

Between River and Sea: What Control a Daily Variation of Physicochemical Properties of Estuary?

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Abstract

Physico-chemical features are among important factor that contributes to the variability of the estuarine environment. This study has been conducted to assess diurnal fluctuations of some physicochemical features in relation to tides in the surface water of Terengganu river estuary. The three stations were set along the area which linked the river to the coastal water where salinity, temperature, dissolved Oxygen, pH, TSS, chlorophyll-a, Phosphate and silicate nutrients were measured at the surface water for every 2 hrs over a period of 12 hrs during spring tide of September 2012. The salinity changes were found to follow the tidal rhythm, while the daily variation of the remaining features were found to be more pronounced than the tidal induced variation. With exception to salinity, gradual increases in all features were observed during the day tides, which generally, decreased from afternoon and early morning. The effect of tidal amplitude which said to be important in determining the extent of variation was more pronounced at lower estuary. The remaining stations were observed to be strongly influenced by the river flow.

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Introduction

Estuaries are considered to be vital natural resources and unique ecosystems at the interface between terrestrial and marine environments. The environmental conditions of estuaries vary essentially due to the short-time effects of tidal cycle on the water system. On a time scale of hours, ebb advection of fresh water and salt water intrusion during the flood determine strong changes of several important Physicochemical parameters of the water column such as salinity (Uncles and Stephens, 1996; Toubance *et al.*, 2013), nutrients

(Montani *et al.*, 1998; Tahir *et al.*, 2008; Kaniz *et al.*, 2014) and total suspended solids (Bimol *et al.*, 2009; Dayang *et al.*, 2012). The extent of such changes will further vary depending on tidal state or amplitude. Other environmental factors such as precipitation rate, winds and currents velocity of both fresh and sea water may greatly confound the situation, resulting to non-linear interactions between the river flow and the incident open sea hydrodynamics at the mouth and so the physicochemical feature of the system. Information on diurnal variations in physicochemical properties of estuarine system is essential to understand the

implications of such changes on various processes like biogeochemical cycling of elements and productivity of estuary (Kumar *et al.*, 20001; Toubance *et al.*, 2013). A number of works have been done on chemical and physical characteristics of some Malaysian estuaries (Suratman *et al.*, 1996; Law *et al.*, 1998; Tahir *et al.*, 2008; Jala *et al.*, 2012; Kaniz *et al.*, 2014; Aris *et al.*, 2014). However the studies concerning diurnal variation of such parameters with respect to tides are few. The present work is an attempt to address such variations in the Terengganu river estuary.

Experimental

The observation was made at Terengganu river estuary, situated on the east coast of peninsular Malaysia facing the South China Sea (Figure 1). The sampling was done during the spring tide to assess the maximum differences in the physicochemical features caused by the tides. The 12 hrs series observation was done on the riverine station (T24), an upper estuarine station (T16) and lower estuary station (T8) *set al.*,ong the study area. With the help of a tide table, the flood tide and ebb tide were marked out of total 12 hrs period starting from 0800 to 2000 hrs.

Surface water temperature, salinity, DO and pH were *insitu* measured at each station using the YSI multi-parameter. Water samples from the three sampling stations were collected, filtered and brought to the laboratory simultaneously. The filter paper were used to analyse TSS and Chlorophyll-a as directed earlier by APHA 1992 and 1998 respectively. The concentrations of inorganic nutrients (DIP and DISi) in the water samples were analyzed using an auto analyzer (Model: Skalar San++) according to the method of Grasshoff and Koroleff (1983). Total nutrients (TP and TSi) and total dissolved nutrients (TDP and TDSi) were determined using potassium peroxydisulfate oxidation method (Grasshoff and Koroleff, 1983).The dissolved organic nutrients (DOP and DOSi) value was taken as the difference between their total dissolved nutrients and particulate nutrients values (TPP and TPSi) were taken as the difference between their total nutrients. The analytical precision was less 1% for DIP, TDSi and TPSi and 2% TDP, TPP and DISi. The measurement and water sample collection were done once in 2 hrs to cover at least one stages of a diurnal tidal cycle.

Results and Discussion

The results of the tidal cycle and general physicochemical parameters monitored during the survey

are shown in figure 2, 3 and 4 respectively. The mean content of each feature relative to tidal fluxes were presented in table 1 and 2.

