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Trace Metal Contents in the Porites Corals of Peninsular Malaysia

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ABSTRACT: The concentration contents of Ca, Mg, Sr and Zn in *Porites* corals from Pulau Langkawi, Pulau Redang and Pulau Tioman were presented. The corals were cleaned and the growth rate examined visually. The growth rate of *Porites* in Malaysia waters was between 5 to 25 mm yr^{-1} and each band was selected for determining the metal contents using the Atomic Absorption Spectrophotometer (AAS). The mean values of Ca (42.1 %), Mg (1184 μg/g), Sr (6276 μg/g) and Zn (60.6 μg/g) were calculated from each annual skeleton band representing the yearly growth. *Porites* coral from Pulau Langkawi shows a high content of Zn (118 μg/g) representing the water surrounding the island was highly polluted and also shows the uptake of Sr and Ca in the coral skeleton was related to the content of Zn, where Sr and Ca contents decreases when the concentration of Zn was more than 50 μg/g. Terrestrial runoff from Sumatera and west coast of Peninsular Malaysia are presumed to be the cause of pollution in Malacca Straits.

Key words: Coral, *Porite,* Trace element, Peninsular Malaysia

INTRODUCTION

Corals have been long recognized as marine bio-monitors, such as rainfall, runoff and upwelling events through the use of $\delta^{18}O$, Ba/Ca, Cd/Ca and Mn/Ca (Linn *et al.,* 1990; Shen *et al.,* 1992; McCulloch *et al.,* 1994; Gagan *et al.,* 1998; Fallon *et al.,* 1999). In the meantime, corals have been used to monitor past sea surface temperature (SST) through chemical, Sr/Ca, U/Ca, Mg/Ca, B/Ca and isotopic $\delta^{18}O$ in the aragonite skeletal lattice (Cole and Fairbanks 1990; Beck *et al.,* 1992; Mitsuguchi 1996; Fallon *et al.,* 1999; McCulloch and Esat 2000). Yet, coral usage in environmental pollutions based on the abundance of trace metals and rare earth elements is less developed (Howard and Brown 1986; Brown 1987; Shen and Boyle 1987; Hanna and Muir 1990; Scott 1990; Sholkvits and Shen 1995; Guzman and Jarvis 1996) as last reported by Bastidas and Garcia in year 1999.

According to Sinclair (2005), trace elements in the skeleton of tropical corals are now widely used as proxies for physical and chemical processes in the world oceans. All these studies have contributed significantly to the understanding of past climate variability, however after more than 120 years of research in this field the exact process by which corals form their skeleton is still not fully understood (Gattuso *et al.,* 1999; Cohen and McConnaugley 2003; Allemand *et al.,* 2004). The aragonite secreted by coral polyps is an orthorhombic form of calcium carbonate ($CaCO_3$) which is less stable than calcite. It can contain various minor and trace elements, mainly divalent cations such as Sr, Ba, Mg, Zn, Pb and Mn (Corrège, 2006). Despite the incorporation mechanism, corals have shown to be good tracers of pollutants in the marine environment (Shen and Boyle 1987; Hanna and Muir 1990; Guxman and Jimenez, 1992; Bastidas and Garcia, 1999). And coral reefs are mostly found in tropical water only. Coral reefs are widely spread around Peninsular Malaysia especially in the west coast. Coral community structures in the west coast of Peninsular Malaysia were dominant with *Porites*

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massive life form, and the east coast with a variety of life form categories of *Montipora* & *Acropora* (Toda *et al.*, 2007). Banded aragonite corals have been useful records of surface water composition changes over time because annual & sub-annual sections can be assigned ages based on growth patterns (Linn *et al.*, 1990). In this study, we used *Porites* corals to determine variation contents of Ca, Mg, Sr and Zn from various sampling stations as a signal for pollution levels.

MATERIALS & METHODS

Malaysia is located at South East Asia (Fig.1). with population over 27 million people. Malaysia's coral reefs extend from the renowned "Coral Triangle" connecting it with Indonesia, Philippine, Papua New Guinea and Australia (Maritime Institute Malaysia 2006). Coral reef types in Malaysia are situated on the Sunday Shelf in relatively shallow water. Most reefs are shallow fringing reefs in the offshore islands. In Malaysia, the conservation of coral reefs is largely achieved through the establishment of marine protected areas. Malaysia has designated 136 marine protected areas including non fishing area, marine parks and marine reserve (Maritime Institute Malaysia 2006).

