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Seasonal Variation of Heavy Metals in Oysters from Darwin Harbor, Northern Territory, Australia

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Darwin Harbor (Fig. 1, Lat. 12°.25′ S, Long. 130° 52′ E) has an area of about 998 Km^2 with main channel depths up to 30 meters and calculated volume at sea level of $2.4X\ 10^9\ m^3$ (Anon 1976). The light industrial development around the harbor includes, a Shell Co. refinery, a cement plant, an acid store, ore loading facilities and the recently abandoned Stroke Hill Power Station. The anthropogenic input is mainly through macerated sewage for a population of about 70,000. Darwin Harbor is largely a well protected natural system relatively undisturbed by exploitation and low in heavy metal concentrations (Peerzada and Ryan 1987, Peerzada and Dickinson 1988 &1989) when compared with Corio Bay, Melbourne, Australia (Smith et al. 1981). The concentration of heavy metals in oysters is a function of water quality, seasonal variation, temperature, salinity, diet, spawning and individual variation (Phillips 1980; Förstner and Wittmann 1983). In an earlier study (Peerzada and Dickinson 1988) the concentration of heavy metals in oysters from Darwin Harbor was determined during the month of August and, in order to understand the seasonal profile of pollutants entering in Darwin Harbor, it was important to monitor heavy metal concentrations over a period of several months. In this study we report the seasonal variation in the concentrations of zinc, lead, cadmium, copper, and iron in oysters over a period of eight months from five different sites in Darwin Harbor. The site selection was based on our previous work (Peerzada and Dickinson 1988), with the exception of Darwin Wharf (Fig 1). Seasonal variation of heavy metals in marine organisms, especially bivalves, has been reported by many workers (Galtstoff 1964; Ireland 1974 ; Talbot 1986). Bryan (1973) found lower concentrations of zinc and manganese in the scallop *Chlamys opercularis* during the spring and summer months and higher concentrations in autum and winter and Phillips (1976) showed that the concentrations of zinc and cadmium in the mussel *Mytilus edulis* in Port Phillip Bay, Melbourne, Australia, were four times higher in winter than in summer . Recently, Talbot (1986) has found similar variations in the oyster *Saccostrea cuccullata* from the Dampier Archipelago, Western Australia. The highest concentrations of zinc and copper were found in the summer month of January and the lowest at the end of winter month of October .

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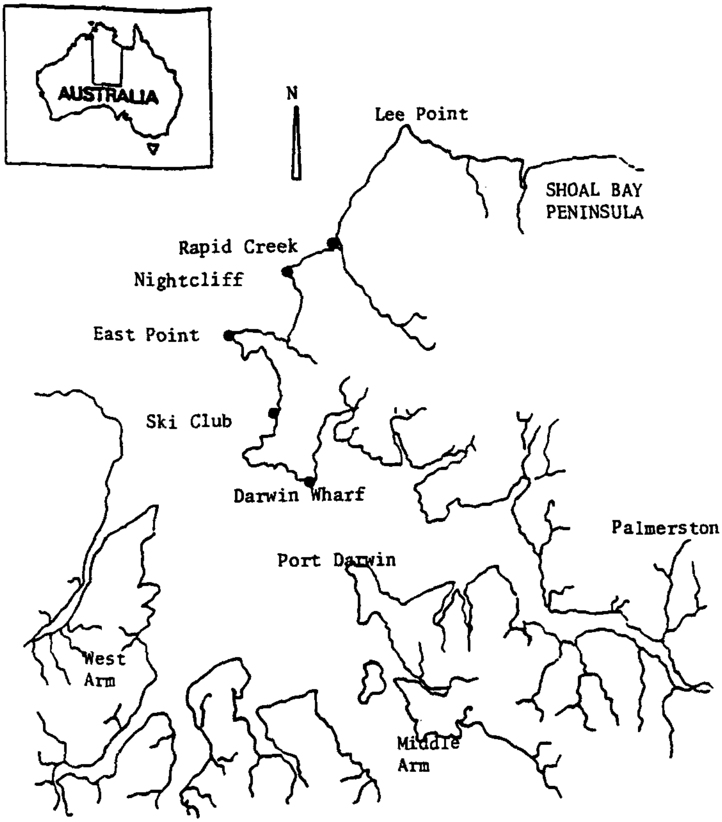

Figure 1. Oyster collection sites in Darwin Harbor

Darwin Harbor lies well within the tropics and is subjected to two weather systems. The dry season extends from April to October approximately, when southeast trade winds prevail, and the wet season extends from November to April, when the northwest monsoon prevails. During the latter period, cyclones can be experienced, particularly in the months of February and March. The annual rainfall measured at Darwin Airport was 1481 mm in 1989 and most of it (98%) fell during the wet season, December to April (Anon 1990).

Sea-surface temperatures of Darwin Harbor shows no great variation between wet and dry seasons. It is virtually constant during the wet season (about 28-29 ^{o}C) and only a few degrees lower during the dry season (25-28 ^{o}C) (Reynolds 1983). Salinity ranges from 27.8 to 35.5 ppt between the months of February and September.