Tides

During the sampling period, at least one lower and one higher tidal levels were predicted (Figure 2). The first high tide, at 1000, was +1.9 m and the expected second high tide, at 2100, was +1.5 m. The difference in tidal height was used to distinguish them as a higher and lower flood tide, respectively. Correspondingly, a high low tide occur at 1600 which was +0.9 m. The largest difference of the tidal level was 1m between 0800 hr and 2000 hr.

Salinity

The diurnal change in salinity with reference to tide is presented in figure 3(a). During the first 2 hrs of measurements, at high flood tide, a strong salinity gradient was observed among the study locations. Salinity was significantly higher at T8 located at the lower part of estuary (Table 1).

Following the ebb flow and the low flood tide, fresh water runoff progressively and strongly reduced the salinity at both Stations. The T24 reported 0.00 ppt during the 12 hrs survey which confirmed that this station is a riverine station and experiences no influence from the sea at any tidal point.

The diurnal change in salinity was found to follow ebb and flood condition. High salinity water import was stronger at the high flood tide than the low flood tide. Correspondingly; salt intrusion was stronger at the higher flood tide than at the lower flood tide (Tahir *et al.*, 2008; Toubance *et al.*, 2013). A low-salinity surface water mass moving down-estuary with the ebb tide led to the decrease of salinity, however the effect of fresh water intrusion to estuary was strongest during evening low flood water causing the decrease in salinity to minimum. This implies that only during high flood tide of spring tide the salt water intrusion become more significant.

The observation also suggests a strong influence of both river and sea water amplitude on salinity distribution. This observation is in disagreement with the report of Uncles and Stephens (1996) and Montani *et al.*, (1998) who showed that only salinity intrusion was a strong function of the tidal state and a weaker function of fresh water inflow.

Temperature

The fluctuation in temperature along TRE was slightly low between the stations and the tides (figure 3(b)). The maximum difference in temperature with the state of tides was only 0.1°C (Table 1). Generally the temperature was observed to be low during the first 2 hrs of high flood tide at the lower part of estuary, increase slightly with the incoming ebb water and decrease with the incoming low flood water. At upper estuary and riverine station, the temperature was measured higher during the two flood phases with slightly low value in ebb tide.

The daily variation of surface water temperature exhibited a maximum value around 1400 - 1700 and the minimum value around 0800 and 2000, thus a gradual increase in temperature was observed during the day tides, which, typically decreased from afternoon and early morning. Similar observation was made earlier by Kaliyamurthy (1976) in Pulicat Lake, Montani *et al.*, (1998) in tidal estuary of the Seto Inland Sea, and Brasileira and Brasileira (2012) in the estuary of the Jaguaribe river. The authors attributed their results with the daily change in atmospheric temperature.

Sharp drop of temperature observed around 1600 was due to heavy rain in the river. It appears, therefore, that atmospheric condition plays an important role in warming and cooling of the studied area, thus overshadowing the differences brought by the tide (Dehari, 2970; sarma *et al.*, 2010).

Dissolved oxygen (DO)

The mid-day water carried more oxygen than the morning and late afternoon water (Figure 3(c)). The variations in DO were greater between the stations than the tidal fluctuation. During the early 2hrs of survey confined to high flood tide, the DO was higher at the lower estuary, intermediate at the upper estuary and slightly low at the river station. The DO concentration starts to decrease with incoming ebb tide and to the maximum at low flood tide down the estuary. The upper estuarine and riverine stations show an increase of DO during ebb tide which decreases in the evening with the surging of low tidal flood.

The DO content of the surface water of Terengganu river estuary was higher during afternoon (1100 - 1600). The high DO in all stations was found to coincide with the peak temperature measured during the survey.

Observations of Qasim and Gopinathan (1969), which showed that the oxygen values began to increase after sunrise and reached the maximum during the early hours of the afternoon, are comparable to the present observations. The authors attributed the oxygen changes to the photosynthetic activity of planktonic and benthic plants. Huggins and Anderson (2005) also lend support to the above explanation. Meanwhile, the lower estuary measured a relatively high mean DO than the rest of stations; this would probably be due to the incursion of well aerated seawater or the higher mixing of air and water due to surface-water agitation by wave action and turbulence (Suratman *et al.*, 1996).

pH

The variations of pH were wider between the stations and between high flood tide and ebb tide (figure 3(d)). at the first 2 hrs of high flood tide, the surface water pH was measured low in all stations, the pH tend to increase with ebb tide and low flood tide at lower estuary. The upper estuarine and riverine stations report a surge of pH with ebb tide which decreases slightly with incoming low flood tide.