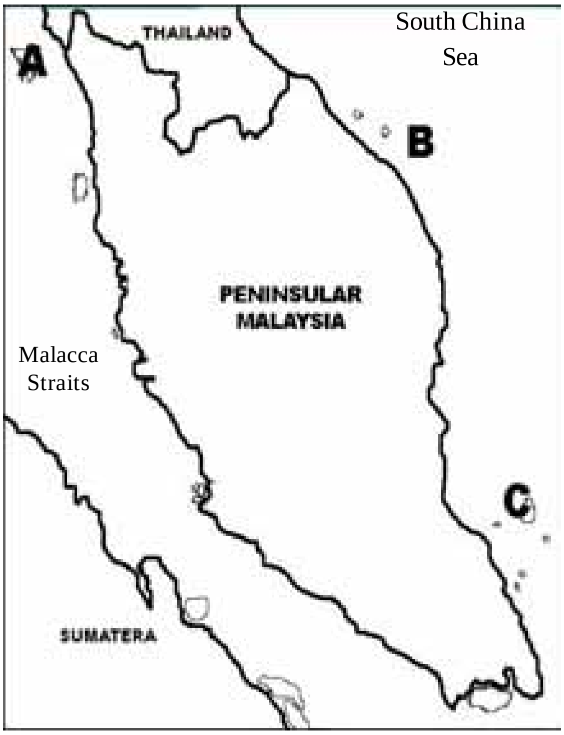

Fig. 1. Map of sampling stations in (A) Pulau Langkawi, (B) Pulau Redang and (C) Pulau Tioman

Pulau Redang was the first island to be declared as marine protected area in 1983. It lies 46 km north-east of Kuala Terengganu state, off the east coast of Terengganu. Further south of east coast of Peninsular Malaysia, lies Pulau Tioman, 32 km off the coast in the state of Pahang. It has eight main villages and the most populated at Kampong Take in the north side. Yet, the densely forested island is still sparsely inhabited and is surrounded by numerous coral reefs. Langkawi is an archipelago of 99 islands at the northern of Malacca Straits, 30 km off the mainland coast as Kedah state. The largest island is Pulau Langkawi with 45,000 populations. Langkawi was declared as tax-free island in 1987 to promote tourism. The island's airport was upgraded and ferry links were increased with other developments.

On August 2004, two coral samples of *Porites* were obtained from Pulau Tioman at 02^{o} 46.76'N, 104^{o} 07.01'E. The size of each coral sample more than 100 mm in diameter was collected from the water depth of 6 m. The *Porites* coral with a size of 101 mm and 7 bands labeled as PPTA and a size of 107 mm with 9 bands as PPTB. Then on September 2004, coral sample was also collected from Pulau Redang (05^{o} 46.46'N 103^{o} 03.59'E). The coral head size was 68 mm in diameter with 9 bands and collected at the water depth of 5 m labeled as PPR.During May 2005, sampling at the west coast of Peninsular Malaysia was done in Pulau Langkawi (06^{o} 09.59'N 099^{o} 48.52'E). The *Porites* coral was collected at the water depth of 1.5 m and the entire colony of 68 mm. The *Porites* coral from Pulau Langkawi (PPL) consists of 7 bands. These corals were prepared for trace metal analysis by washing with de-ionizer distilled water (DDH_2O) and weak acid (0.02M HNO_3) to remove surface contamination.

Massive *Porites* corals were cut into 2 cm slices using a diamond saw. The slices were washed with DDH_2O. After drying the slices, the coral was examined visually to identify chronological (yearly) bands (Fig. 2). Then, every layer was cut by small diamond saw and grounded using an agate mortar. About 0.5 g of powder samples were taken from each layer for analysis. Each of the power samples was dissolved in 5 ml of hydrofluoric acid, 10 ml of nitric acid and 3 ml of perchloric acid on the hotplate for 2 hours. After dissolution, dried sample continue adding with 50

