waters of India (Roy et al. 2002). Thus, it is likely that high PHC accumulation during June coupled with optimum temperature for microbial degradation of PHC can lead to higher BOD values in the study area. However, the other DOC components also may have direct impact on BOD, since we have not studied DOC during this study, it is difficult to interpret.

Many authors reported diatoms, the members of bacillariophyceae to dominate the phytoplankton community of coastal Bay of Bengal (Madhupratap et al. 2003; Paul et al. 2008; Naik et al. 2011). Our microscopic analysis also supports this view. Chla concentrations and phytoplankton cell numbers were well correlated with Si concentrations and this is because of the dominance of diatoms. Diatom growth in the marine environment can be directly dependent on dissolved silicate concentrations (Sarthou et al. 2005). The significant correlation between phytoplankton cell number and Chla indicates that micro-phytoplankton is the major contributing genera within the entire phytoplankton community. Si:N ratio seemed to play a dominant role in diatom growth in this area. In general, several marine diatoms have a relatively balanced N:Si ratio (1:1) within their biomass (Brzezinski, 1985; Martin-Jézéquel et al. 2000). Thus, increasing or decreasing Si:N ratios have a significant impact on diatom growth and physiology. The observed positive correlation between Si:N ratios and Chla is consistent with this hypothesis. In Jan, Si:N average value was close to 1:1 and the dominating phytoplankton species were mainly smaller in size. On contrary low Si:N values were consistent with low phytoplankton biomass and cell numbers. Conversely, in Dec, significant amount of Si supply probably through freshwater input increased the ratio of Si:N to almost double which was coupled with significant enhancement in biomass and cell counts. The observed linear correlation between Si:N ratio and Chla revealed a slope of 1.04 which also indicates that the requirement of Si:N in this bay is close to 1:1.

The significant enhancement in *S. costatum* cells during Dec was a unique feature. *S. costatum* is a cosmopolitan diatom species and has been identified as a most abundant diatom in the coastal waters (Hasely 1973). The occurrences of *Skeletonema costatum* bloom in Dec could be presumably because of 1) lowering of the salinity 2) enhancement in Si:N ratios in this coastal bay. Nevertheless, Gilpin et al. (2004) reported from a mesocosm study at Trondheims fjord, Norway that variable Si:N ratios did not affect *S. costatum* growth in the experimental nutrient enrichment. However, the author reported the dominance of *S. costatum* in all treatments irrespective of Si:N ratios and the fjord water salinity was reduced due to freshwater runoff in

spring/summer. However, there are several reports stating the coupling between S. costatum bloom and rainfall. A similar bloom was recorded in Jiaozhou Bay, China by Huo et al. 2005. The author stated that low saline water and eutrophic condition helped S. costatam to proliferate. In the same study increase in phytoplankton Chla was also associated with pH increase which is also consistent with our observation. Recently, a S. costatum bloom has been reported from an Indian estuary in the southeast India which was also coupled with heavy rainfall and dilution of the seawater during August-September 2014 (Vasudevan et al. 2014). Li et al. (2009) reported the occurrence of S. costatum bloom from the Hongsha Bay of Sanya, South China Sea and it was associated with increased nutrient concentrations induced by heavy rainfall in that area. Borkman and Smyda (2009) analysed a very long term time series data set (over 38 years) on S. costatum bloom observed in lower Narragansett Bay, Rhode Island, USA. The authors noticed a clear negative correlation between the secchi disk transparency and S. costatum bloom indicating that this chain forming centric diatom species bloomed under low light condition. Biswas et al (2010) reported from a long term observations of phytoplankton data set from a mangrove dominated estuarine system of India (NW Bay of Bengal) that S. costatum blooms were noticed during the turbid monsoonal months when silicate concentrations and TSM were significantly high. Machado et al. (2014) investigated the impact of small scale turbulence under low nutrient condition (nitrate) in a temperate coastal embayment, Western Australia and observed that mainly the chain forming diatom including Skeletonema sp. were able to benefit by siliceous chain formation under turbulent and low nutrient condition.

Consistent lower values of N:P relative to the classical Redfield values of 16:1 (Redfield, 1963) indicates that in the study area the supply of DIN is lesser relative to the phosphate and hence phosphate limitation was never noticed. Biswas et al. (2010) also reported a data set over a decadal scale from a mangrove associated estuarine system that N:P were consistently lower than the classical 16:1 ratios. Presumably because of higher rates of DIP loading relative to DIN combined with higher consumption rates of DIN. Very recently, Ray et al. (2014) analysed the biogeochemical cycle of nitrogen in a tropical mangrove ecosystem, east coast of India through a box model and the author concluded that nitrogen could be largely limiting in the mangrove dominated aquatic system. In Dec noticeable low values of DIN could be because of drawing down of DIN by the phytoplankton community. Nutrient exhaustion is a common phenomenon during a phytoplankton bloom in the coastal areas. Huo et al. (2005) also reported significant nutrient depletion in the post *S. costatum* bloom phase in Jiaozhou Bay, China.

