DISTRIBUTION OF SOME HEAVY METALS IN SELECTED COMPONENTS OF A CORAL REEF ECOSYSTEM AT CAPE RACHADO, MALAYSIA

by

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ABSTRACT

The coral reef ecosystem at Cape Rachado, is the only remaining fringing coral reef along the west coast of Peninsular Malaysia. The reef represents an interesting ecosystem with diverse flora and fauna and possesses a critical geographical location at the Straits of Malacca. The reef ecosystem especially the associated seaweed flora, was shown to be sensitive to development when increased silt levels led to loss of sensitive species of seaweeds. As yet, no study of heavy metal distribution and bioaccumulation in the coral reef area has been done. This study was aimed to investigate the distribution and bioaccumulation of iron, copper, zinc and lead in seawater, sediment, seaweeds (*Sargassum baccularia*, *Padina tetrastomatica* and *Turbinaria conoides*), soft coral (*Sinularia* sp.) and sea cucumber (*Holothuria atra*). The effect of environmental parameters on metal bioaccumulation in the different trophic and taxonomic levels was investigated.

Seawater, sediment, three brown seaweed species (*Sargassum baccularia*, *Padina tetrastomatica* and *Turbinaria conoides*), soft coral (*Sinularia* sp.) and sea cucumber *Holothuria atra* were collected from the intertidal area at selected sites (B&C) of the Cape Rachado coral reef ecosystem over a period of 14 months.

Metals (dissolved) in seawater were preconcentrated using Chelex 100 resin at pH of 5.10 ±0.01 prior the instrumental analysis. Surface sediments (>2 mm size) were used for total metal concentration measurement. The dissolution of sediment samples was achieved with a mixture of nitric, perchloric and hydrofluoric acids in covered Teflon vessels. Reflux digestion technique was applied to achieve the complete

digestion of biological samples using a mixture of nitric acid and hydrogen peroxide. The concentration of iron, copper, zinc and lead in the various components of the Cape Rachado coral reef ecosystem were measured using the ICP-AES. No significant difference was observed in most of the environmental parameters and metal concentrations between the two study Sites B and C. Metal concentrations in various components of Cape Rachado showed temporal changes over the study period as a response to the short-term environmental changes over time.

The concentration of iron in seawater over the study period was 0.0128 ± 0.0036 µg ml^{-1} for Site B and 0.0176 ± 0.0144 µg ml^{-1} for Site C. Copper concentration in seawater over the study period was 0.0010 ± 0.0003 µg ml^{-1} for Site B and 0.0010 ± 0.0005 µgml^{-1} for Site C. Zinc concentration in seawater was 0.0098 ± 0.0059 µg ml^{-1} for Site B and 0.0104 ± 0.0049 µg ml^{-1} for Site C. Lead concentration in seawater was 0.0048 ± 0.0025 µ g ml^{-1} for Site B and 0.0047 ± 0.0023 µg ml^{-1} for Site C.

The concentration of iron in sediment was 4560.0286 ± 1799.7433 µg g^{-1}dry wt for Site B and 2137.9571 ± 401.0338 µg g^{-1}dry wt for Site C. Copper concentration in sediment was 1.3991 ± 0.6611 µg g^{-1}dry wt for Site B and 0.2451 ± 0.0881 µg g^{-1}dry wt for Site C. Zinc concentration in sediment was 11.7215 ± 6.621 µg g^{-1}dry wt for Site B and 4.2484 ± 4.3578 µg g^{-1}dry wt for Site C. Lead concentrations in sediment were 4.8321 ± 1.9908 µg g^{-1}dry wt and 1.3347 ± 0.9287 µg g^{-1}dry wt, for Sites B and C respectively.