There appears a wide range of fluctuation in pH with regard to tidal stages. The low pH was observed with flood tide and increased to the maximum with the peak ebb tide. The increase in pH concedes with the peak temperature (photosynthetic hours) for both stations. The observation of Zhang *et al.*, (2013), which showed that the pH moved in line with the diurnal trends of temperature, falling to the lowest values at 0600 am and rising to the highest between 12:00 and 15:00, when the temperature reached the peak of the day at Sanya Bay, is comparable to the present observation. The authors attributed the pH change to the photosynthesis process of biological community. Usually the photosynthetic consumption of carbon dioxide (CO₂) can drive pH to high levels, thus pH may be higher during daylight hours when photosynthesis is at maximum. The major drive of pH fluctuations between stations was the net photosynthesis, respiration and decomposition process, which probably depend on the relative abundance of biological communities at each location (Dickson, 2010). The time and amount of sewage discharge from the surroundings (Subin and Husna, 2013, which feature the river, and, to some extent the upper estuary, was predicted to lower the relative pH of these stations. However, the buffering capacity of the estuary (Elliot *et al.*, 2008) resulting from seawater intrusion produced a comparable pH at lower part of estuary.

Table.1 The mean content of salinity, temperature, DO, pH, TSS and Chlorophyll-a relative to tidal fluxes

| Feature | Tides | Stations | | |
|----------------|--------|-------------|-------------|-------------|
| | | T8 | T16 | T24 |
| Salinity (ppt) | Flood* | 26.4 ± 5.94 | 0.60 ± 0.57 | 0.00 ± 0.00 |
| | Ebb | 12.6 ± 13.9 | 0.33 ± 0.58 | 0.00 ± 0.00 |
| | Flood | 4.00 ± 1.41 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| Temperature | Flood* | 29.5 ± 0.35 | 28.7 ± 0.21 | 29.0 ± 0.07 |
| | Ebb | 29.7 ± 0.25 | 28.5 ± 1.13 | 28.7 ± 1.34 |
| | Flood | 29.3 ± 0.07 | 28.7 ± 0.85 | 29.2 ± 0.07 |
| DO | Flood* | 5.41 ± 0.30 | 3.87 ± 0.52 | 3.69 ± 0.10 |
| | Ebb | 5.19 ± 0.50 | 4.04 ± 0.26 | 3.88 ± 0.09 |
| | Flood | 4.74 ± 0.02 | 3.78 ± 0.03 | 3.84 ± 0.07 |
| pH | Flood* | 6.06 ± 0.33 | 6.59 ± 0.30 | 6.64 ± 0.03 |
| | Ebb | 6.11 ± 0.26 | 7.12 ± 0.90 | 6.87 ± 0.55 |
| | Flood | 6.24 ± 0.16 | 7.11 ± 0.16 | 6.48 ± 0.25 |
| TSS | Flood* | 61.5 ± 27.6 | 26.0 ± 2.83 | 17.0 ± 4.24 |
| | Ebb | 77.7 ± 64.4 | 28.3 ± 19.6 | 14.0 ± 10.5 |
| | Flood | 25.5 ± 12.0 | 18.5 ± 9.19 | 9.50 ± 3.54 |
| Chlorophyll-a | Flood* | 8.25 ± 6.79 | 15.3 ± 13.7 | 6.46 ± 1.60 |
| | Ebb | 2.83 ± 2.04 | 6.42 ± 4.61 | 3.91 ± 1.60 |
| | Flood | 1.54 ± 0.56 | 2.77 ± 1.50 | 3.55 ± 1.28 |

* representing the High flood tide.

Table.2 The mean concentrations of DIP, DOP, TPP, DISi, DOSi and TPSi relative to tidal fluxes