After analysing the physicochemical and biological parameters of three sampling months, this is likely that Jan was a post-bloom phase of phytoplankton with moderate cell number and smaller diatoms (*Thalassiosira decipiens*, *Thalassionema nitzschioides* and *Thalassiothrix frauenfeldii*) dominated with 10.8% dinoflagellate relative contribution. Roberts et al. (2003) investigated the effects of different N:Si ratios on phytoplankton community in the Trondheims fjord, Norway. The authors observed that autotrophic dinoflagellate dominated under high N:Si treatments at the end of the experiment. In June the low biological activity could be due to

higher salinity and temperature; dinoflagellate relative contribution decreased to 8.17 and further decreased to 0.2% in Dec.

Conclusions:

We conclude from this three time series observations that the physicochemical parameters of Kakinada bay can be highly fluctuating due to monsoonal influence. Biological oxygen demand, petroleum hydrocarbon and dissolved oxygen values indicate that during the sampling time there was no severe pollution stress noticed in this bay. The magnitude of the major nutrient input and their ratios can largely influence microalgal diversity in this bay. Kakinada bay was found to be enriched with dissolved inorganic phosphate relative to dissolved inorganic nitrogen. Diatoms dominate the phytoplankton community all seasons, *Skeletenoma cotatum*, a centric diatom was detected to form bloom during December when low saline water occupied the entire bay in its surface waters. However, there was a distinct change in microalgal diversity between three sampling times. It is likely that high biological, chemical and physical activity may play a vital role in nutrient and organic matter mineralization which ultimately dilute pollutants concentrations in this bay.

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References:

- Amund OO, Igiri CO. Biodegradation of petroleum hydrocarbons under tropical estuarine conditions. World J Microb Biot 1990; 6(3): 255 -262.
- APHA (American Public Health Association). Standard methods for the examination of water and waste water. 21st ed. Washington: APHA; 2005; 3–15.
- Atlas RM. Effects of Temperature and Crude Oil Composition on Petroleum Biodegradation. Applied J Microb 1975; 30(3):396 -403.
- Biswas H, Dey M, Ganguly D, De TK, Ghosh S, Jana TK. Comparative Analysis of Phytoplankton Composition and Abundance over a Two-Decade Period at the Land–Ocean Boundary of a Tropical Mangrove Ecosystem. Estuaries and Coasts 2010; 33: 384–394.
- Borkman D, Smayda T. Multidecadal (1959–1997) changes in *Skeletonema* abundance and seasonal bloom patterns in Narragansett Bay Rhode Island USA. J Sea Res 2009; 61: 84–94.
- Bruce M. Mahoney, Harold H. Haskin. The effects of petroleum hydrocarbons on the growth of phytoplankton recognised as food forms for the eastern oyster, *Crassostrea virginica gmelin*. Environmental Pollution Series A Ecological and Biological 1980; 22(2):123–132. DOI:10.1016/0143-1471(80)90188-9
- Brzezinski MA. The Si-C-N ratio of marine diatoms-interspecific variability and the effect of some environmental variables. J Phycol 1985; 21: 347–357.

- Carter CM, Ross AH, Schiel DR, Howard-Williams C, Hayden B. In situ microcosm experiments on the influence of nitrate and light on phytoplankton community composition J Exp Mar Bio Ecol 2005; 326 (1): 1–13. http://dx.doi.org/10.1016/j.jembe.2005.05.006
- Cerniglia CE. Biodegradation of polycyclic aromatic hydrocarbon. Biodegradation 1992; 3: 51-68.
- Chouksey MK., Kadam AN, Zingde MD. Petroleum hydrocarbon residues in the marine environment of Bassein–Mumbai. Marine Pollut Bull 2004; 49(7-8):637 -647.
- Cloern JE. Phytoplankton bloom dynamics in coastal ecosystem: A review with some general lessons from sustained investigation of San Francisco Bay California: Rev Geophys 1996; 127-168.
- Codispoti LA, Friederich GE, Iverson RL, Hood DW. Temporal changes in the inorganic carbon system of the south-eastern Bering Sea during spring 1980. Nature 1982; 296: 242 245. doi:10.1038/296242a0
- Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens K.E, Lancelot C, Likens GE. Controlling eutrophication: nitrogen and phosphorus. Science 2009; 323: 1014–1015.
- Conley D. Biogeochemical nutrient cycles and nutrient management strategies. Hydrobiologia 2000; 410: 87-96.
- Desikachary TV. Atlas of Diatoms: Marine diatoms of the Indian Ocean region. 1987; Vol.11. Madras Science Foundation Madras
- Diaz RJ, Rosenberg R. Spreading Dead Zones and Consequences for Marine Ecosystems. Science 2008; 321: 926.
- Dickson AG et al. Reference materials for oceanic CO2 analysis: A method for the certification of total alkalinity. Mar Chem 2003; 80: 185–197.
- Elmgren R, Larsson U. Eutrophication in the Baltic Sea area: Integrated coastal management issues. *In* B. Von Bodungen and R. K. Turner [eds.] Science and integrated coastal management. Dahlem Univ. Press 2001; p 15–35.
- Géraldine Sarthou Timmermans K.R, Blain S, Tréguer P. Growth physiology and fate of diatoms in the ocean: a review. J Sea Res 2005; 53: 25–42.
- Gilpin LC, Davidson K, Roberts E. The influence of changes in nitrogen: silicon ratios on diatom growth dynamics. J Sea Res 2004; 51(1):21-25.
- Grasshoff KM, Ehrhardt, Krembing K. Methods of seawater analysis. 3rd ed. Germany: Verlag Chemic; 1993.
- GuipengYG, Zhang L, Sun X, Jing W. Photochemical degradation of crude oil in seawater. Chinese J Oceanogr Limnol 2006; 34(3): 264-269
- Harayama S, Kishira H, Kasai Y, Shutsubo K. Petroleum Biodegradation in Marine Environments. J Mol Microbiol Biotech 1999; 1(1): 63-70.
- Harris G.P. *Phytoplankton ecology: structure function and fluctuation*. Chapman & Hall New York: 384: 1986. http://dx.doi.org/10.1007/978-94-009-4081-9
- Hasely GR. Morphology and taxonomy of *Skeletonema costatum* (Bacillariophyceae). Norw. J. Bot. 1973; 20: 109–137.
- Hasle GR, Syvertsen EE, Throndse, J, Steidinger, KA, Tangen K. and Heindal BR. Identifying Marine Phytoplankton (Kindle Edition). In: Tomas, RC, editor. Academic Press: 1997.
- Head IM Jones DM, Röling WFM. Marine microorganisms make a meal of oil. Nature Reviews Microbiol 2006; 4: 173-182.
- Huo WY, Shu Jian J. Outbreak of *Skeletonema costatum* Bloom and Its Relations to Environmental Factors in Jiaozhou Bay China. WSEAS Int. Conf. on Environment Ecosystems and Development Venice Italy November 2005; 2-4: 205-210.

