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BEHAVIOUR OF WATER QUALITY PARAMETERS DURING EBB TIDE IN DUNGUN RIVER ESTUARY, TERENGGANU

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Abstract: A study has been carried out to determine the behaviour of selected water quality (WQ) parameters in Dungun river estuary. Samplings were carried out twice during October 2001 under similar tidal conditions (ebb tide) whereby samples were collected as a function of salinity i.e. along the salinity gradients from 0 ppt (freshwater end-member) to 31 ppt (coastal water end-member). WQ parameters monitored were the general physical parameters (viz. temperature, pH, dissolved oxygen, suspended solids and redox potential), dissolved metals (copper, cadmium and lead), dissolved nutrients (nitrogen- and phosphate-based nutrients) and chlorophyll-a. The physical water quality parameters were measured *in situ* using a multi-parameter data logger whilst nutrients and chlorophyll-a analyses were carried out based on the colorimetric method. Dissolved metals were analysed using GF-AAS technique following the pre-concentration step using APDC-MIBK method. Results in general indicated that most of the parameters measured appear to behave non-conservatively with salinity. In the case of nutrients, with the exception of nitrate which exhibited removal behaviour, all other nitrogen- and phosphorus-based nutrients, exhibited addition behaviour in the estuary. Cadmium and lead were also found to behave in a non-conservative manner in the estuary i.e. positive deviation was observed for cadmium whilst lead exhibited a negative deviation from the theoretical dilution line. These observations suggest that the estuary act as a source for cadmium but a sink for lead. Copper on the hand exhibited a linear relationship with salinity indicating a conservative distribution along the estuary. Results obtained in the present study clearly show the different behaviour of a given water quality parameter in the estuary and also illustrate the important role played by Dungun River estuary in modifying the nutrient and metal concentrations during the transportation from the river to the coastal waters.

KEYWORDS: Water quality, physical parameters, dissolved nutrients, dissolved metals, Dungun river estuary.

Introduction

Estuary is a complex system because it is a place where mixing occurs between natural waters of different chemical composition and physico-chemical properties. The most common approach to examining the behaviour of constituents entering an estuarine system is to compare their distribution with that predicted for simple mixing of water bodies during which the constituent is conserved. Salinity is used as an indicator of conservative mixing and a constituent that exhibits a linear relationship with it is assumed to be conserved.

Liss (1976) has proposed a model to demonstrate the conservative and non-conservative behaviour of a given constituent in an estuary from a simple mixing of a two-component system that is single source of river and seawater, respectively. The constituent is said to mix conservatively if the plotted data fall on a straight line joining the end-members of the mixing series, often called the theoretical dilution line. The slope of the theoretical dilution line will be positive for a component more concentrated in seawater than river water (Figure 1(a)) and negative where the river water is enriched in the constituent concerned relative to seawater (Figure 1(b)). A deviation from theoretical dilution line of dilution (i.e. a curvilinear relationship) may, depending upon the direction of the curvature, indicate a losses or gains of material during mixing; a curvature above the theoretical dilution line is generally indicative of the non-conservative behaviour by addition to the water whilst a curvature below the dilution line is indicative of removal from the water during the mixing process. The above characterization of a given constituent of an estuary with respect to salinity is a standard procedure for chemical investigations in estuaries. Based on this model, many

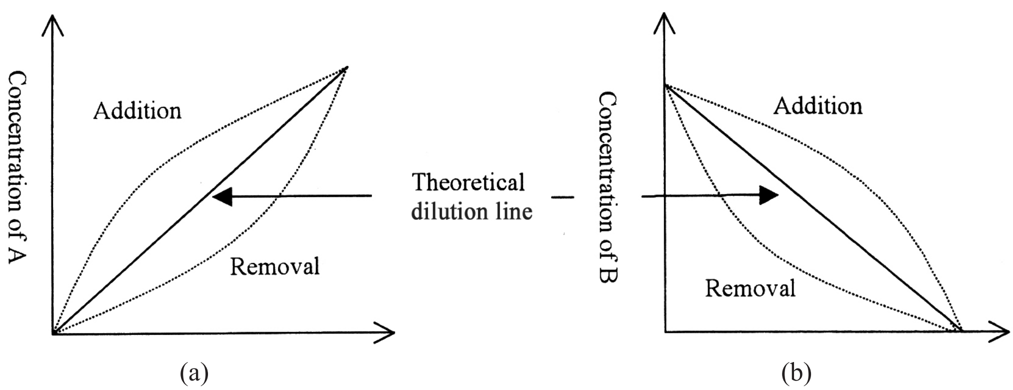

Figure 1: Relationship between concentration of dissolved component and a conservative index of mixing (Liss, 1976).