| Feature | Tides | Stations | | |
|---------|--------|-----------------|-----------------|-----------------|
| | | T8 | T16 | T24 |
| DIP | Flood* | 0.31 ± 0.01 | 0.47 ± 0.02 | 0.48 ± 0.02 |
| | Ebb | 0.36 ± 0.03 | 0.48 ± 0.05 | 0.38 ± 0.05 |
| | Flood | 0.36 ± 0.01 | 0.44 ± 0.10 | 0.31 ± 0.11 |
| DOP | Flood* | 0.27 ± 0.01 | 0.48 ± 0.02 | 0.51 ± 0.02 |
| | Ebb | 0.35 ± 0.22 | 0.59 ± 0.25 | 0.94 ± 0.22 |
| | Flood | 0.79 ± 0.36 | 0.96 ± 0.29 | 0.97 ± 0.73 |
| TPP | Flood* | 0.52 ± 0.02 | 0.73 ± 0.02 | 1.26 ± 0.04 |
| | Ebb | 0.23 ± 0.19 | 1.41 ± 0.54 | 1.40 ± 0.25 |
| | Flood | 0.76 ± 0.60 | 1.11 ± 0.77 | 1.52 ± 1.46 |
| DISi | Flood* | 7.751 ± 0.00000 | 14.45 ± 0.00000 | 17.95 ± 0.00000 |
| | Ebb | 8.083 ± 0.00000 | 12.87 ± 0.00000 | 19.30 ± 0.00000 |
| | Flood | 9.933 ± 0.00000 | 10.93 ± 0.00000 | 7.632 ± 0.00000 |
| DOSi | Flood* | 60.11 ± 0.00000 | 289.4 ± 0.00000 | 105.4 ± 0.00000 |
| | Ebb | 48.29 ± 0.00000 | 265.0 ± 0.00000 | 316.8 ± 0.00000 |
| | Flood | 386.5 ± 0.00000 | 904.3 ± 0.00000 | 351.6 ± 0.00000 |
| TPSi | Flood* | 110.5 ± 0.00000 | 155.9 ± 0.00000 | 167.8 ± 0.00000 |
| | Ebb | 212.4 ± 0.00000 | 105.0 ± 0.00000 | 82.93 ± 0.00000 |
| | Flood | 209.3 ± 0.00000 | 121.4 ± 0.00000 | 209.2 ± 0.00000 |

* representing the High flood tide.

Fig.1 Study area and location of sampling station along Terengganu river estuary: T8 (Lower estuary), T16 (Upper estuary) and T24 (river station)