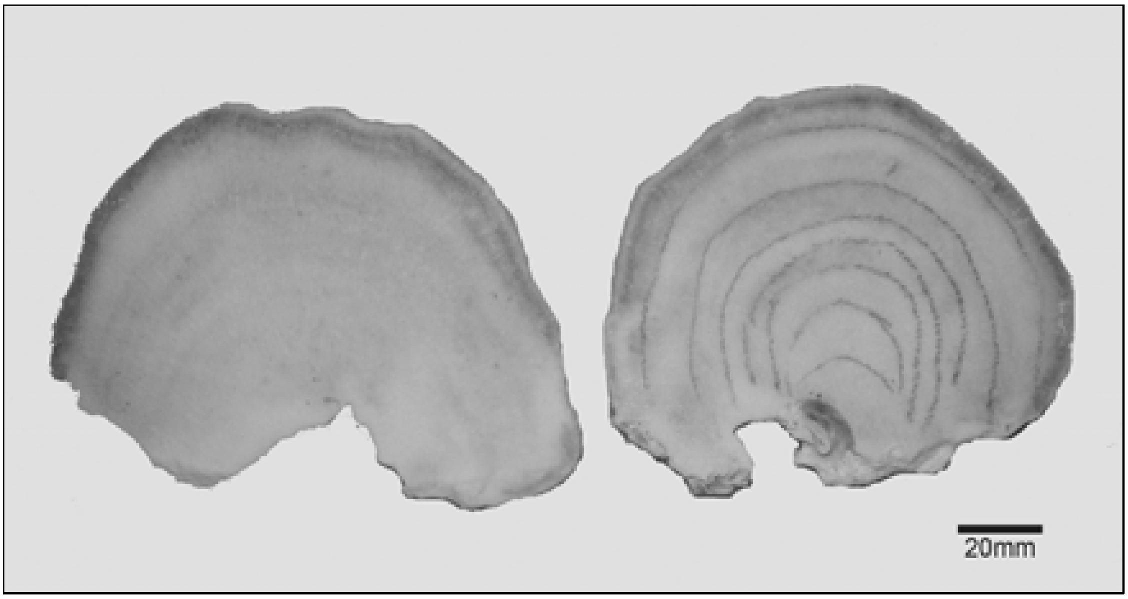

Fig. 2. A print of *Porites* coral from Pulau Redang. The right coral is mark to indicate the banding of the coral. The coral was samples along the major growth axis

ml of 0.5 M nitric acid and determine the concentration of trace metals using the Atomic Absorption Spectrometry (AAS). This procedure was evaluated with Standard Reference Material 1633b (Coal Fly Ash) with the percentage value of similarity 87% to 113%.

RESULTS & DISCUSSION

Porites corals growth rate obtained from this study is in the range of 5 to 25 mm yr^{-1} (Table 1). The growth rate depends on the location and the environment of the coral reef. The water quality of Pulau Langkawi is totally different from Pulau Redang and Pulau Tioman. The physical parameter for each sampling station is shown in (Table 2). The temperature and salinity is still in the range of coral reef distribution although the salinity in Pulau Langkawi is slightly higher than Pulau Redang and Pulau Tioman.The variation of Zn shows that Pulau Langkawi and Pulau Redang have an increasing trend in the year of 1999 to 2001 for Pulau Langkawi and 1997 to 2001 for Pulau Redang (Fig.3). Meanwhile, the level of Zn in Pulau Langkawi is the highest (> 57.3 µg/g) compare to Pulau Redang with content between 31.8 µg/g to 48.3 µg/g. *Porites* at Pulau Tioman shows lowest content of Zn with the average of 23.6 µg/g. The content of Zn in Pulau Tioman shows variation of up and down in PPTB in the year of 1996 to 2001. While in the PPTA shows decreased from 1998 to 2001 but after year 2001 the content of Zn increase gradually for both corals.

Table 1. Growth rate in millimeter (mm) of *Porites* coral at different sampling location

Year	Growth rate (mm/yr)			
	PPTA	PPTB	PPR	PPL
2005	-	-	-	10
2004	13	10	7	9
2003	12	11	10	6
2002	10	10	6	7
2001	10	12	5	11
2000	13	12	5	15
1999	18	12	7	10
1998	25	12	8	-
1997	-	8	5	-
1996	-	20	-	-

(-) is not measured

Table 2. Physical parameter of temperature, salinity and turbidity in each station

Station	Pulau Langkawi	Pulau Redang	Pulau Tioman
Temperature (°C)	31.33	30.06	31.38
Salinity (psu)	33.54	31.77	31.89
Turbidity (NTU)	7.08	NA	NA
pH	9.11	7.88	7.82