- Hur J, Kong DS. Use of synchronous fluorescence spectra to estimate biochemical oxygen demand (BOD) of urban rivers affected by treated sewage. Environ Technol 2008; 29(4): 435–444.
- Hylland K. Polycyclic Aromatic Hydrocarbon (PAH) Ecotoxicology in Marine Ecosystems. J Toxicol Env Health 2006; Part A: 69(1-2).
- Jiang Z, Tyrrell PT, Hydes DJ, Dai M, Hartman SE. Variability of alkalinity and the alkalinity-salinity relationship in the tropical and subtropical surface ocean. Global Biogeochem Cycles 2014; 28. doi:10.1002/2013GB004678
- Kirk JTO. Light and Photosynthesis in Aquatic Ecosystem. Cambridge University Press Cambridge Britain 1994; 57–71.
- Kwak J, Khang B, Kim E, Kim H. Estimation of Biochemical Oxygen Demand Based on Dissolved Organic Carbon UV Absorption and Fluorescence Measurements. Journal of Chemistry 2013; ID 243769: 9 pages. http://dx.doi.org/10.1155/2013/243769
- Laws EA. Aquatic Pollution: A Introductory Text. John Wiley and Sons Inc. New York: 2000; 432–479.
- Lee K, Tong LT, Millero FJ, Sabine CL, Dickson AG, Goyet C, Park GH, Wanninkhof R, Feely RA, Key RM. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. Geophys Res Lett. 33: 2006. L19605 doi:10.1029/2006GL027207
- Leterme SC, Seuront L, Edwards M. Differential contribution of diatoms and dinoflagellates to phytoplankton biomass in the NE Atlantic Ocean and the North Sea. Mar Ecol Prog Ser. 2006; 312: 57–65. http://dx.doi.org/10.3354/meps312057.
- Li C, Zhu B, Chen H, Liu Z, Cui B, Wu J, Li B, Yu H, Peng M. The Relationship between the *Skeletonema* costatum Red Tide and Environmental Factors in Hongsha Bay of Sanya South China Sea. J Coast Res 2007; 25 (3): 651-658.
- Li Y, Zhao Y, Peng S, Zhou Q, Ma LQ. Temporal and spatial trends of total petroleum hydrocarbons in the seawater of Bohai Bay China from 1996 to 2005. Mar Pollut Bull 2010; 60:238–243.
- Machado DA, Marti CL, Imberger J. Influence of microscale turbulence on the phytoplankton of a temperate coastal embayment Western Australia. Estuar Coast Shelf S 2014; 20:80-95.
- Mackay AP, Hodgkinson M. Assessment of the impact of naphthalene contamination on mangrove fauna using behavioural bioassays. Bull Environ Contam Toxicol 1996; 56:279 -286.
- Madhupratap M et al. Biogeochemistry of the Bay of Bengal: physical chemical and primary productivity characteristics of the central and western Bay of Bengal during summer monsoon 2001. Deep-Sea Res Part II 2003; 50: 881-896.
- Martin-Jézéquel V, Hildebrand M, Brzezinski MA. Silicon metabolism in diatoms: Implications for growth. J Phycol 2000; 36: 821–840.
- McCreary JP, Kundu, PK, Molinari RL. A numerical investigation of the dynamics thermodynamics and mixed-layer processes in the Indian Ocean. Progress Oceanogr 1993; 31: 181–244.
- Millero FJ, Lee K, Roche M. Distribution of alkalinity in the surface waters of the major oceans. Mar Chem 1998; 60(1–2): 111–130.
- Milliman JD, Meade RH. World-wide delivery of river sediment to the oceans. Journal of Geology 1983; 91:1–21.
- Murata A et al. Impact of a spring phytoplankton bloom on the CO₂ system in the mixed layer of the north-western North Pacific. Deep-Sea Res. II 2002; 49:5531–55.
- Naik RK, Anil AC Narale DD, Chitari RR, Kulkarni VV. Primary description of surface water phytoplankton pigment patterns in the Bay of Bengal. J Sea Res 2011; 65:435–441.
- Nayar S, Goh BP, Chou LM, Environmental impacts of diesel fuel on bacteria and phytoplankton in a tropical estuary assessed using in situ mesocosms. Ecotoxicology 2005; 14(3): 397-412.