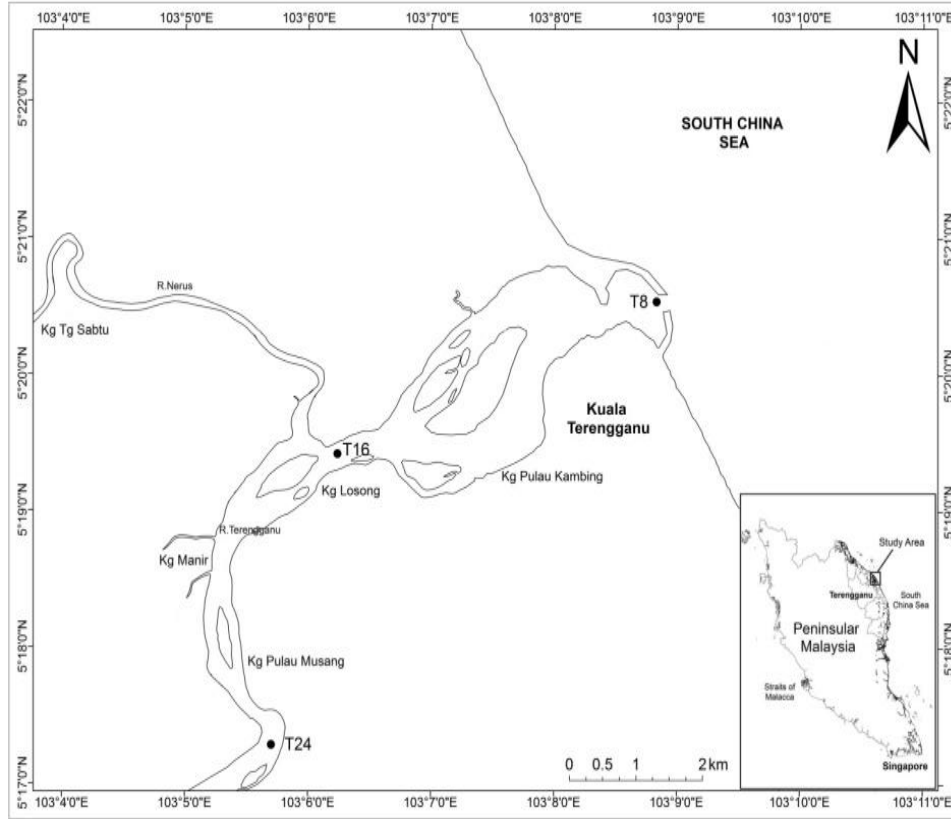


Fig.2 Spring tide cycle during 12 hours survey of September 2012

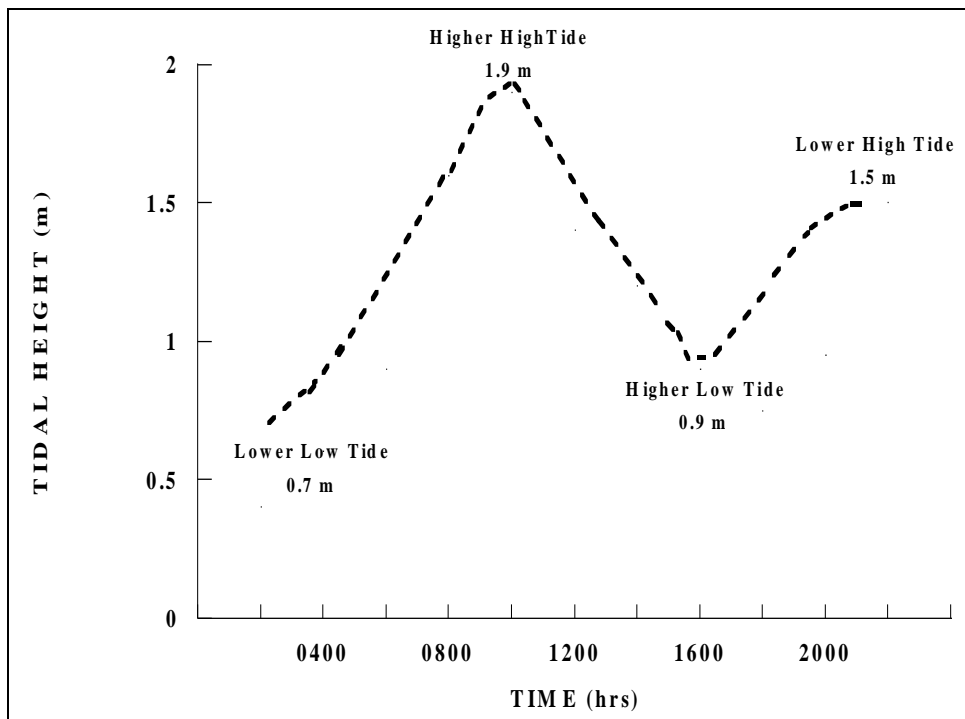


Fig.1 Diurnal variation of salinity (a), surface water temperature (b), DO (c), pH (d), TSS (e) and chl a (f)