studies have been made in order to evaluate the conservative and non-conservative behaviour in the estuarine environment (Morris *et al.*, 1981; Emmerson, 1989, Eyre, 1994).

A study has been carried out to determine the concentrations of the physical, nutrients and selected dissolved trace metals (copper, cadmium, lead) parameters along the whole estuarine system of the Dungun River estuary. In addition, the behaviour of these parameters during mixing in the estuary will also be evaluated using the model proposed by Liss (1976). This paper summarises the results obtained from this study which had been previously reported elsewhere (Mohd Tahir *et al.*, 2004, 2005).

Experimental

The Dungun River is located at the district of Dungun, Terengganu. This river is approximately 75 km in length and receives runoffs from its main tributaries such as Telemboh, Lok, Kelmin, Loh and Perlis Rivers before discharging into South China Sea (Figure 2). The catchment covers an area of approximately 4414 km^2 and the land use within the catchment is predominantly rural and agricultural activities. The tides in this river are of semi-diurnal in nature with a tidal range of about 1.0-3.5 m.

This tidal range was measured during the low and high water near the river mouth. The river is rather narrow with a width of about 100-150 m at the river mouth. Except at the coastal area, the depth of the estuary is about 3-5 m.

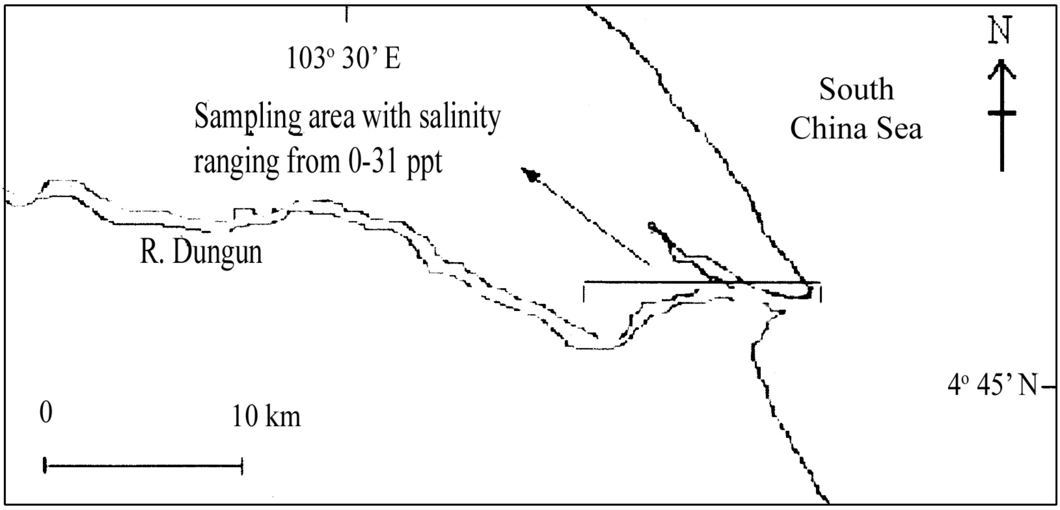

Figure 2: Sampling stations in the Dungun River estuary

In this study, sampling stations were not fixed according to longitude-latitude coordinates because salinity was used as the conservative index. Consequently, samples were collected along the salinity gradients from 0 ppt (freshwater end-member) until 31 ppt (coastal water end-member) at the middle of the river by using a boat. Since the boat was not anchored during samples collection, small amount of drift occurred around the sampling points; changes in the salinity values during the drift for the respective sampling points were small i.e. + 1 ppt (data not shown). Samples were collected on 9/10/01 and 30/10/01 under similar tidal condition , namely during the ebb water using a Van Dorn sampler at a depth of 1 meter from the surface water, filtered through 0.45 μm membrane filters and introduced into 1 L polyethylene bottles. Temperature, Dissolved Oxygen (DO), pH and Redox Potentials (Eh) were measured *in situ* using YSI multiparameter data logger. Phosphorus-(orthophosphate and Total Dissolved Phosphate (TDP) and nitrogen-based nutrients (nitrite, nitrate, ammonia and Total Dissolved Nitrogen (TDN)) were determined based on the colorimetric method (Grasshoff, 1983) whilst Total Suspended Solids (TSS) and chlorophyll-a were based on standard methods (APHA, 1985). Dissolved Cu, Cd and Pb were determined after preconcentration-complexation treatment. The metals were complexed with 1% ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutylketone (MIBK) in Teflon separatory funnels. After phase separation, the water was discarded and the complexes in the MIBK were extracted back into 2M HNO^3 and stored in polypropylene test tubes. Trace metal analysis was then performed by GFAAS. Spikes were added to some samples to determine the extraction efficiency, which was better than 90% for all metals investigated.