The concentration of iron in *Sargassum baccularia* was 214.0714 ± 68.7573 µg g^{-1} dry wt for Site B and 207.2571 ± 84.3032 µg g^{-1}dry wt for Site C. Copper concentration in *S. baccularia* was 2.3228 ± 0.3845 µg g^{-1}dry wt for Site B and $2.4388 \pm$

0.4363 μg g^{-1}dry wt for Site C. Zinc concentration in *S. baccularia* was 31.3530 ± 10.3130 μg g^{-1}dry wt for Site B and 34.9917 ± 17.4516 μg g^{-1}dry wt for Site C. Lead concentration in *S. baccularia* was 12.2906 ± 5.1182 μg g^{-1}dry wt for Site B and 13.48831 ± 4.9554 μg g^{-1}dry wt for Site C.

The iron concentration in *Padina tetrastomatica* was 1241.0000 ± 609.7023 μg g^{-1}dry wt for Site B and 1452.9286 ± 549.6211 μg g^{-1}dry wt for Site C. Copper concentration in *P. tetrastomatica* was 4.2794 ± 0.6184 μg g^{-1}dry wt for Site B and 4.6688 ± 0.3381 μg g^{-1}dry wt for Site C. Zinc concentration in *P. tetrastomatica* was 51.5467 ± 14.0208 μg g^{-1}dry wt for Site B and 48.1943 ± 24.1921 μg g^{-1}dry wt for Site C. Lead concentration in *P. tetrastomatica* was 20.4077 ± 7.9308 μg g^{-1}dry wt for Site B and 20.4003 ± 4.8775 μg g^{-1}dry wt for Site C.

The concentration of iron in *Turbinaria conoides* was 78.5914 ± 30.7812 μg g^{-1}dry wt for Site B and 80.1329 ± 45.2190 μg g^{-1}dry wt for Site C. Copper concentration in *T. conoides* was 1.7714 ± 0.8155 μg g^{-1}dry wt for Site B and 1.7310 ± 0.3146 μg g^{-1}dry wt for Site C. Zinc concentration in *T. conoides* was 17.4129 ± 5.1629 μg g^{-1}dry wt for Site B and 19.1961 ± 11.6552 μg g^{-1}dry wt for Site C. Lead concentration in *T. conoides* was 11.4236 ± 4.4433 μg g^{-1}dry wt for Site B and 11.4631 ± 5.4325 μg g^{-1}dry wt for Site C.

The concentration of iron in *Sinularia* sp.was 22.2886 ± 6.2627 μg g^{-1}dry wt for Site B and 28.5857 ± 11.1942 μg g^{-1}dry wt for Site C. Copper concentration in *Sinularia* sp. was 7.7979 ± 0.5686 μg g^{-1}dry wt for Site B and 8.1750 ± 0.8876 μg g^{-1}dry wt for Site C. Zinc concentration in *Sinularia* sp. was 23.3129 ± 3.9785 μg g^{-1}dry wt for

Site B and 25.8257 ± 9.1998 for Site C. Lead concentration in *Sinularia* sp. was 25.4300 ± 1.0982 μg g^{-1}dry wt for Site B and 25.6629 ± 3.7704 μg g^{-1}dry wt for Site C.

The concentration of iron in *Holothuria atra* was 28.5433 ± 7.4755 μg g^{-1}dry wt for Site C. Copper concentration in *H. atra* was 2.7702 ± 0.8099 μg g^{-1}dry wt for Site C. Zinc concentration in *H. atra* was 37.2385 ± 29.0852 μg g^{-1}dry wt for Site C. Lead concentration in *H. atra* was 21.4335 ± 11.7456 μg g^{-1}dry wt for Site C.

Metal concentrations in seawater and sediment were within the range of metal concentrations in areas with no history of metal contamination, suggesting that Cape Rachado is a relatively unpolluted area as far as Fe, Cu, Zn and Pb are concerned.

All the four metals studied were ranked similarly in their distribution within the three seaweed species and proportional to seaweed thallus surface area as follows: *P. tetrastomatica* > *S. baccularia* > *T. conoides*, indicating the role of seaweed surface area in metal accumulation.

Bioconcentration factors for iron for all components ranged from 1622 to 89752. Bioconcentration factors for copper for all components ranged from 1751 to 7987. Bioconcentration factors for zinc for all components ranged from 1810 to 4947. Bioconcentration factors for lead for all components ranged from 2409 to 4560.