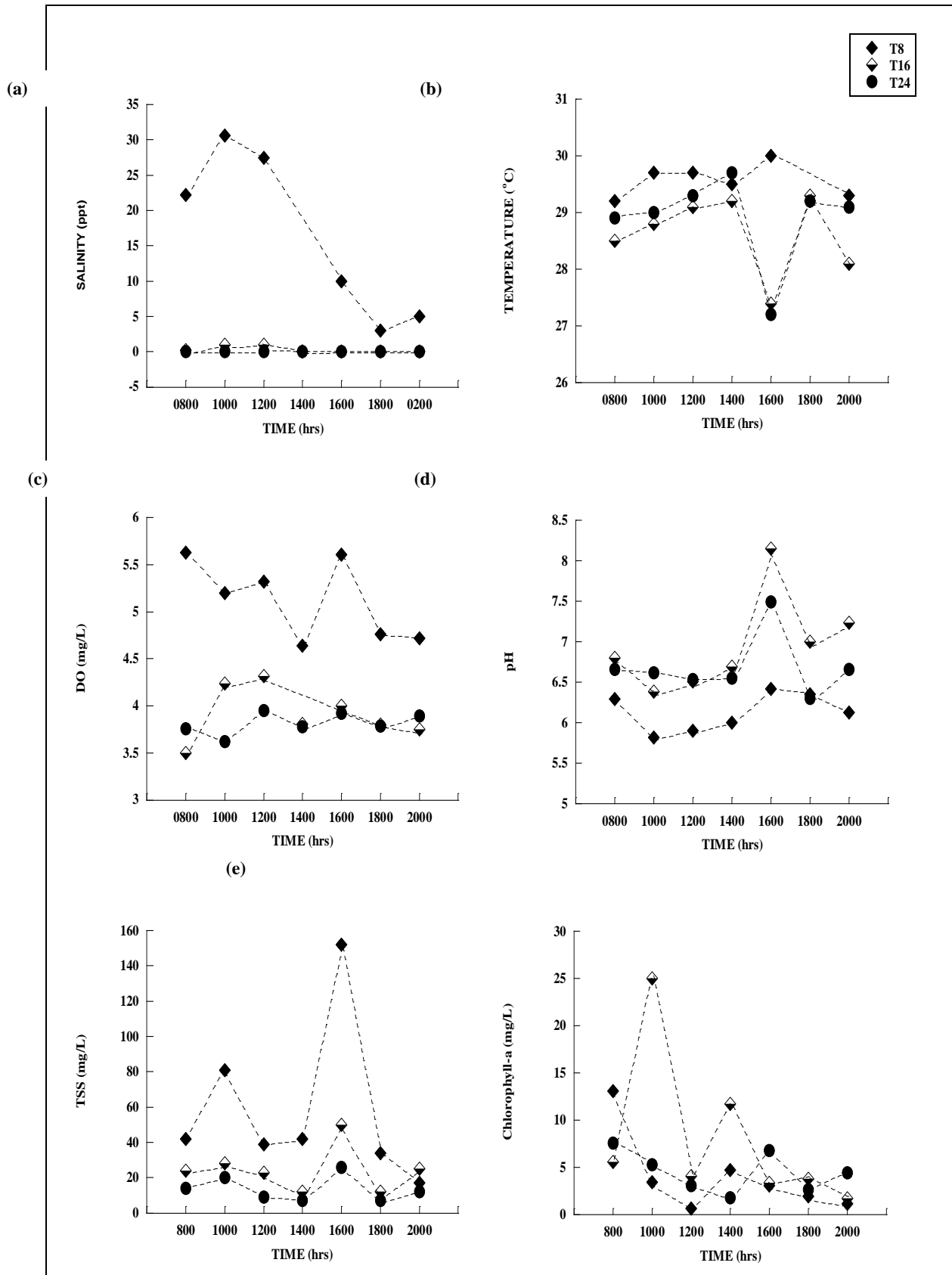
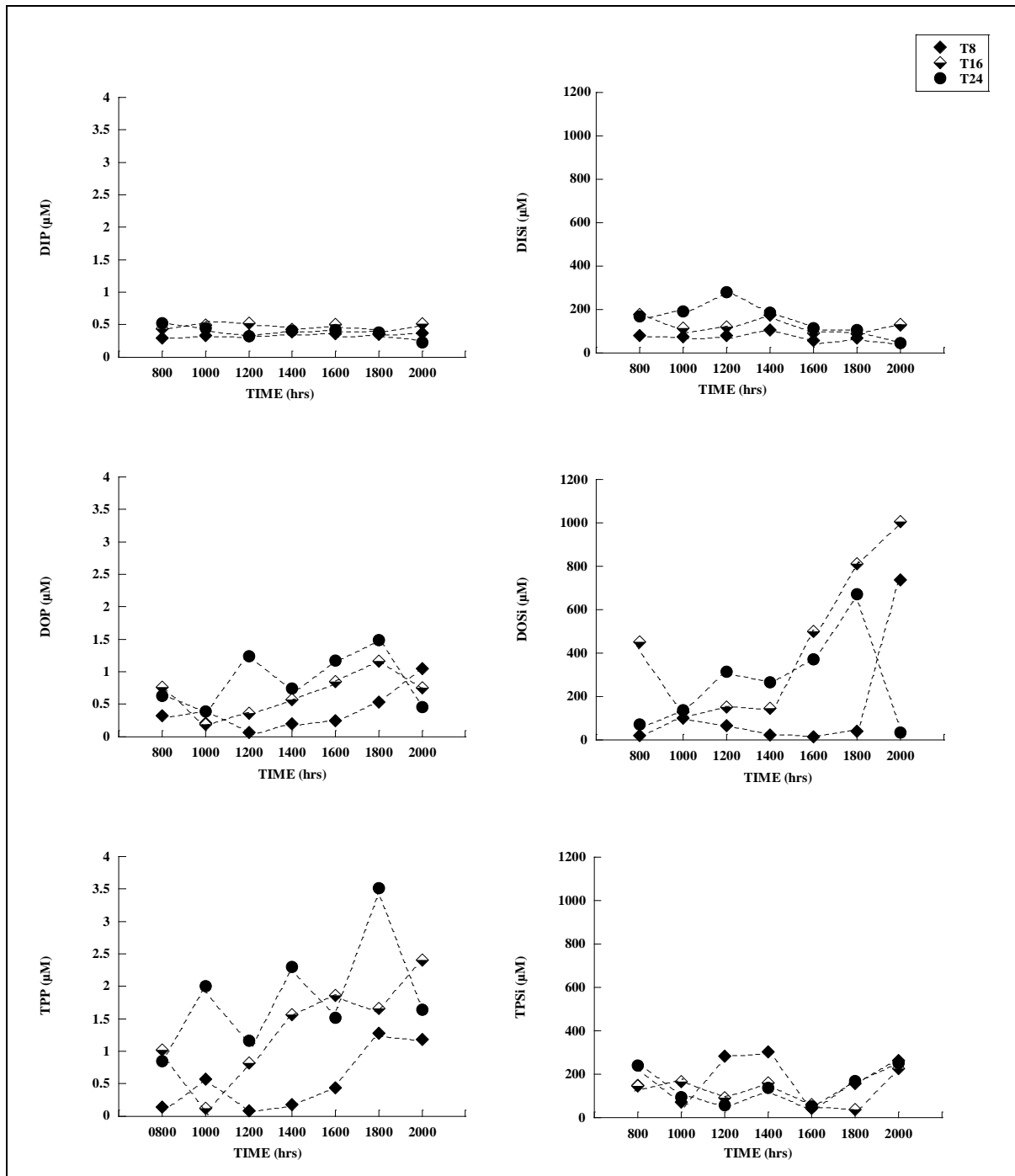