Results and discussion

Data obtained for the two sampling were plotted against the salinity. Figure 3 shows the mixing curve for the physical parameters current data whereas Figure 4 and 5 show the mixing curves for the nutrient and metals parameters, respectively. The range of the concentrations and behaviours of the parameters studied for both survey were summarised in the Table 1.

Physical parameters

During both sampling periods, the temperatures variations were rather small (27.04-30.66 ^{o}C). Temperatures of the estuary increased consistently from the freshwater end-member to coastal water end-member indicating a conservative mixing by this parameter. The pH values varied from 6.06 recorded at freshwater end-member to 8.02 recorded at coastal water end-member. For both surveys, the pH-salinity plot shows an upward curvature, which indicates addition of pH values in the estuarine region. A non-conservative behaviour was also observed for TSS and chlorophyll-a where an addition of these parameters occurred in the estuarine area. In general, their concentrations were more variable during both sampling periods with a markedly higher concentrations observed at low salinity region (0-15 ppt) for both parameters; their concentration ranges from 4.4-54.4 mg/L and 0.13-0.66 mg/m3, respectively. Similarly, a non-conservative behaviour was also observed for DO and Eh parameters, but their behaviours showed a removal trend within the estuary. The DO concentrations observed ranges from about 82.2 % of saturation in freshwater end-member to 110.5 % of saturation in coastal water end-member for both surveys although DO concentrations recorded on 9/10/01 were slightly higher that the sampling carried out on 30/10/01. As in the case of DO, the Eh values also showed variation between sampling data. Sampling on 30/10/01 recorded significantly higher values (131.3-285.7 mV) that the values (23.7-82.5 mV) recorded on 9/10/01.

Table 1: Range of the concentrations and behaviours of the parameters studied for both survey

Parameters	Values/Concentrations	Behaviour
Temperature	27.04 – 30.66 0C	Conservative
pH	6.06 – 8.02	Non-conservative (addition)
DO	82.2 – 110.5 % saturation	Non-conservative (removal)
Eh	23.7 – 285.7 mV	Non-conservative (removal)
TSS	4.4 – 54.4 mg/L	Non-conservative (addition)
Chlorophyll-a	0.13 – 0.66 mg/m^3	Non-conservative (addition)
Orthophosphate	2.15 – 18.64 μg/L P	Non-conservative (addition)
TDP	23.90 – 115.20 μg/L P	Non-conservative (addition)
Nitrite	0.2 – 2.2 μg/L N	Non-conservative (addition)
Nitrate	24.6 – 188.6 μg/L N	Non-conservative (addition)
Ammonium	10.8 – 296.1 μg/L N	Non-conservative (addition)
TDN	40.4 – 649.1 μg/L N	Non-conservative (addition)
Copper	0.10 – 0.23 μg/L	Conservative
Cadmium	0.11 – 0.32 μg/L	Non-conservative (addition)
Plumbum	0.09 – 0.45 μg/L	Non-conservative (removal)