- Officer CB, Ryther JH. The possible importance of silicon in marine eutrophication. Mar Ecol Progr Ser 1980; 3: 83–91.
- Parab SR Reena A. Pandit, Arun N. Kadam, Madhavi M. Indap. Effect of Bombay high crude oil and its water-soluble fraction on growth and metabolism of diatom Thalassiosira sp. Indian Journal of Geo Marine Science, 2008; 37(3): 251-255.
- Paul JT, Ramaiah N, Sardessai S. Nutrient regimes and their effect on distribution of phytoplankton in the Bay of Bengal; Mar Environ Res 2008. DOI- 10.1016/j.marenvres:05.007
- Rabalais NN, Nixon SW [eds.] Dedicated issue. Nutrient over-enrichment in coastal waters: Global patterns of cause and effect. Estuaries 2002; 25(4B): 639–900.
- Ray R, Majumder N, Das S, Chowdhury C, Jana T K. Biogeochemical cycle of nitrogen in a tropical mangrove ecosystem east coast of India. Mar Chem 2014; 20: 33–43.
- Reader HE, Stedmon CA, Kritzberg ES. Seasonal contribution of terrestrial organic matter and biological oxygen demand to the Baltic Sea from three contrasting river catchments. Biogeosciences 2014; 11: 3409–3419.
- Reynolds CS. Phytoplankton periodicity: the interactions of form function and environmental variability. Freshwater Biol 1984; 14: 111-142.
- Rimet F, Bouchez A. Biomonitoring river diatoms: implications of taxonomic resolution. Ecol. Indic. 2012; 15 (1): 92–99. http://dx.doi.org/10.1016/j.ecolind.2011.09.014
- Roberts EC, Davidson K, Gilpin LC. Response of temperate microplankton communities to N:Si ratio perturbation. J Plankton Res 2003; 25(12):1485 -1495.
- Roberts EC, Davidson K, Gilpin LC. Response of temperate microplankton communities to N: Si ratio perturbation. J Plankton Res 2003; 25: 1485–1495.
- Roy S, Hens D, Biswas D, Kumar R. Survey of petroleum-degrading bacteria in coastal waters of Sundarban biosphere reserve. World J Microbiol BioT 2002; 18: 575 -581.
- Saramun S, Wattayakorn G. Petroleum hydrocarbon contamination in Seawater along the western coast of Philippines. In proceedings of the Third Technical Seminar on Marine Fishery Resources Survey in the South China Sea: Area III. SEAFEDC Bangkok 2000; 316-320.
- Schaffner IR, Juneau AA. In-Situ Air Sparging Without Inorganic Nutrient Amendment: An Effective Bioremediation Strategy for Treating Petroleum-Contaminated Groundwater Systems. In: The Ninth National Outdoor Action Conference on Aquifer Remediation Ground Water Monitoring & Geophysical Methods: National Ground Water Association p. 101-115.
- Sharma SL, Pant A. Crude Oil degradation by a marine actinomycetes Rhodococcus. Ind J Geo Mar Sci 2001; 30:146-150.
- Shetye SR, Gouveia AD, Shankar DS, Shenoi SC, Vinayachandran PN, Sundar D, Michael GS, Nampoothiri G. Hydrography and circulation in the western Bay of Bengal during the northeast monsoon. J Geophys Res 1996; 101:14011–14025.
- Smayda TJ. Novel and nuisance phytoplankton blooms in the sea: evidence for a global epidemic. In Grane'li E. Sundstrom B. Edler L. and Anderson D. M. (eds) Toxic Marine Phytoplankton. Elsevier New York: 1990; 29–40.
- Smith RC, Ainley D, Baker K, Domack E, Emslie S, Fraser B, Kennett J, Leventer A, Thompson EM, Stammerjohn S, Vernet M. Marine Ecosystem Sensitivity to Climate Change BioScience 1999; Vol. 49(5):393-404.
- Smith VH. Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. Limnol Oceanogr 1996; 51(1 part 2) 2006: 377–384.
- Stolte W, McCollin T, Noordeloos A, Riegman R. Effect of nitrogen-source on the size distribution within marine-phytoplankton populations. J Exp Mar Biol Ecol 1994; 184: 83–97.