Fig.2 Diurnal variation of phosphate and silicate nutrients along TRE



TSS

The marked diurnal variations in TSS content with reference to tide were observed (Figure 3(e)). In the first 2 hrs of measurements, at high flood tide, the mid-mean values of TSS concentration was observed in all stations. The concentration was observed to increase at lower and

upper estuary during ebb tide, followed the decrease at the riverine station. The TSS was then decrease to the minimum in all stations during the low flood water.

In hourly time scale the tidal advection under the ebb and flood tide conditions transport freshwater and salt water to the estuary, which results in a strong diurnal change in

TSS content. The TSS concentrations were more during ebb tide than the flood tide, this indicate that the influx of TSS into this estuary is seaward, which principally depends on the river flow. The result is in agreement with those reported at Itajai-Acu estuary (Schettini and Carvalho, 1998), Caboriuestuary (Siegle *et al.*, 2009) and Mangatalestuary (Yusop, 2007). Thus far the TSS was found higher at the high water of the flood tide than for the low flood tide. This observation attributed to the resuspension of the bottom sediments caused by strong currents generated from the large tidal range during high flood of spring tide. Similar observation was reported elsewhere by Suratman *et al.*, (1996) at Selangor River, Bimol *et al.*, (2009) at Sempadi river estuary and DayangSiti Maryam (2012) at Manngatal estuary.

Chlorophyll-a

In the first 2 hrs of high water of the flood tide, the concentrations of chlorophyll-a were higher at all stations and decreased gradually with the incoming ebb tide and low water of the flood tide (figure 3f)). However, the T16 and T24 showed a higher concentration than the T8 station suggesting that the spreading of this pigment is seaward.

A number of studies that examined the diurnal change of chlorophyll-a with the tide have been conducted. For example Yin and Harrison (2000) reported a higher chlorophyll-a content during the flood tide than the ebb tide, indicating a loss of the pigment from the water column, which was likely due to feeding by benthic organisms. Naik *et al.*, (2012), however, related this observation to the species diversity and phytoplankton density, which seemed to increase and decrease with the flood and ebb water, respectively. Although the same trend has been observed in the present study, the justification provided by the two aforementioned studies was slightly inappropriate for the scenery; it is thought that the tidal mixing of water or resuspension of phytoplankton from surface sediment, particularly during the high flood tide, results in high chlorophyll-a content in the surface water. This phenomenon has been well explained earlier by Qasim and Gopinathan (1969), Anderson *et al.*, (1983) and Shikata *et al.*, (2008). Further observation show the diurnal peaks of chlorophyll-a during the daytime than the night. This may be because of the ambient temperature and light at daytime are among the important parameters for their production peaks in the day hours, which decreased to the minimum during the late hours of the evening (Qasim and Gopinathan, 1969 and Senthilkumar *et al.*, (2008).