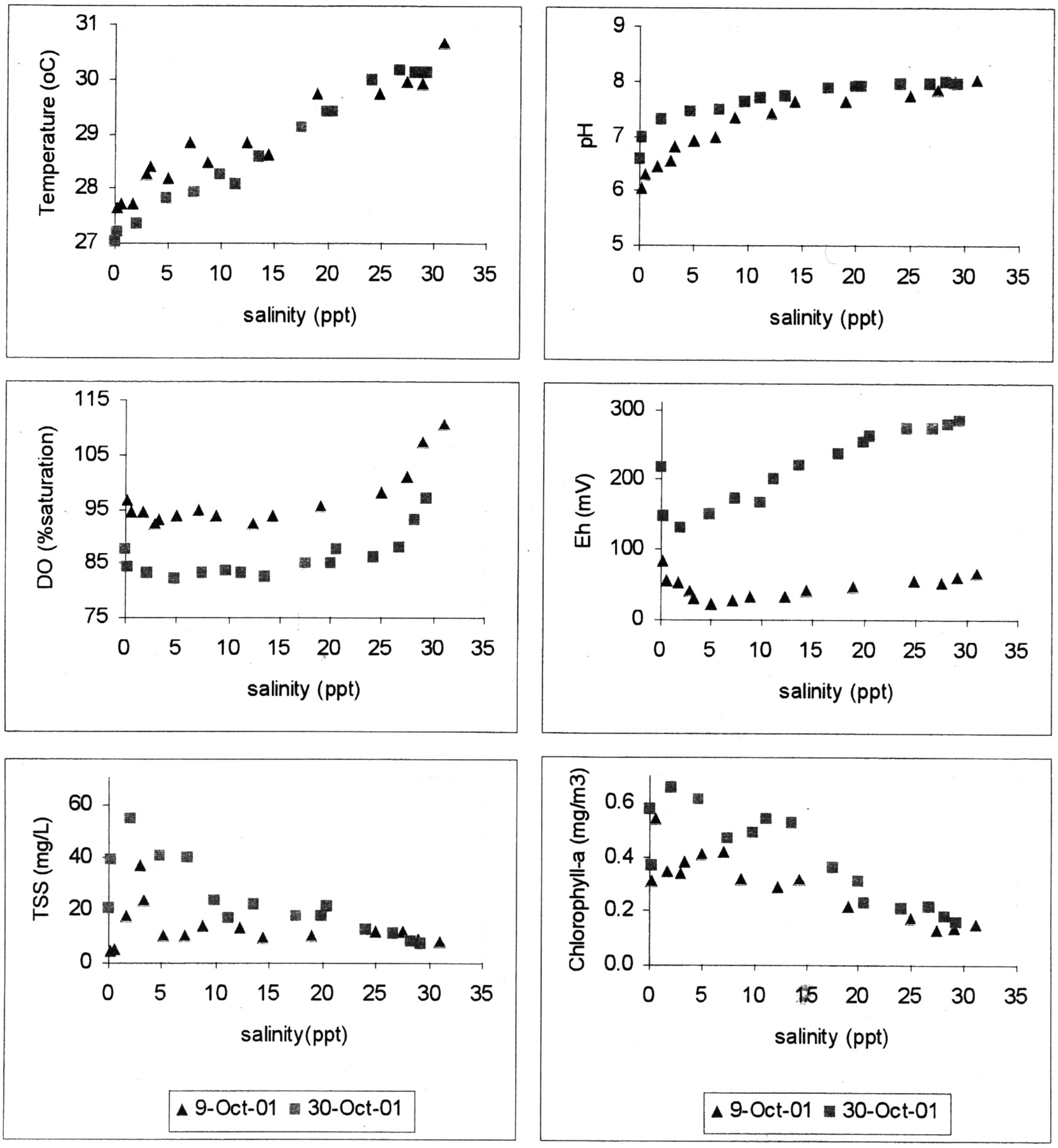

Figure 3: Mixing curves for the physical parameters in the Dungun River estuary

Phosphorus-based nutrient

The concentrations of orthophosphate and TDP in Dungun River estuary varied between 2.15-18.64 µg/L P and 23.90-115.20 µg/L P, respectively. Freshwater end-member recorded a higher value of orthophosphate and TDP compared to the coastal water end-member. The relatively high concentration values of orthophosphate were recorded during the sampling on 30/10/01 compared to 9/10/01. However for TDP, no obvious differences were observed between the two sampling periods.