- Sullivan AB, Snyder DM, Rounds SA. Controls on biochemical oxygen demand in the upper Klamath River Oregon. Chem Geolo 2010; 269:12–21.
- Tahir NM, Abdullah AR, Shanmugam S. Determination of total hydrocarbon concentration in coastal waters and sediments off the east coast of Peninsular Malaysia. <u>Env Geochem Health</u> 1997; 19(2): 67-71.
- UNESCO manual for monitoring oil and dissolved dispersed petroleum hydrocarbon in marine waters and on beaches, Manuals and Guide No. 13 (IOC-UNESCO, Paris), 1984; 35.
- Unger D, Ittekkot V, Schafer P, Tiemann J, Reschke S. Seasonality and inter-annual variability of particle fluxes to the deep Bay of Bengal: Influence of riverine input and oceanographic processes. Deep-Sea Res. II 2003; 50: 897–923.
- Utermohl H. Zur Vervollkommung der quantitativen Phytoplankton- Methodik. Mitteilungen der Internationale Vereinigung für theoretische und angewandte. Limnologie 1958; 9:1–38 (German).
- Vasudevan S, Arulmoorthy MP, Balachandar K, Harikumar S, Ashok prabu V. Extensive bloom of phytoplankton *Skeletonema costatum* in Vellar Estuary Parangipettai Tamilnadu Southeast Coast of India. Int J Currt Trends Res 2014; 3 (2):154-157.
- Venkatachalapathy R, Veerasingam S, Rajeswari V. Distribution and Origin of Petroleum Hydrocarbons in Pichavaram Mangrove Swamp Along Tamilnadu Coast Bay of Bengal India. Geochem International 2012; 50 (5): 476–480.
- Wattayakorn G. Petroleum Pollution in the Gulf of Thailand: A Historical Review. Coast Mar Sci 2012; 35(1):234-245.
- Weiss R.F. The solubility of nitrogen, oxygen and argon in water and seawater: Deep-Sea Research 1970; vol. 17: 721-735. http://water.usgs.gov/owq/rfweiss.paper.pdf

Table 1: Variability of all parameters (physiochemical and biological) during three times series observations at Kakinada bay in surface (Sur = 0m) and subsurface (Sub = 4.5m). Minimum, maximum and average values (n =10-12) with standard deviations are given here for three sampling periods in January, June and December, 2012. Phytoplankton cell counts were only done from the surface waters and hence diversity values were calculated only for surface waters.

counts were only done in		Jan'12		1000	, or o daround	June'12				Dec'12			
		Max	Min	Average	Stdev	Max	Min	Average	Stdev	Max	Min	Average	Stdev
Temp (°C)	Sur	26.23	24.75	25.63	0.38	30.01	28.14	28.88	0.65	28.75	22.97	25.80	1.76
	Sub	26.42	25.20	25.75	0.34	30.33	27.91	28.51	0.63	27.06	23.21	25.77	1.44
Salinity (PSU)	Sur	28.91	28.10	28.49	0.25	35.18	33.88	34.30	0.34	28.71	27.10	27.82	0.56
	Sub	28.95	28.16	28.65	0.21	35.65	34.05	34.45	0.45	28.69	27.40	27.94	0.44
pН	Sur	8.13	8.02	8.08	0.03	8.23	8.02	8.13	0.06	8.22	8.10	8.16	0.03
	Sub	8.14	8.00	8.08	0.04	8.19	8.01	8.12	0.05	8.26	8.11	8.16	0.04
Alk (μmol L ⁻¹)	Sur	2204	2118	2166	21.4	2472	2329	2379	35	2185	2024	2106	42.67
	Sub	2170	2142	2158	7.8	2390	2299	2360	22	2155	2051	2107	28.45
TSM (mg L ⁻¹)	Sur	71	35.33	48.50	10.84	67.67	30.00	50.85	11.79	73.50	44	58.55	8.59
	Sub	106	37.00	58.90	24.59	77.00	39.00	53.24	11.15	100.50	44.5	76.14	16.12
DO (mg L ⁻¹)	Sur	7.75	6.33	6.78	0.40	6.63	5.20	5.70	0.32	7.30	5.53	6.47	0.60
	Sub	6.80	6.01	6.41	0.24	5.98	4.89	5.52	0.37	7.17	5.28	6.13	0.55
BOD (mg L ⁻¹)	Sur	1.91	0.55	1.19	0.43	2.35	0.14	1.02	0.57	0.93	0.15	0.46	0.23
	Sub	1.47	0.40	0.93	0.34	2.18	0.86	1.40	0.49	0.76	0.34	0.50	0.14
O ₂ % of saturation	Sur	111.86	89.65	97.73	5.99	104.12	81.96	89.58	5.08	106.51	78.77	93.11	10.01
	Sub	98.59	86.10	92.74	3.77	93.81	76.36	86.29	5.74	98.69	73.15	87.35	7.64
PHC (μg L ⁻¹)	Sur	13.37	1.69	7.52	4.41	17.60	1.86	8.67	4.49	9.80	1.49	6.48	2.62
	Sub	12.53	0.88	4.93	3.88	29.44	1.08	15.88	8.68	9.73	1.35	4.19	2.49
DIN (μmol L ⁻¹)	Sur	11.31	8.14	9.65	1.10	14.15	11.13	12.79	0.94	9.77	5.65	7.27	1.51
	Sub	12.3	9.8	10.9	0.8	18.6	11.2	14.6	2.2	8.7	4.61	7.05	1.24
NO ₃ ⁻¹ (μmol L ⁻¹)	Sur	9.33	6.84	8.15	0.88	11.97	9.18	10.52	0.77	8.14	2.87	5.20	1.89
	Sub	9.15	7.28	8.53	0.49	16.10	8.99	12.13	2.12	6.45	1.53	4.38	1.68
$NO_2^{-1}(\mu mol L^{-1})$	Sur	1.10	0.46	0.71	0.18	1.31	0.37	0.71	0.29	0.64	0.15	0.33	0.16
	Sub	1.77	0.30	1.14	0.42	1.15	0.39	0.80	0.25	0.90	0.20	0.46	0.18