Phosphate

The average values of each P species relative to the sampling stations and their diurnal trend were shown in Table 2 and figure 3 respectively. During the first two hours of peak flood, the DOP, DIP and TPP were lower at T8. The trend was reversed during the ebb tide. With the low water of the flood tide the concentration of each species increased relatively to the P-surge from the river. Relative to this observations, the river water seemed to be a major source of all P-species to the estuary and the transportation of this nutrient relied more on the river flow rather than the tidal cycle; however, the minimal influence of the tide that was observed during the high water of spring tide at T8 was influenced by the P fluctuation from T16, which interconnects the two rivers and estuary. The increase in the P content at T16 might directly or indirectly come from T24 since the two stations were quite far from each other, thus the river flow intensity must be there to ensure the supply of P-species at T16. T24 became an independent station with respect to T16 and T8. For the three stations, T16 and T24 seemed to possess more P than the rest suggesting the retention of this nutrient, which then became an essential source downstream.

The fluctuations in the phosphate levels seemed to be more perturbing. Lillebø *et al.*, (2002) reported a higher P efflux during the first hour of tidal flood with a sharp or linear decrease at high tide and incoming ebb phase. The authors explain his observation that, the higher phosphate efflux rates in the first hours may result from the contact of the incoming seawater, with lower phosphate concentration and lower temperature, with the rich warm superficial (low tide pools) or interstitial water. These differences of P-content between the two waters may promote the phosphorus efflux to the incoming water column by diffusion and/or convection process. The differences will be attenuated as the tide comes in, and phosphate efflux rates smoothly decrease. During the tidal ebb, the efflux rates showed a sharp, sometimes linear decrease. This is because the air-exposed sediments have a substantially higher phosphate sorption capacity than the submerged sediments, thus reducing the P-content from the low water ephemeral pools formed. In contrast, Naik *et al.*, (2012) found an increase in the P concentration during the ebb phase, with an inverse relationship between salinity and P-nutrient, suggesting that the increase in P-nutrient at this tidal point was due to river input. In respect of the Terengganu River estuary, the ebb-flood change in P-nutrient might probably be affected by river flow.

However, the high P reported during the high water of the flood tide could be attributed to the resuspension of the surface sediments resulting in its high concentration at the surface water.

Silicate

The DOSi, DISi and TPSi were found to be lower at T8, the trend was reversed for DISi and TPSi during the ebb tide of the first two hours of sampling. The DOSi tends to decrease following its decrease at T16. Temporarily, the riverine stations reported higher content of Si-species in the flood and ebb phase. With the coming low tide of high water, the DISi at T8 was observed to increase with a decrease from T16 and T24 while DOSi and TPSi increased with the increase of the concentration at T16 and T24 (figure 3).

The general observation of diurnal variation of Si in the study area shows no clear-cut relation between the Silicate concentration and tidal phase. Observation of Kumar *et al.*, (2000) showed both high and low concentrations during all tidal phases in the Mulki Estuary, which is comparable to the present surveillance. The authors concluded the absence of a relationship between the two variables (Si and tidal rhythm). In addition, the river stations showed a higher Si concentration than the estuary. This observation comes from the fact that the rivers are the major vectors of large-scale redistributions of Si between continents and the ocean via estuaries, transporting large quantities to marine waters (Tre'guer and De La Rocha 2013; Carey and Fulweiler, 2014). Apart from weathering, which is known to be the ultimate source of silica for the river and estuaries, human activity can add to the observed high Si in the study area. Conley *et al.*, (2008) reported that land-use activities have an influence on Si concentrations in adjacent rivers. In the Terengganu River estuary, the most forested watersheds are those of the Nerus and Terengganu Rivers with the largest surface area devoted to agriculture. Although the impact of the agriculture on the water geochemistry differs strongly from one stream to another its impact seemed to be high in the Nerus River since both cultivated crops and pasture land (included in grasslands) are the biomes of most Si sequestration. Urbanization and development may also affect the riverine Si, particularly DSi concentrations that come from partially treated sewage systems and wastewater enriched in DSi due to the use of washing powders (Meunier *et al.*, 2011); this is featured in Terengganu River and its estuary. Other features like sand digging, sand embankments and the presence of

water treatment plan dragging, may also be superimposed, translating into high Si content in the area.

The freshwater inflow along Terengganu river estuary was a vital course of estuary physicochemical properties dynamics as indicated by the strong changes of all features at individual stations on a time scale of 2 hrs. The effect of the tidal amplitude was observed at lower estuary merely at high tide of spring tide. The higher values of nutrients in riverine stations suggest that, the river can be an important source on nutrients for the estuary and adjacent sea.

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