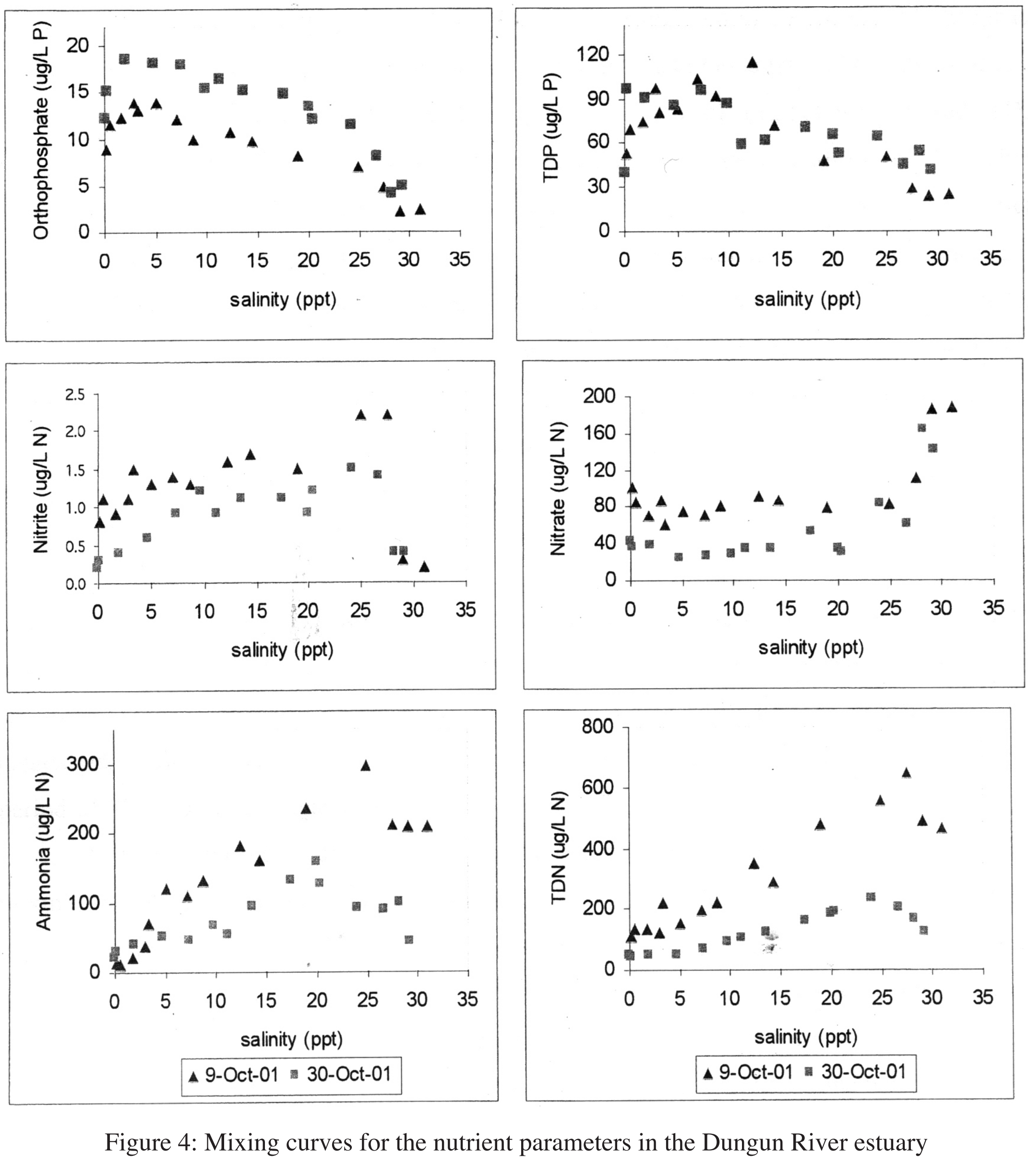

Figure 4: Mixing curves for the nutrient parameters in the Dungun River estuary

The behaviour of orthophosphate and TDP parameters along the salinity gradient during the estuarine mixing, as shown by the orthophosphate-salinity and TDP-salinity plots, revealed a non-conservative behaviour with an addition trend for both nutrients. There were several factors which could explain an addition of phosphate in this area. One of the factors could be from the Dungun town and a small jetty built for fish landed situated at the estuarine region. It is possible that the domestic sewage from that town and effluents from the activities at the jetty were discharge directly into the estuarine area, which raises the phosphate concentrations. The physical parameters such as pH and DO have also been found to influence the phosphate concentrations in natural waters. The adsorption process which led to low dissolved phosphate contents in natural waters is favoured under low pH (Carritt and Goodgal, 1954) value and vice versa. The reason could be used to explain an addition of orthophosphate and TDP concentrations observed at the estuarine area which recorded also an addition of pH value. Studies have also founded that under anoxic condition (i.e low DO contents), phosphate which adsorbed on suspended solids will be released to water column (Lopez-Hernandez and Burnham, 1978). As a result, the phosphate concentrations in the water column will be high. In general, the present observation shows that there is an inverse trend between DO contents and phosphate concentrations in the estuarine area. The phosphate concentrations were found to be higher at the estuarine area with lower of DO contents.

Nitrogen-based nutrient