* NA = below detection limit

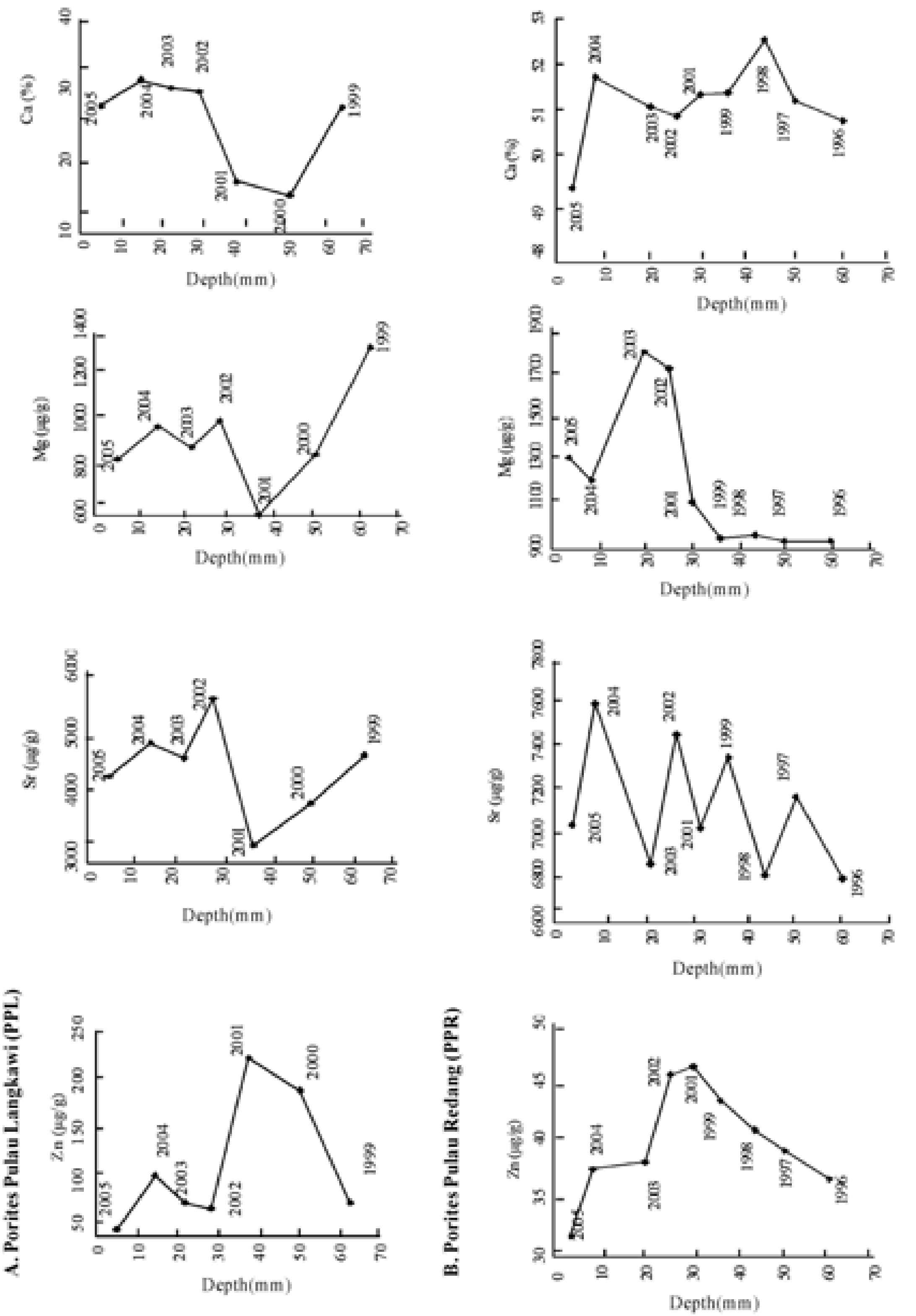

Fig. 3. Distribution of Zn, Sr, Mg and Ca in the various bands of *Porites* corals during this study-Continues