MATERIALS AND METHODS

Absolute taxonomy of oysters from Darwin Harbor has not been established, therefore samples of oysters (*Saccostrea sp)* were collected monthly from March to October from five different locations in Darwin Harbor, (Fig 1). The oysters were placed in separate, labelled plastic bags and kept frozen at -10 ^{o}C until analyzed. As the oysters were small (3-4 cms in length; 2-3 cms in width), composite samples of 4-6 individuals were used for analysis. At least 20-30 specimen were collected from each location. When defrosted, the oysters were shucked, drained and weighed into digestion tubes, and 20 mL of concentrated nitric acid (Aristar) was added to each tube and digested at 60-80 ^{o}C for 2-3 hours. When the clear solution was cooled, the volume was made up to 50 mL in a volumetric flask with deionized water. Filtration of the digest was unnecessary. The samples were placed in acid-washed polyethylene screw-top sample bottles and analyzed within 24 hours by flame spectroscopy using a Varian AA 1475. The background absorption was found to be low and no correction was made. Detection limits in $\mu g\ g^{-1}$ were: cadmium-0.02, copper- 0.01, zinc-0.02, iron-0.02 and lead-0.1. The accuracy of the method used was established with Canadian dogfish liver reference material DOLT-1. Triplicate analyses gave the following results:

Sample DOLT-1	Zn	Cu	Cd	Fe
CertifiedValues $\mu g\ g^{-1}$	92.50	20.80	4.18	712.00
	±2.30	±1.20	±0.28	±48.0
Concn. found μg g-1	102.24	18.89	3.84	780.92
	±8.93	±3.05	±0.04	±11.23

RESULTS AND DISCUSSION

Measured levels in oysters for five metals determined at five locations; Rapid Creek, East Point, Darwin Wharf, Nightcliff and Ski-Club, on a monthly basis (March to October) from Darwin Harbor are presented in Figs. 2-4. Concentrations of zinc were highest (804-1139 $\mu g\ g^{-1}$) in the oysters from Darwin Wharf (Fig. 2). Industrial activities at Darwin Wharf include a small cement plant, a small oil refinery, an acid store, ore loading and holding facilities for a mine (zinc, lead and silver ore) and shipping activities. A monthly zinc concentration profile for Darwin Wharf showed a downward trend during most of the dry season gradually increasing in the months of September and October due to early rain. The concentration of zinc remained elevated during the wet season months of March and April . The lowest level of zinc (804 $\mu g\ g^{-1}$) was found during the months of July and August when the surface water temperature of Darwin Harbor dropped to 24.5 ^{o}C as compared to the wet season constant temperature of 28.9 ^{o}C . The highest level of zinc (1139 $\mu g\ g^{-1}$) was present in the month of April. The reproductive cycle of the organism is an important parameter when studying seasonal variations of tissue trace-metal concentrations. The levels tend to increase during the spawning period when the water temperature is high and decrease during the period of gametogenesis when the temperature is lower (Talbot 1986). The body weight of the organism is also known to be related to the incidence of spawning (decreases) and gametogenesis (increases) (Boyden 1974). No relationship was found between the body weight of the organism and zinc concentration at Darwin Harbor. Intermittent spawning of oysters in the tropical environment has been described by Phillips (1980), therefore an average body weight could be expected throughout the year that shows no relationship to the level of trace metals. Higher concentrations of zinc during the wet season could be attributed to the freshwater runoff from the land. Hart et al.(1987) found that elevated levels of copper, zinc and lead entered the water catchment of Northern Territory during the wet season and decreased during the dry season. Higher concentrations of zinc at Darwin Wharf, as compared to other locations, reflect the very contaminated nature of this site.

