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A DISSOLVED AND PARTICULATE ZN IN THE TERENGGANU RIVER ESTUARY, SOUTHERN SOUTH CHINA SEA (MALAYSIA)

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Abstract: The distribution and behaviour of dissolved and particulate Zn during estuarine mixing was determined in the Terengganu River and its estuary, which enters the southern South China Sea. Surface water samples were collected during a transect at the full range of salinities region, and filtered through acid-cleaned cellulose acetate 0.45 µm filters. Dissolved and particulate Zn was determined using preconcentration-complexation treatment of the filtrate and acid digestion of the filters, respectively. The results showed that the range of concentration of dissolved and particulate Zn was 36-387 (mean=137+94) µg/L and 3-652 (mean=79+129) µg/L, respectively. The concentrations of dissolved and particulate Zn were higher in the freshwater end-member suggesting a riverine input to the estuarine area. Both dissolved and particulate Zn behaved non-conservatively, with negative deviation from the theoretical conservative mixing line in the estuary, suggesting that the estuary acts as a sink for this metal with the removal process accounting for 69-99%.

KEYWORDS: Zn, Distribution, Non-conservative behaviour, Removal, southern South China Sea

Introduction

During the transportation of dissolved and particulate metals from fresh water to the sea, they will pass through an estuarine region characterised by a strong gradient in ionic strength (salinity), pH and redox potentials. During estuarine mixing, a range of physico-chemical processes occur and as a result the distribution of metals in the water column undergoes modification. The distribution during the mixing can be characterised using a metal-salinity graph (Liss, 1976) which has been used by many researchers to study estuarine mixing (Holliday and Liss, 1976; Norhayati *et al.*, 2003; Karbassi *et al.*, 2008; Jian and Wen, 2009). The salinity of the estuarine is used as a conservative index of mixing. The metals behave conservatively if the graph exhibits a straight line between the two end-members (theoretical dilution). Any deviation above or below this line indicates addition or removal, respectively, to or from the water (Liss, 1976).

In this paper, the distribution and behaviour of Zn in the Terengganu River estuary is examined (Figure 1). Zn has been an issue of concern, especially in the marine environment because of enhanced human activities in coastal areas (Holliday and Liss, 1976; Dassenakis *et al.*, 1997; Fang *et al.*, 2006; Karbassi *et al.*, 2008; Song *et al.*, 2010). Zn is a highly persistent metal and can be toxic in trace amounts (Langston, 1990). Thus, the distribution and behaviour of Zn in marine systems, especially in the estuarine environment, should be assessed to aid the understanding of the nature and extent of anthropogenic influence. However, little is known about this metal in the present study area. The Terengganu River estuary is located at the east coast of Peninsular Malaysia and drains into the southern South China Sea. This estuary receives runoffs from two river systems i.e. the Terengganu and Nerus Rivers. The tides in these rivers are semi-diurnal with a tidal range of 0.5-2.0 m.

Materials and Methods

Surface (~0.5 m) water samples were collected along the salinity gradients from 0 ppt to 33 ppt at the middle of the river using a Van Dorn sampler. Sampling stations were not in fixed

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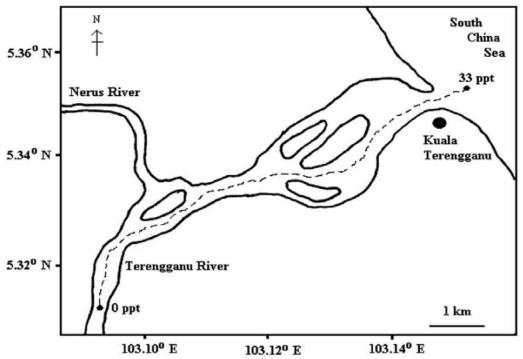

Figure 1: Location of Kuala Terengganu River estuary. (Samples were taken along the dashed line.)

locations during this study because the samples were taken according to salinity values acting as a conservative index (Liss, 1976). Samples were collected on 4th August 2008 (first sampling) and 28th September 2008 (second sampling) with both sampling dates having similar tidal conditions i.e. sampling took place around high water on spring tides. The samples were stored in acid-washed high-density polyethylene bottles and placed in a cooler during transportation to the laboratory. Upon arrival at the laboratory, the samples were immediately vacuum filtered in a 'Class 100' laminar air-flow bench, using acid-cleaned cellulose acetate 0.45 µm pore size filters. Filtrates were then acidified to pH 2 with concentrated HNO_3 (a.g.). The particulate matters collected on the filters were air dried in the laminar flow bench, then sealed in glass Petri dishes and stored in desiccators until analysis. Dissolved Zn (DZn) was determined after preconcentration-complexation treatment and analysed by graphite furnace atomic absorption spectrophotometry (GFAAS) (Mangnusson and Westerlund, 1981). Particulate Zn (PZn) was measured by GFAAS following digestion in HNO_3-HCl-HF (Chen and Ma, 2001). The detection limit for Zn analyses was 1.0 µg/L. Spikes were added to some samples to determine the extraction efficiency, which was better than 90%.