$NH_4^{+1}(\mu mol L^{-1})$	Sur	1.46	0.27	0.79	0.30	2.11	0.92	1.56	0.34	2.45	0.97	1.74	0.49
	Sub	2.00	0.57	1.22	0.48	2.16	0.73	1.67	0.36	3.30	0.55	2.21	0.85
PO ₄ -3(μmol L ⁻¹)	Sur	2.54	0.43	1.18	0.60	1.78	1.06	1.35	0.27	0.96	0.48	0.67	0.14
	Sub	3.17	0.62	1.71	0.82	2.35	1.01	1.58	0.36	0.79	0.32	0.57	0.18
Si (μmol L ⁻¹)	Sur	12.45	6.38	10.52	1.81	9.86	3.48	5.54	2.19	24.63	12.71	16.63	3.46
	Sub	13.02	7.74	10.94	1.56	11.92	3.74	6.37	2.70	18.86	13.95	15.60	1.41
N:P	Sur	21.8	4.4	10.1	4.9	12.5	7.5	9.7	1.6	17.8	6.26	11.23	3.30
	Sub	16.63	3.28	7.90	3.83	14.87	5.72	9.80	2.96	19.71	7.14	13.40	4.28
Si:N	Sur	1.30	0.76	1.09	0.18	0.88	0.25	0.44	0.21	3.21	1.71	2.32	0.43
	Sub	1.26	0.65	1.01	0.17	1.06	0.21	0.45	0.23	3.02	1.73	2.27	0.38
Chla (µg L ⁻¹)	Sur	2.19	0.66	1.16	0.41	1.00	0.13	0.51	0.27	4.92	0.98	2.47	1.21
	Sub	2.72	0.66	1.25	0.53	1.35	0.31	0.89	0.31	5.20	0.14	1.90	1.31
Phyto cell L ⁻¹	Sur	20250	2250	9088	4986	12000	1540	4525	3110	234000	29000	99339	63607
Diversity index (H)	Sur	2.07	0.85	1.36	0.35	1.60	0.84	1.22	0.26	1.25	0.26	0.83	0.29

Table 2: Correlation coefficients values along with number of samples, type of correlation and levels of significance between various physicochemical and biological parameters during the study period at Kakinada bay.

Parameters	Type of correlation	Correlation	Number of	Probability
		coefficients (R ²)	samples (n)	level (p)
Dissolved oxygen Vs Salinity	Linear negative	0.403	74	< 0.001
Salinity Vs total alkalinity	Linear positive	0.917	74	< 0.001
PHC Vs. BOD	Linear positive	0.195	74	< 0.05
PHC Vs Salinity	Linear positive	0.245	74	< 0.05
DIN Vs Chla	Polynomial negative	0.242	74	< 0.05
Si Vs Chla	Exponential positive	0.696	74	< 0.001
Si Vs Cell No.	Exponential positive	0.571	37	< 0.001
Si:N Vs Chla	Logarithmic positive	0.508	37	< 0.01
Cell No. Vs Chla	Exponential positive	0.521	37	< 0.001

Table 3: Relative % of different phytoplankton general in the surface waters Kakinada bay during January, June and December, 2012