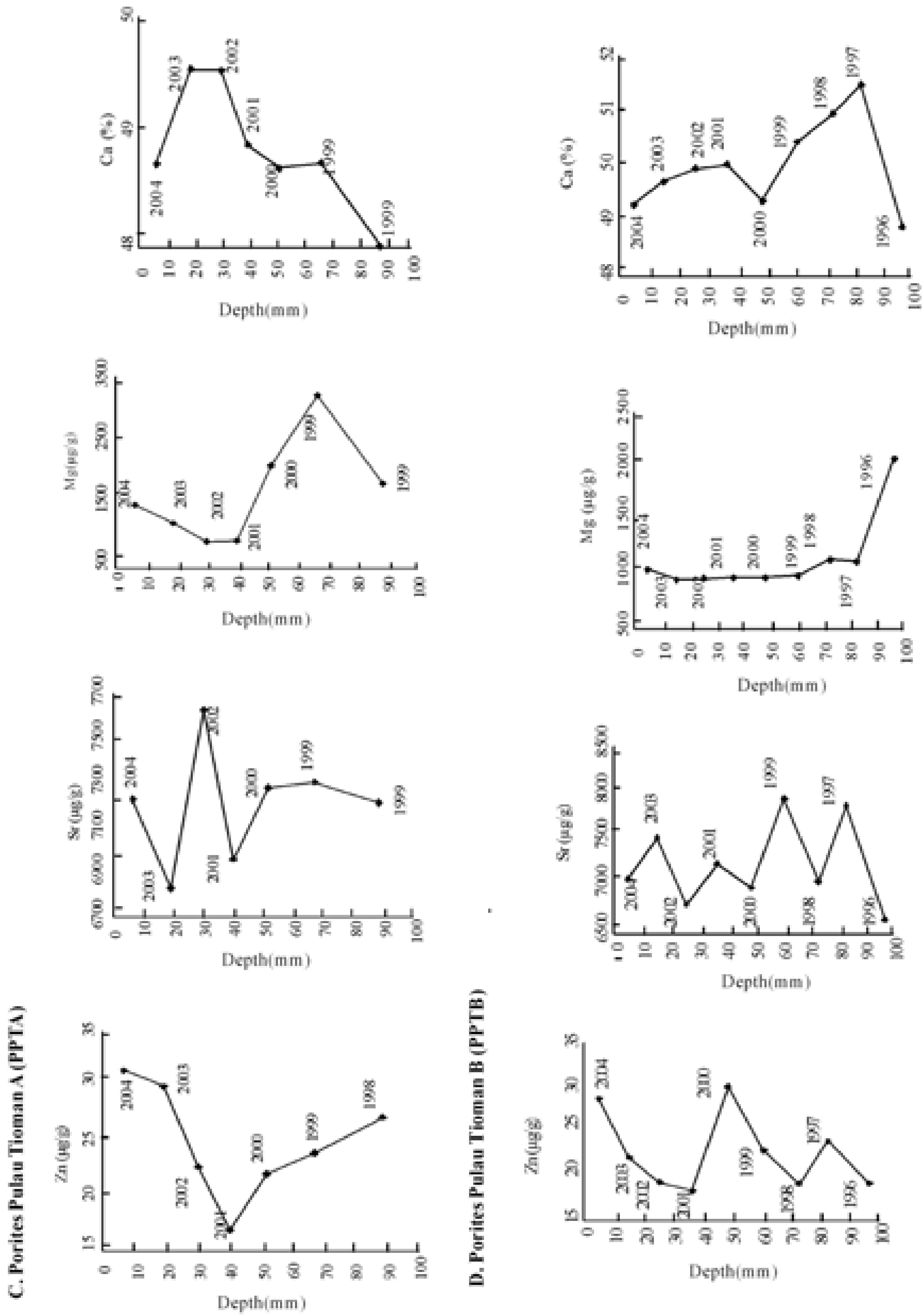

Fig. 3. Distribution of Zn, Sr, Mg and Ca in the various bands of *Porites* corals during this study-Continuation