Results and Discussion

Concentrations of DZn and PZn against salinity for each of the sampling periods are shown in Figure 2. The concentrations of DZn ranged

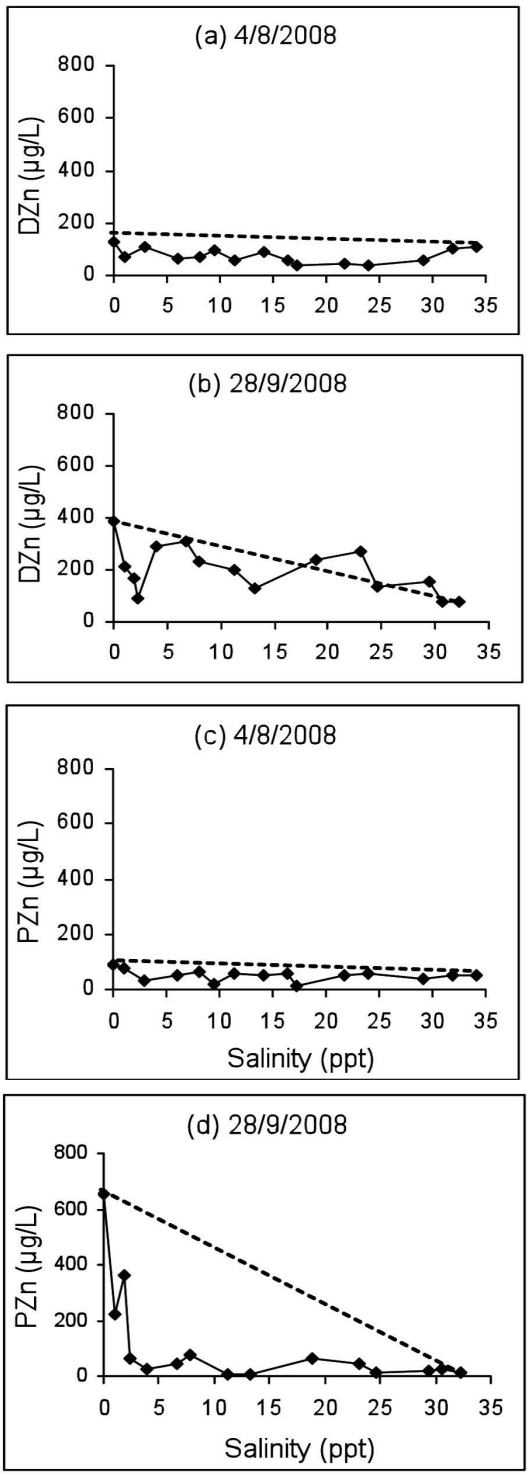

Figure 2: Dissolved (DZn) and particulate (PZn) Zn concentrations vs. salinity.

from 36-131 µg/L and 74-387 µg/L for first and second samplings, respectively. In addition, the concentrations of PZn ranged from 13-92 µg/L (first sampling) and 3-652 µg/L (second sampling). In general, higher concentrations of this form of metal were recorded at the riverine end-member compared to sea water, especially during the second sampling. Both forms of Zn showed non-conservative removal over the whole salinity range, with exception of DZn during second sampling which exhibited a slight addition at higher salinity regions.

In comparison with other estuaries, the mean concentration of DZn (137 + 94 µg/L) was significantly higher compared to Tay River, Scotland (1.5 µg/L) (Owens and Balls, 1997) and Acheloos River, Greece (2.9 µg/L) (Dassenakis *et al.*, 1997) estuaries. However, the mean concentration of PZn (79 + 129 µg/L) was lower compared to the Daugava estuary, Baltic Sea (Yurkovskis and Poikane, 2008) with mean concentrations of 429 µg/L and the Danube estuary, north-western Black Sea which recorded a mean concentration of 248000 µg/L (Guieu *et al.*, 1998). Higher concentrations of Zn recorded in the upstream region, especially during the second sampling, were probably due to the input from both anthropogenic activities and natural sources. Many studies have shown the same distribution with higher concentration of metals upstream relative to the downstream region (Holiday and Liss, 1976; Norhayati *et al.*, 2003; Suratman *et al.*, 2009). The composition of the surface freshwater system is strongly influenced by nearby activities and the chemical composition of the rock/sand in the area. By contrast, if there is an input of metals in the related coastal region, it will be masked due to the large dilution by sea water, leading to low concentrations of metals.

Significantly higher concentrations of dissolved and particulate Zn were recorded at the riverine end-member during the second sampling. This was probably as a result of heavy rainfall event during the day before the sampling. This type of event will contribute to high concentration of metals content at the upstream region through the runoff from land. A similar observation has been recorded at Changjiang River, China which recorded high metal concentrations in the river during the flood season (Song *et al.*, 2010). Comparison between dissolved and particulate forms showed that significantly higher concentrations of Zn were recorded in the latter form. When metals are released into the aquatic environment, they will generally bind to the particulate matter that is incorporated into the sediments after settling. This leeds to higher concentration of metals in dissolved compared to particulate form as observed at other study areas (Suratman *et al.*, 2009).

The present study shows significant removal of dissolved and particulate Zn in the Terengganu River estuary, indicating non-conservative behaviour (i.e. deviation from theoretical dilution line) during estuarine mixing. However, the Zn removal trend was less pronounced during the first sampling (DZn, 69%; PZn, 86%) compared to the second sampling (DZn, 81%, PZn, 99%). In general, the highest removal was found for PZn between the salinities of 0-5 ppt. The process responsible for this removal needs further investigation, but earlier studies have attributed this phenomenon to the influence of ionic strength, pH, turbulence, suspended solids and algae (Dassenakis *et al.*, 1997; Matagi *et al.*, 1998; Hatje *et al.*, 2003).

Conclusion

This study on the distribution and behaviour of Zn in Terengganu River estuary showed high concentrations of dissolved and particulate Zn in the freshwater regions compared to associated coastal waters. It is suggested that anthropogenic input and runoff from land during heavy rain contributed to high Zn concentration at the freshwater end-member. The results also revealed the non-conservative behaviour shown by both dissolved and particulate Zn with removal occurring predominantly in the low salinity region. This behaviour warrants further study in order to aid the improved understanding of the removal process in the estuary.

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