Jan		June		Dec		
Name of the species	Relative%	Name of the species	Relative%	Name of the species	Relative %	
Thalassiosira decipiens	39.83	Thalassiosira decipiens	18.6	Thalassiosira decipiens	1.80	
Thalassionema nitzschioides	20.37	Thalassionema nitzschioides	21.9	Thalassionema nitzschioides	24.56	
Thalassiothrix frauenfeldii	2.02	Thalassiothrix frauenfeldii	19.3	Thalassiothrix frauenfeldii	2.32	
Cheatoceros sp.	5.37	Chaetoceros sp.	1.7	Cheatoceros sp.	0.29	
Navicula sp	3.52	Navicula sp.	1.9	Navicula sp.	2.64	
Coscinodiscus sp.	2.66	Coscinodiscus sp.	7.3	Coscinodiscus sp.		
Skeletonema costatum		Skeletonema costatum		Skeletonema costatum	64.77	
Synedra sp.	0.17	Synedra sp.		Synedra sp.	1.90	
Pseudo-nitzschia seriata	1.80	Pseudo-nitzschia seriata	1.1	Pseudo-nitzschia seriata	0.41	
Pleurosigma elongatum	0.75	Pleurosigma elongatum	2.8	Pleurosigma elongatum	0.09	
Nitzschia sp.	0.17	Nitzschia sp.	0.3	Nitzschia sp.	0.27	
Guinardia striata	0.45	Guinardia striata		Guinardia striata		
Ditylum brightwellii		Ditylum brightwellii	0.7	Ditylum brighwellii	0.05	
Rhizosolenia setigera		Rhizosolenia setigera	0.2	Rhizosolenia setigera	0.30	
Leptocylindrus danicus		Leptocylindrus danicus	2.0	Leptocylindrus danicus		
Paralia sulcate	0.33	Paralia sulcate		Paralia sulcate		
Astroinella japonica		Astroinella japonica	0.3	Astroinella japonica		
Odentella sinensis		Odentella sinensis	0.7	Odentella sinensis		
Bacteriastrum delicatulum		Bacteriastrum delicatulum		Bacteriastrum delicatulum	0.05	
Gyrosigma sp.		Gyrosigma sp.		Gyrosigma sp.	0.06	
Hemidscus sp.	0.17	Hemidscus sp.		Hemidscus sp.		
Other dinoflagellate	1.89	Other dinoflagellate	0.6	Other dinoflagellate		
Protoperidinium sp.	7.04	Protoperidinium sp.	7.6	Protoperidinium sp.	0.05	
Prorocentrum micans	1.97	Prorocentrum micans		Prorocentrum micans	0.01	
Ceratium furca		Ceratium furca		Ceratium furca	0.05	
Others	11.50	Others	13.1	Others	0.18	

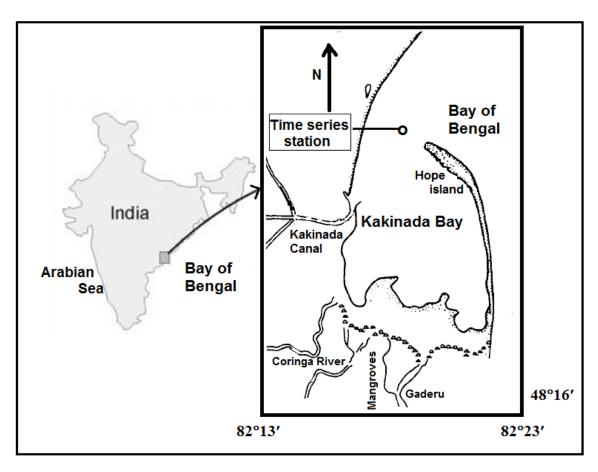


Fig 1: Map showing the station location where the time series observation has been conducted.

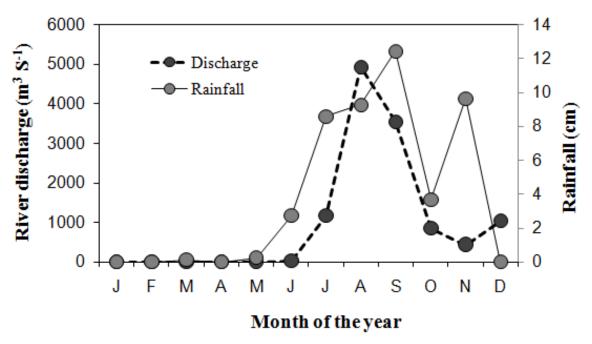


Fig. 2: River discharge and rainfall data during the year 2012 over Andhra Pradesh

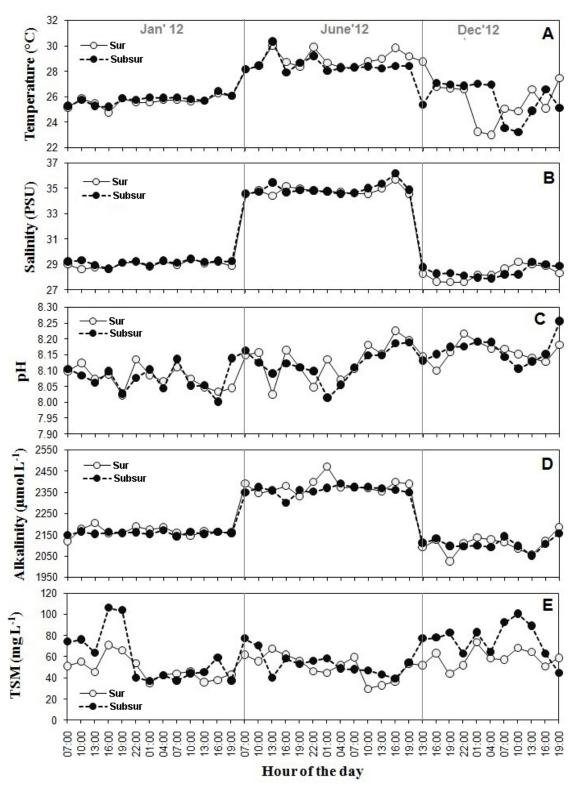


Fig. 3: Variability in surface and subsurface water temperature (a), Salinity (b), pH(c), total alkalinity (d) and total suspended matter (TSM) (e) during three time series observations at Kakinada Bay in January, June and December, 2012. The gray line in the figures shows the sampling duration between individual time series measurements.