The content of Sr in Pulau Tioman is in the average of 7207 µg/g for PPTA and 7238 µg/g for PPTB while the concentration for PPR is slightly low with an average of 7127 µg/g. Then the lowest content (4478 µg/g) was found in PPL sample. Similar trend also happen with the content of Ca in all the samples. The Ca content in PPL is in the range of 15.5 % and 31.5 %. Meanwhile PPR is in the range of 49.5 % and 52.6 %. The contents of Ca in PAPT and PBPT were in the average of 48.9 % and 50.0%.The content of Mg for PPL is similar to the Sr trend with ranging from 606 µg/g to 1334 µg/g. PPR shows higher content of Mg with an average of 1213 µg/g. PPTA shows the highest content of Mg comparing to other corals with 3205 µg/g at the depth of 67 mm or equivalent to the year of 1999. Meanwhile for PPTB, the content of Mg is at the average of 1000 µg/g at the surface till the depth of 79 mm. Then, it increase to 2071 µg/g at the deepest layer of 107 mm.The *Porites* sp. from Pulau Langkawi (9.7 mm yr^{-1}) and Pulau Redang (7.5 mm yr^{-1}) have lower growth rate compare to Pulau Tioman with an average of 13 mm yr^{-1}. This means that the coral in Pulau Tioman calcified faster than other places where the PBPT growth in 9 years for 107 mm while the PPR reach only 68 mm of the same age. Calcification of coral much depends on the surrounding water parameters, terrestrial runoff and stress. Temperature is an important tool affecting calcification rate in coral. However in this study, temperature is at the average of 31°C and the coral growth from each places are different.The differences of salinity in Pulau Langkawi from other islands might cause stress to the coral. Meanwhile the pH reading for Pulau Langkawi is high (9.11) because of the limestone at the surrounding water. The erosion of limestone ($CaCO_3$) increases the pH in the surrounding water. There is no study yet on the effect of pH on the coral reef. But the coral in Pulau Langkawi also face other stress such as high sedimentation rate. It is noted that millions of tons of sediment particles are transported annually by major rivers of the east coast of Sumatra and the west coast of Peninsular Malaysia to the coastal water of the Malacca Straits (Soegiarto, 2000).Comparing Zn content to other places, Pulau Tioman and Pulau Redang are between the range of 2.25 to 42 µg/g as likes the Papua New Guinea and Vanezuela high with the sediment loads (Table 3). Zn content in PPL is triple higher than other places. This shows the surrounding water of Pulau Langkawi is highly polluted. Hija River coral with highest content of 34.3 µmol/mol of Zn also serves as a pollution indicator. Zinc is enriched in the coral skeleton relative to seawater (distribution coefficient D_{Zn}=11; Shen & Boyle 1988). The loads of Zn into seawater are mainly from terrestrial runoff and soil.Zn and Pb are mostly used as anthropogenic and pollution monitoring in coral. Lead appears to be bound directly into the calcium in the coral lattice and is enriched relative to the seawater (distribution coefficient D_{Pb}=2.3; Shen & Boyle 1987, 1988). The effect of Zn to the calcification is less known. This study shows that Zn appears to be absorbed in coral lattice when Zn reaches a certain level and decrease the ability of absorbing Sr and Ca in the coral lattice. Fig. 4. shows the content of Sr, Mg and Ca that decreases when the content of Zn was more than 50 µg/g. This study has found that the uptake of Sr and Ca that used as SST proxy is not influences by the content of Zn. According to Sinclair (2005), if the temperature condition become more extreme, the enzymes that transport Ca ions would become less efficient, resulting in a lowering of the active Ca^{2+} transport and a decreasing calcification rate. The result shown in Figure 4 indicate the Sr and Ca is affected by the high Zn content and yet the Sr/Ca ratio (0.014 - 0.017) is still in the range comparing to the Rea Sea (0.022) and Davies Reef (0.019). This indicates that the coral is a good proxy for SST and also as pollution indicator at the same time.This result of Sr is almost similar to the studies in Davies Reef, Great Barrier Reef with 7463 µg/g (Sinclair *et al.*, 1998). The content of Ca in PPR (51.3%) and PPT (49.4%) is in the range from Davies Reef (38.3%) and Rea Sea (58.4%). The content of Ca in PPL is 25.75%. Since Sr and Ca is widely used as proxy for sea surface temperature, the trend of Sr and Ca should be similar because of the ratio (Sr/Ca) is use to calculate the SST. This study shows the uptake of Sr and Ca in the coral skeleton is related to the content of Zn. Unlike Zn, Sr lies long residence time in the ocean or static behavior over the short time scales of glacial cycles. Sr is added to the ocean by rivers and hydrothermal exchange and removes from the ocean by carbonate deposition, both in the form of aragonite and calcite (Stoll &

Schrag, 1998).Comparing the metals content at PPTA and PPTB, the average content is almost the same but the yearly content is different. This shows that the ability of each corals for metal up taking is different and also they are few meters apart. Differences in the metal profiles of the Ihatub corals imply that the location and depth of the coral samples are important factors to consider even if distances of only a few hundred meters separate them (David 2003). It also stated that high metal levels on the outermost 5 mm of coral samples is probably due to metals associated with tissue that remains in the organic rind of the corals. But this situation does not happen in this study. The outer layer of each coral did not state high metal content. The methods of rinsing the corals with de-ionizer distill water (DDH_2O) and weak acid (0.02M HNO_3) is useful to remove surface contamination.