Bioconcentration factors of the four metals in the three seaweed species were ranked similarly to the metal concentration ranks in the seaweed species and metal concentration ranking in seawater and sediment (Fe > Zn >Pb > Cu). The higher the ambient metal concentration the higher is the metal accumulation and bioconcentration factor in seaweeds. The bioconcentration factors obtained here are low reflecting the low ambient metal concentrations of the study area rather than the metal-species accumulation ability.

For soft coral and sea cucumber, different ranking for the bioconcentration factors of the metals was obtained, with Cu > Pb > Zn > Fe in soft coral and Pb > Zn > Cu > Fe for sea cucumber. This suggests the presence of certain regulation processes in metal accumulation. Soft coral showed a particular affinity for Cu while sea cucumber showed higher affinity for Pb.

Metal bioaccumulation was shown to be more affected by the past ambient environmental parameters including metal concentration rather than the concurrent or present parameters. The effect of environmental parameters on metal bioaccumulation is biotic species-metal specific. Synergistic interaction with the binding sites and the increase in metal binding affinity were also observed.

Heavy metal contamination can be indicated by metal content in seaweeds. Seaweeds indicate concurrent and time-integrated responses (bioaccumulation) of metal concentration in the environment. The findings suggest the potential of using the two seaweed species: *Sargassum baccularia* and *Padina tetrastomatica* as biomonitors for the heavy metals concerned.

ABSTRAK

Ekosistem terumbu karang di Cape Rachado merupakan terumbu karang 'fringing' yang terakhir wujud di pantai barat Semenanjung Malaysia. Terumbu ini mewakili suatu ekosistem yang menarik dengan pelbagai flora dan fauna, dan mempunyai lokasi geografi yang kritikal di Selat Melaka.

Ekosistem terumbu ini, terutama flora rumpai laut yang berkaitan, didapati sensitif kepada pembangunan di mana paras enapan menyebabkan kehilangan spesis rumpai laut yang sensitif. Sehingga kini, belum ada kajian logam berat di kawasan ini. Kajian ini bertujuan menyiasat distribusi dan bioakumulasi ferum, kuprum, zink dan plumbum di dalam air laut, sedimen, rumpai laut (*Sargassum baccularia, Padina tetrastomatica*), karang laut (*Simularia* sp.) dan gamat (*Holothuria atra*). Kesan parameter alam sekitar ke atas bioakumulasi logam pada paras trofik dan taksonomik yang berlainan telah disiasat.

Air laut, sedimen dan tiga spesis rumpai laut perang (*Sargassum baccularia*), karang lembut dan gamat (*Holothuria atra*) dikumpul daripada kawasan 'intertidal' di tapak (B&C) di ekosistem terumbu karang Cape Rachado sepanjang tempoh 14 bulan.

Logam-logam (terlarut) dalam air laut dipekatkan terlebih dahulu menggunakan resin Chelex 100 pada pH 5.10 ± 0.01 sebelum analisa instrumental. Sedimen-sedimen permukaan (saiz > 2 mm) digunakan bagi ukuran kepekatan logam total/keseluruhan. Disolusi sampel-sampel sedimen dicapai dengan campuran asid-asid nitrik, perklorik dan hidrofluorik dalam vesel-vesel Teflon bertutup. Teknik-teknik penghadaman refluks digunakan untuk mencapai penghadaman lengkap sampel-sampel biologi

menggunakan suatu campuran asid nitrik dan hidrogen peroksida. Kepekatan ferum, kuprum, zink dan plumbum dalam komponen-komponen berbeza di ekosistem terumbu karang Cape Rachado diukur menggunakan ICP-AES. Tiada perbezaan signifikan diperhatikan dalam kebanyakan parameter-parameter alam sekitar dan kepekatan-kepekatan logam berat antara kedua-dua site B dan C. Kepekatan logam dalam pelbagai komponen di Cape Rachado menunjukkan perubahan temporal sepanjang tempoh kajian sebagai respon kepada perubahan-perubahan alam sekitar jangka pendek dengan masa.