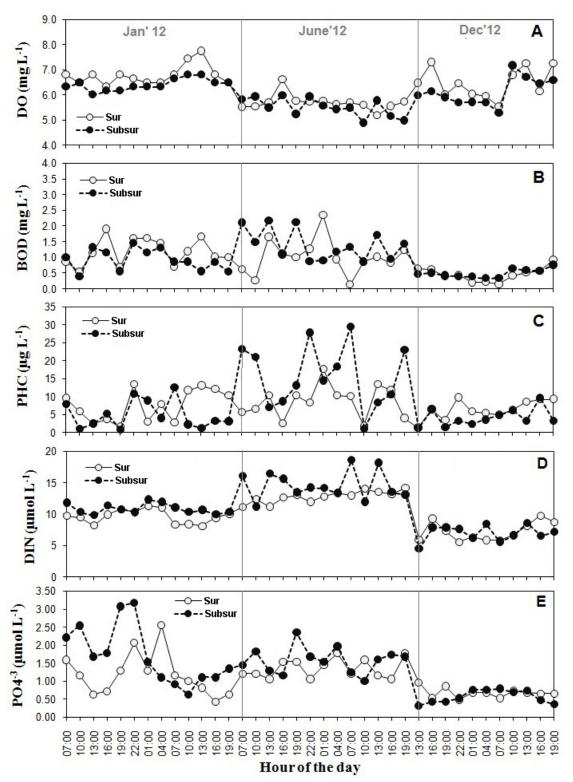


Fig. 4: Variability in surface (0m) and subsurface (average 4.5m) water DO (a), BOD (b), PHC (c), DIN (d) and PO₄⁻³ (e) during three time series observations at Kakinada Bay in January, June and December, 2012. The gray line in the figures shows the sampling duration between individual time series measurements.

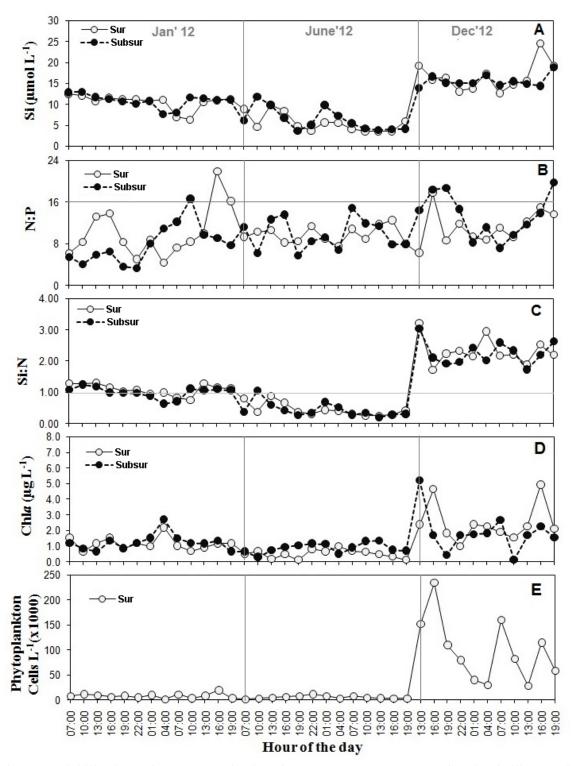


Fig. 5: Variability in surface (0m) and subsurface (average 4.5m) water dissolved silicate (Si) (a), the ratios of N:P (b), N:SI (c), total Chla (d) and phytoplankton cells (e) during three time series observations at Kakinada Bay in January, June and December, 2012. The gray line in the figures shows the sampling duration between individual time series measurements.

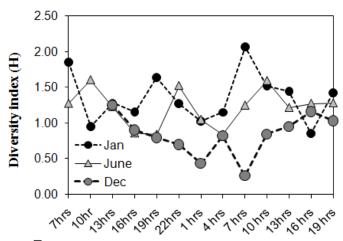


Fig. 6: Diversity index (\overline{H}) values of phytoplankton community during January, June and December in Kakinada bay from the surface waters.

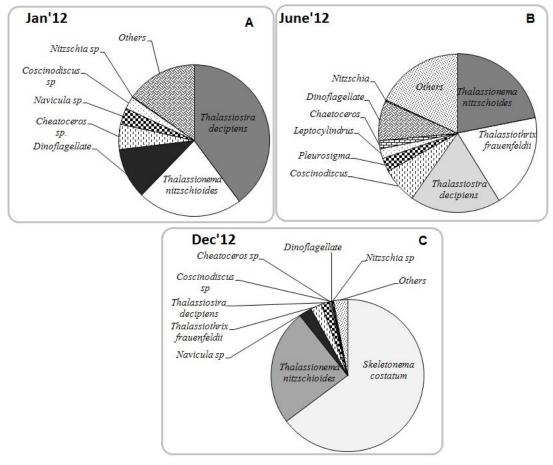


Fig. 7: Relative % of major contributing genera of phytoplankton community in January (a), June (b) and December (c) from surface waters of Kakinada bay. The values were calculated from the diel cycle measurement for 36 hours.