Table 3. Trace elements concentration reported for *Porites* corals

Location	Zn (µg/g)	Mg (µg/g)	Sr (µg/g)	Ca (%)	Comments– Reference
Pulau Tioman	23.73	1402.60	7222.89	49.43	This study
Pulau Redang	39.96	1213.73	7127.71	51.25	This study
Pulau Langkawi	118.03	936.75	4478.38	25.75	This study
Hija River, Okinawa	34.3	-	-	-	(Ramos *et al.,* 2004)
Misima Island, Papua New Guinea	2.25-19.9	-	-	-	High sediment (Fallon *et al.,* 2002)
Vanezuela	3-42	-	-	-	High sediment (Bastidas & Garcia 1999)
Davies Reef, Great Barrier Reef	-	960	7463	38.32	(Sinclair *et al.,* 1998)
Red Sea	3.38	140	12000	54.2	Unpolluted (Hanna & Muir 1989)
Red Sea	9.28	417	16000	58.4	Polluted (Hanna & Muir 1989)
Thailand	1.4-3.7	-	-	-	(Brown, 1987)

(-) is not measured

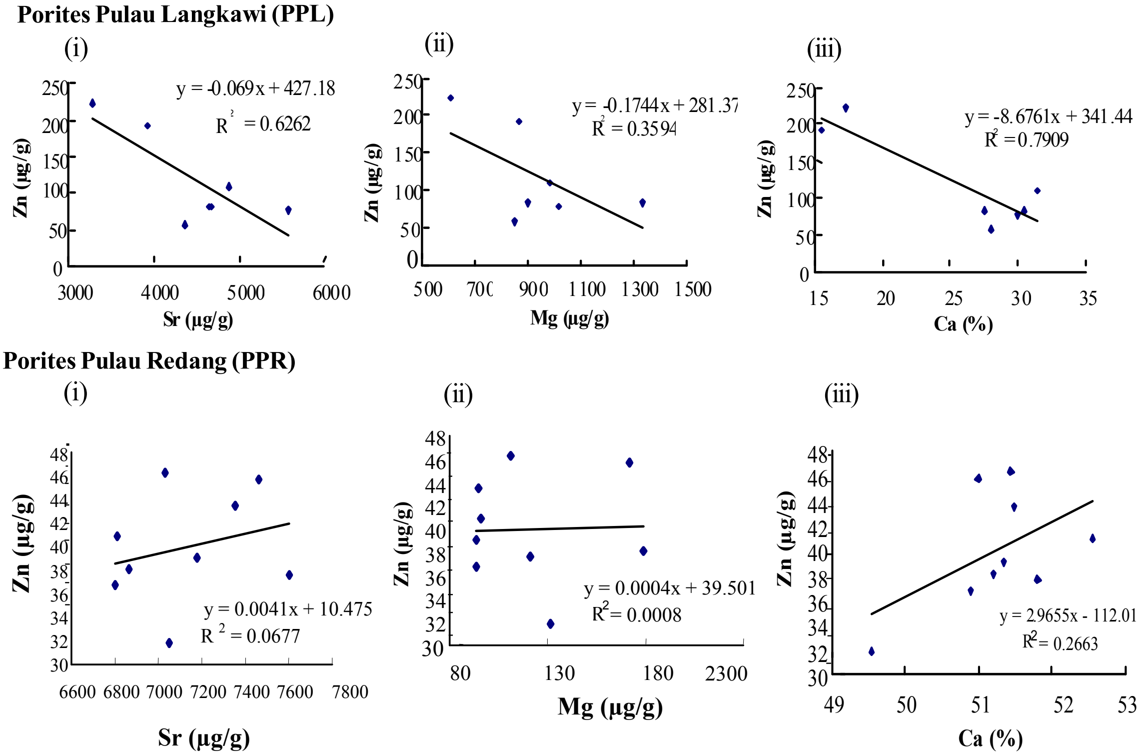

Fig. 4. Relationship between Zn with Sr, Mg and Ca at each sampling sites-Continues