During the present study, nitrite concentrations were in the range of 0.2-2.2 µg/L N and for nitrate, the concentrations values ranged from 24.6-188.6 µg/L N. Concentrations recorded for ammonia and TDN ranged from 10.8-296.1 µg/L N and 40.4-649.1 µg/L N, respectively. The results also indicate that the concentrations for all nitrogen-based nutrients during the sampling period on 30/10/01 were slightly higher compared to 9/10/01.

With the exception of nitrate which showed the removal trend during the estuarine mixing, the others three nitrogen-based nutrients showed an addition especially at the higher salinity region (20-31 ppt). Similar with those observed for phosphorus-based nutrient, the additions of most of the nitrogen-based nutrients were probably the sewage discharge from Dungun town and the activities at the fish landed jetty. DO content in a water column has been shown to play an important role in the nitrogen-based nutrients concentrations where generally, higher ammonia levels are found in water column with low DO content (Baird and Pereyra-Lago, 1992). This has been mainly attributed to rapid conversion of the oxides forms of nitrogen compounds such as nitrate to ammonia in water with low DO content. In the present study, the mixing profile clearly shows a significant removal of DO and nitrate occurring in the Dungun River estuary.

In contrast, comparison between other nitrogen compounds-salinity plots and DO-salinity plot indicate a clear inversion correlation. Biological assimilation by phytoplankton/benthic communities has also been cited as possible mechanism for nitrate removal in the water column (Johannes *et al.*, 1994). In this present study, the concentrations of chlorophyll-a have been used as indicator of biological data. Result obtained in the present study showed an inverse correlation between chlorophyll-a and nitrate concentrations. Thus, this observation could well suggest that the removal of nitrate in the estuary has also been attributed to consumption of nitrate by phytoplankton/benthic communities.