Kepekatan ferum di dalam air laut sepanjang kajian dijalankan adalah 0.0128 ±0.0036 μg ml^{-1} pada Tapak B dan 0.0176 ±0.0144 μg ml^{-1} pada Tapak C. Kepekatan kuprum di dalam air laut sepanjang kajian dijalankan adalah 0.0010 ±0.0003 μg ml^{-1} untuk Tapak B dan 0.0010 ±0.0005 μg ml^{-1} pada Tapak C. Kepekatan zink pula adalah 0.0098 ±0.0059 μg ml^{-1} pada tapak B dan 0.0140 ±0.0049 μg ml^{-1} pada Tapak C. Manakala kepekatan plumbum pula adalah 0.0048+0.0025 μg ml^{-1} pada Tapak B dan 0.0047 ±0.0023 μg ml^{-1} pada Tapak C.

Kepekatan ferum dalam sedimen adalah 4560.0286 ±1799.7433 μg g^{-1} berat kering pada Tapak B dan 2137.9571 ±401.0338 μg g^{-1} berat kering pada Tapak C. Kepekatan kuprum dalam sedimen adalah 1.3991 ±0.6611 μg g^{-1} berat kering pada Tapak B dan 0.2451 ±0.0881 μg g^{-1} berat kering pada Tapak C. Kepekatan zink dalam sedimen pula adalah 11.7215 ±6.621 μg g^{-1} berat kering pada Tapak B dan 4.2484 ±4.3578 μg g^{-1} berat kering pada Tapak C. Kepekatan plumbum dalam sedimen pula adalah 4.8321 ±1.9908 μg g^{-1} berat kering dan 1.3347 ±0.9287 μg g^{-1} berat kering pada Tapak B dan Tapak C, masing-masing.

Kepekatan ferum di dalam *Sargassum baccularia* adalah 214.0714 ±68.7573 μg g^{-1} berat kering pada Tapak B dan 207.2571 ±84.3032 μg g^{-1} berat kering pada Tapak C. Kepekatan kuprum di dalam *S. baccularia* adalah 2.3228 ±0.3845 μg g^{-1} berat kering pada Tapak B dan 2.4388 ±0.4363 μg g^{-1} berat kering pada Tapak C. Kepekatan zink dalam *S. baccularia* adalah 31.3530 ±10.3130 μg g^{-1} berat kering pada Tapak B dan 34.9917 ±17.4516 μg g^{-1} berat kering pada Tapak C. Kepekatan plumbum dalam *S. baccularia* adalah 12.12906 ±5.1182 μg g^{-1} berat kering pada Tapak B dan 13.48831 +4.9554 μg g^{-1} berat kering pada Tapak C.

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Kepekatan ferum di dalam *Turbinaria conoides* adalah 78.5914 ±30.7812 μg g^{-1} berat kering pada Tapak B dan 80.1329 ±45.2190 μg g^{-1} berat kering pada Tapak C. Kepekatan kuprum di dalam *T. conoides* adalah 1.7714 ±0.8155 μg g^{-1} berat kering pada Tapak B dan 1.7310 ±0.3146 μg g^{-1} berat kering pada Tapak C. Kepekatan zink dalam *T. conoides* adalah 17.4129 ±5.1629 μg g^{-1} berat kering pada Tapak B dan

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Kepekatan ferum di dalam *Sinularia* sp. adalah 22.2886 ±6.2627 μg g^{-1} berat kering pada Tapak B dan 28.5857 ±11.1942 μg g^{-1} berat kering pada Tapak C. Kepekatan kuprum di dalam *Sinularia* sp. adalah 7.7979 ±0.5686 μg g^{-1} berat kering pada Tapak B dan 8.1750 ±0.8876 μg g^{-1} berat kering pada Tapak C. Kepekatan zink dalam *Sinularia* sp. adalah 23.3129 ±3.9785 μg g^{-1} berat kering pada Tapak B dan 25.8257 ±9.1998 μg g^{-1} berat kering pada Tapak C. Kepekatan plumbum dalam *Sinularia* sp. adalah 25.4300 ±1.0982 μg g^{-1} berat kering pada Tapak B dan 25.6629 ±3.7704 μg g^{-1} berat kering pada Tapak C.