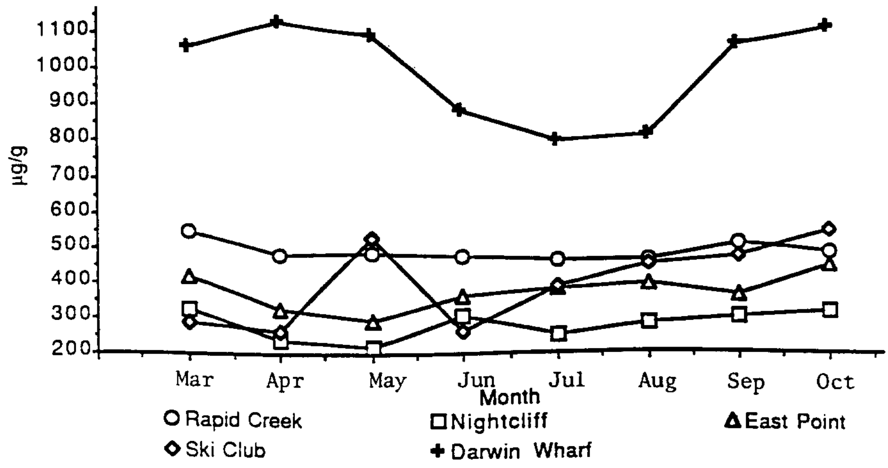

Figure 2. Fluctuation of Zn at five sites of Darwin Harbor

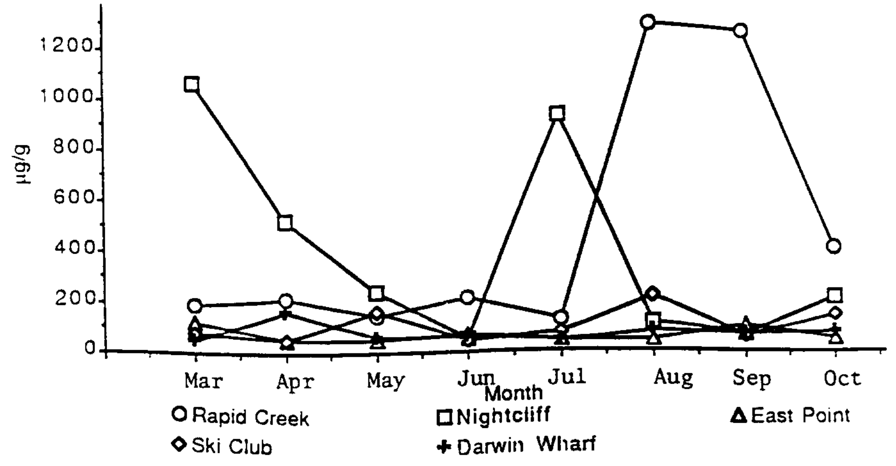

Figure 3. Fluctuation of Fe at five sites of Darwin Harbor

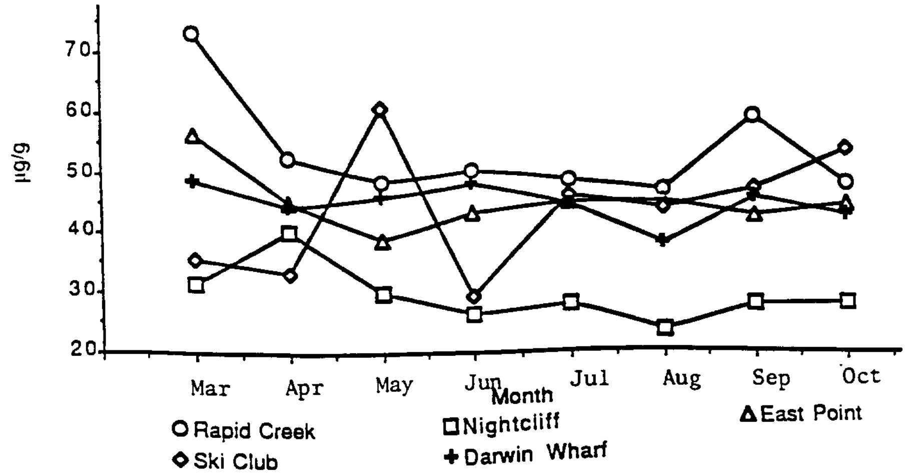

Figure 4. Fluctuation of Cu at five sites of Darwin Harbor

There was a sharp increase in zinc concentration in the month of May, a drop in June and then a gradual increase till October at Ski-Club. All boats at Ski-Club are taken out of the water during the wet season (December to April) because of the possibility of a cyclone and go back in the water during the month of May therefore showing a sharp increase of zinc concentration in the month of May followed by a gradual increase from June to October. Most of the other sites showed little fluctuation in the levels of zinc in oyster, during the period of monitoring (March-October) (Fig 2).

Lead was found only at Darwin Wharf. Its concentration was unusually high and the maxima and minima during the wet/dry season exhibited a difference of three fold; the difference for zinc was half the amount . The highest concentration of lead was found in the month of April (83.30± 16.30 $\mu g\ g^{-1}$), as was the case for zinc, and the lowest level (17.30± 6.60 $\mu g\ g^{-1}$) followed a similar pattern. No lead was detected at other sites. Darwin Wharf also had a higher concentration of cadmium (0.86-1.32 $\mu g\ g^{-1}$) when compared to the other sites. The concentration of iron did not change significantly over eight months at East Point, Ski-Club and Darwin Wharf (Fig. 3) while Nightcliff and Rapid Creek showed a large increase in the month of July and August indicating some contamination of these locations. A correlation was also found for iron concentration with body weight of the organism at Nightcliff. As the iron concentration decreased during the months of June, August-October (dry season) the body weight of the organism increased. A similar relationship was observed for the higher concentration of iron to lower body weight during the wet season. No body weight to concentration relationship was found for other sites.

Copper concentration did not vary much during this study at most sites (Fig. 4). A slightly higher level of copper occured during the wet season followed by an almost constant lower reading for rest of the period. Only Ski-club, Fig. 4) showed a sharp increase in the level of copper concentration for May, a drop in June followed by a gradual increase till October. A similar pattern in change of concentrations for zinc was found at this location indicating an increase in the number of moored boats. Bately et al. (1990) recently found a similar elevation in concentration of copper, zinc and tributyltin from the use of marine antifouling paints and discussed its impact on oysters of NSW, Australia.

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