Trace metals concentrations

As in the case of physical and nutrients parameters, trace metals gradients in estuaries can be better expressed in terms of their concentrations versus a conservative index such as salinity. Figure 5 shows the relationship between trace metals and salinity during the estuarine mixing. The results showed there was a linear relationship between Cu with salinity, indicating a conservative behaviour for this metal. On the other hand, an addition and removal were observed for Cd and Pb, respectively. This indicates non-conservative behaviour for these two metals where the Dungun River estuary acts as a source for Cd but a sink for Pb. Reported results for trace metals behaviour in estuaries differ considerably. For examples, Cu was reported to behave conservatively in the Amazon estuary (Boyle *et al.*, 1982), but non-conservatively with removal behaviour in the San Francisco Bay estuary

(Eaton, 1979) and an addition in South-eastern U.S estuaries (Windom *et al.*, 1983). Cu and Pb have also been reported to be conservative in Rhone River estuary (Elbaz-Poulichet *et al.*, 1996). In contrast, an addition of Cd was observed at the same study area. Removal of Cu and Cd was recorded at the upper Tay estuary (Owens and Balls, 1997). These observations clearly suggest that behaviour of metals in estuaries is a complex phenomenon and can vary from one estuary to another and/or from one region to another. It is suggested that non-conservative behaviour of the trace metals in the mixing zone of an estuary may be due to ion exchange, variation of ionic strength, adsorption and biological uptake (Burton, 1976; Liss, 1976).

Conclusion

The result revealed the non-conservative behaviour shown by most of the parameters studied for both surveys. Only nitrate showed a removal trend whereas the other nutrients showed the addition during the estuarine mixing. The trace metals-salinity diagram also revealed the different behaviour shown by the trace metals. It is possible that there exist some mechanisms by which the parameters studied were removed from or added to the estuary. Further research should be conducted to investigate such mechanism.

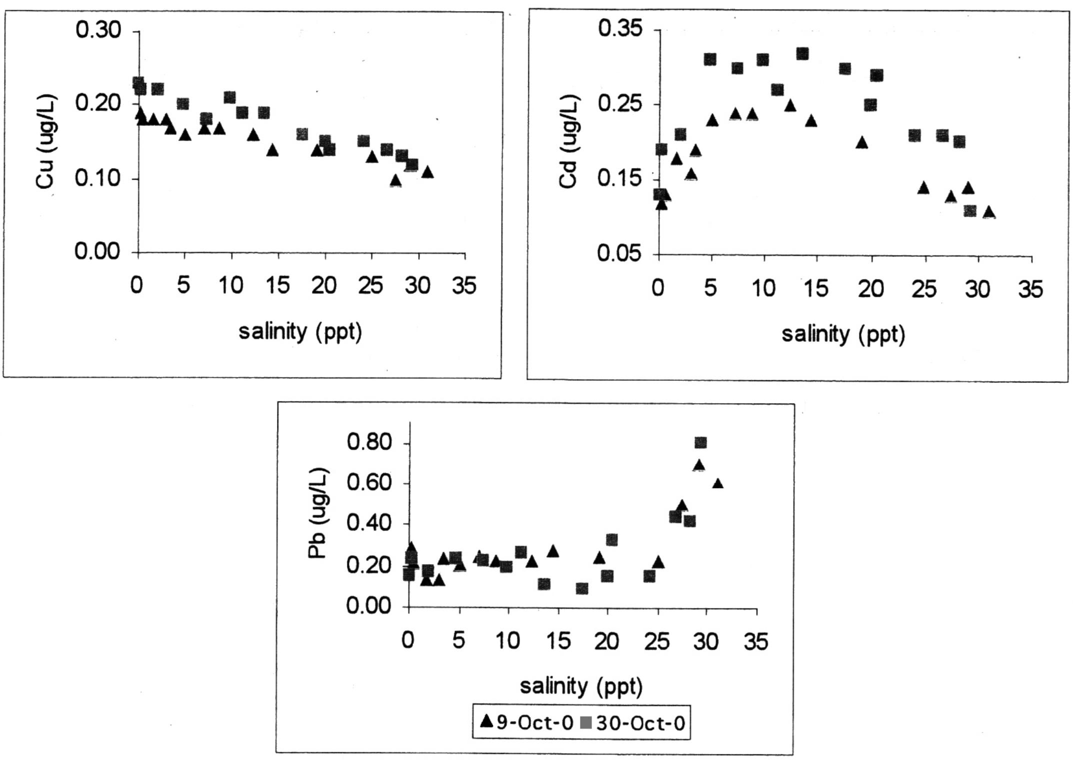

Figure 5: Mixing curves for the nutrient parameters in the Dungun River estuary

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