Kepekatan ferum di dalam *Holothuria atra* adalah 28.5433 ±7.4755 μg g^{-1} berat kering pada Tapak C. Kepekatan kuprum di dalam *H. atra* adalah 2.7702 ±0.8099 μg g^{-1} berat kering pada Tapak C. Kepekatan zink di dalam *H. atra* adalah 37.2385 ±29.0852 μg g^{-1} berat kering pada Tapak C. Kepekatan plumbum di dalam *H. atra* adalah 21.4335 ±11.7456 μg g^{-1} berat kering pada Tapak C.

Kepekatan logam dalam air laut dan sedimen berada dalam renj kepekatan logam di kawasan-kawasan yang tiada sejarah kontaminasi logam. Ini mencadangkan bahawa Cape Rachado adalah secara relatifnya kawasan yang tidak tercemar dengan Fe, Cu, Zn dan Pb.

Kesemua empat logam yang dikaji dijujukkan serupa dalam distribusi mereka dalam ketiga-tiga spesis rumpai laut dan berkadar kepada luas permukaan talus seperti berikut: *P. tetrastomatica* > *S. baccularia.* > *T. conoides*, menunjukkan peranan luas permukaan rumpai laut dalam akumulasi logam.

Julat-julat faktor biokonsentrasi bagi ferum untuk semua komponen adalah dari 1622 hingga 89752. Julat-julat faktor biokonsentrasi bagi kuprum untuk semua komponen adalah dari 11751 hingga 7987. Julat-julat faktor biokonsentrasi bagi zink untuk semua komponen adalah dari 1810 hingga 4947. Julat-julat faktor biokonsentrasi bagi plumbum untuk semua komponen adalah dari 2409 hingga 45602.

Faktor-faktor biokonsentrasi keempat-empat logam dalam ketiga-tiga spesis rumpai laut dijujukkan serupa kepada jujukan kepekatan logam dalam spesis rumpai laut dan jujukan kepekatan logam dalam air laut dan sedimen (Fe > Zn > Pb > Cu). Semakin tinggi kepekatan logam ambien, semakin tinggi akumulasi logam dan faktor biokonsentrasi dalam rumpai laut. Faktor-faktor biokonsentrasi didapati di sini adalah rendah, lebih membayangkan kepekatan logam ambien yang rendah kawasan kajian daripada kebolehan akumulasi logam spesis.

Bagi karang lembut dan gamat jujukan yang berbeza bagi faktor biokonsentrasi logam-logam didapati, dengan Cu > Pb > Zn > Fe bagi karang lembut dan Pb > Zn > Cu > Fe bagi gamat. Ini mencadangkan kewujudan suatu proses regulasi dalam akumulasi logam. Karang lembut menunjukkan afiniti bagi Cu manakala gamat menunjukkan afiniti yang lebih tinggi bagi Pb.

Bioakumulasi logam didapati lebih dipengaruhi oleh parameter alam sekitar ambient yang lepas, termasuk kepekatan logam daripada parameter selari dan masakini. Kesan parameter alam sekitar ke atas bioakumulasi logam adalah spesifik spesis biotik-logam. Interaksi sinergistik dengan tapak-tapak pengikatan dan pertambahan dalam afiniti pengikatan logam juga diperhatikan.

Pencemaran logam berat boleh ditunjukkan oleh kandungan logam dalam rumpai laut. Rumpai laut menunjukkan respon-respon konkuren dan berintegrasikan masa (bioakumulasi) kepekatan logam dalam alam sekitar. Penemuan ini mencadangkan potensi menggunakan dua spesis rumpai laut: *Sargassum baccularia* dan *padina tetrastomatica* sebagai biomonitor bagi logam-logam berat berkenaan.

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