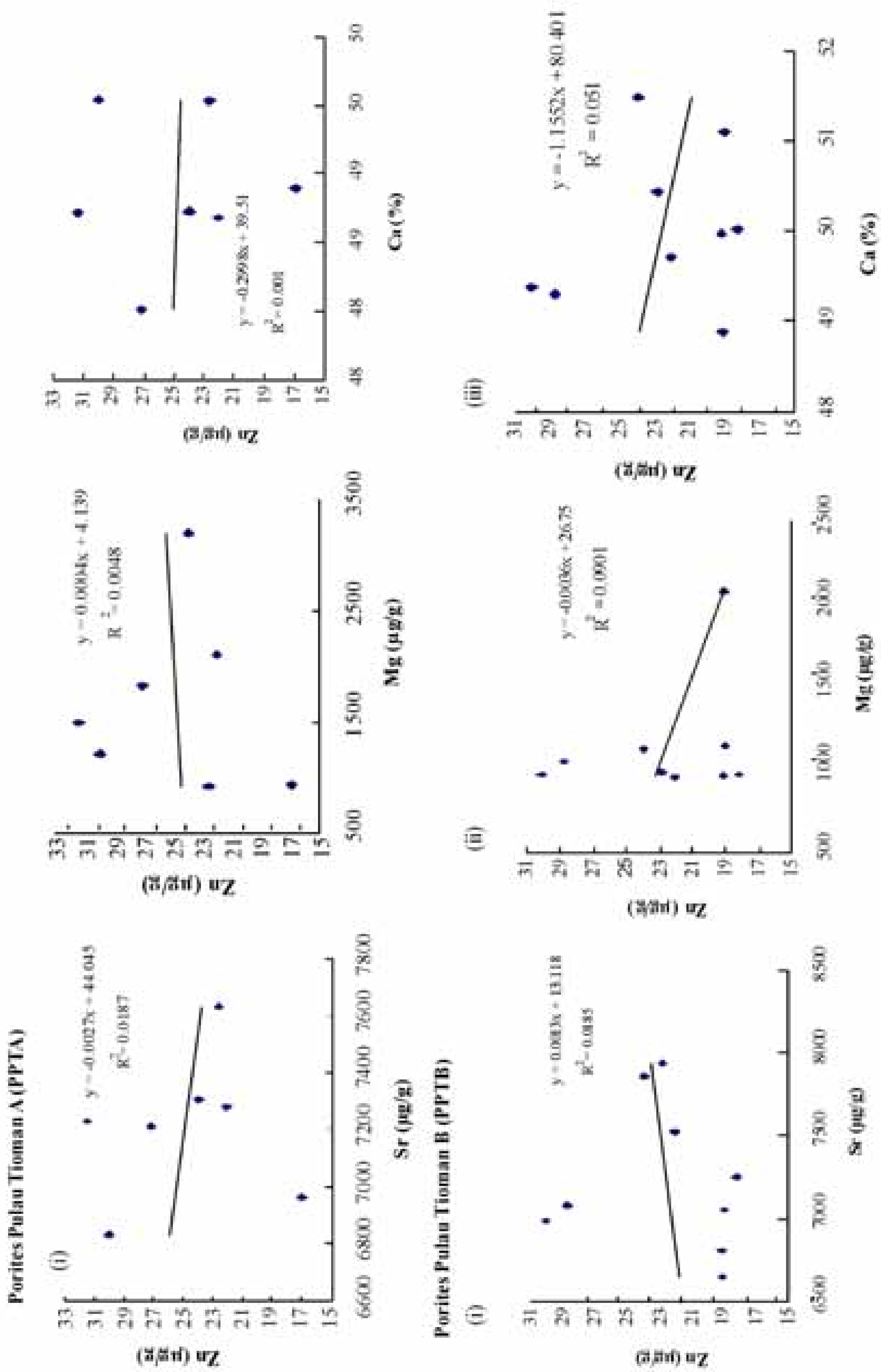

Fig. 4. Relationship between Zn with Sr, Mg and Ca at each sampling sites-Continues

CONCLUSION

Hard coral such as *Porites* sp widely found in Malaysia waters have growing rate ranged from 5 mm yr^{-1} to 25 mm yr^{-1}. The mean values of Ca, Mg, Sr and Zn were fluctuated from each annual skeleton band representing the yearly growth. *Porites* coral from Pulau Langkawi shows a high content of Zn representing the water surrounding the island was highly polluted and also shows the uptake of Sr and Ca in the coral skeleton was related to the content of Zn, where Sr and Ca contents decreases when the concentration of Zn was more than 50 µg/g. Study also found that the uptake of Sr and Ca as indicator for sea surface temperature proxy was not influences by the content of Zn. Finally, in the stress marine environment conditions, *Porities* species very useful as bio-pollution indicator for trace elements uptake and sediment loading as showed by Pulau Langkawi corals. Most of the sediment loading in the Malacca Straits was coming from the west coast Peninsular Malaysia and Sumatera Island.

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