

Status of Heavy Metals in Surface Sediments of the Western Part of the Johor Straits Using a Sediment Quality Guideline

¹Syaizwan Zahmir Zulkifli, ^{2,3}Ferdaus Mohamat-Yusuff, ¹Ahmad Ismail,
¹Azizul Aziz, ⁴Asnor Azrin Sabuti and ⁵Che Abd Rahim Mohamed

¹Department of Biology, Faculty of Science,

Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

²Department of Environmental Sciences, Faculty of Environmental Studies,

Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

³Environmental Forensics Research Centre, Faculty of Environmental Studies,

Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

⁴Department of Marine Science, Kulliyah of Science, International Islamic University Malaysia (IIUM),

Jalan Sultan Ahmad Shah, Bandar Indera Mahkota, 25200 Kuantan, Pahang, Malaysia

⁵School of Environmental and Natural Resources Sciences, Faculty of Sciences and Technology,

Universiti Kebangsaan Malaysia, 43650 Bangi, Selangor, Malaysia

Abstract: Cu, Zn, Ni and Pb concentrations in surface sediments collected from 10 stations in the western part of the Johor Straits were determined. Samples were acid digested and metal concentrations were determined by atomic absorption spectrometry (AAS). The obtained results showed that Zn had the highest concentration ($111.7 \pm 78.8 \mu\text{g/g}$) among the selected metals, followed by Pb ($28.4 \pm 30.0 \mu\text{g/g}$), Cu ($21.8 \pm 15.8 \mu\text{g/g}$) and Ni ($16.4 \pm 15.6 \mu\text{g/g}$). Sediments collected in stations near the Johor Causeway had higher metal concentrations than those from other stations. A station near the Johor Causeway had significantly higher metal concentrations than other stations. Metal concentrations also exceeded the limit set by a sediment quality guideline. This could be due to semi-static water flow and an anoxic environment in the area. A comparison with previous studies also revealed continuous increases in metal concentrations in sediments of the western part of the Johor Straits.

Key words: Heavy Metals • Sediments • Sediment Quality Guideline • Johor Straits

INTRODUCTION

Heavy metal contamination in aquatic ecosystems is one of the most challenging pollution issues due to the toxicity, abundance, persistence and subsequent bioaccumulation of heavy metals [1]. Hence, there is an increasing concern about the input of heavy metals and their effects on human and ecosystem health, which also has led to increased monitoring of metal concentrations and studies of the fates of heavy metals in the environment [2, 3].

Sediments are a critical sink for numerous anthropogenic chemical contaminants [4]. These chemicals can originate from point- or non-point sources, such as agriculture, industries, urban areas, transportation, recreation and other activities [5-7].

Scientists have recommended the use of sediment as a tool to assess the impact of human activities on the aquatic environment [8].

The Johor Straits is as an important site for comprehensive, integrated studies on chemical pollution, particularly heavy metals, due to its strategic location, ecological importance, potential for development in the future and its past history of heavy metal contamination [9]. It is a narrow, shallow waterway that is less than 6 km across and less than 25 m deep [10]. The seawater temperature ranges from 28–30°C and water salinities due to runoff resulting from abundant rainfall range from 15-20‰. The Johor Strait has abundant with fish and shellfish resources that are important for the diets and economies of the people of Malaysia and Singapore. With more than three million people living along the coastal area of the

Straits of Johor, as well as rapid development in the area, continuous monitoring should be conducted to further understand the current status and chemical behaviours of heavy metals in the area. Present study aimed to determine Cu, Zn, Ni and Pb concentrations in surface sediments collected from stations in the western part of the Johor Straits and use the Interim Sediment Quality Guideline (ISQG) to estimate the possibility that there are toxic effects of these metals on sediment-dwelling organisms.

MATERIALS AND METHODS

Surface Sediments Were Collected in October 2013 from Ten: locations in the western part of the Johor Straits (Fig. 1) using a 9×9×9 inch Ekman grab sampler. The top 3 to 5 cm of the surface sediments were collected in triplicate at the respective sampling sites. Each sediment sample was placed in an acid-washed polyethylene bag and kept frozen (-20°C) prior to further analysis. Analytical procedures used in the present study were as follows. The reagents used were all of analytical grade and certified for high purity. Samples were dried in an oven at 60°C for at least one day until a constant dry weight was obtained. Afterwards, the samples were agitated with a ceramic mortar and pestle. The fine fraction was obtained after sieving through a 63 μ m mesh sieve and it was shaken vigorously to ensure homogeneity. All sieved samples were kept in sealed, acid-washed polyethylene containers prior to chemical analysis.

To determine heavy metal contents in the sediments, the direct aqua regia method was applied in this study, as previously described [11,12]. In brief, about 1 g of dried sediment sample was weighed and placed in a digestion tube. Afterwards, a combination of concentrated nitric acid (BDH Aristar Grade (69%), VWR, Singapore) and concentrated perchloric acid (BDH Aristar Grade (60%), VWR) in a 4:1 ratio was added to each digestion tube filled with sediments. Next, each digestion tube was placed vertically in a digestion block for 1 h at 40°C and the temperature was increased to 140°C for 3 h. After 3 h of digestion, the samples were left to cool at room temperature and then diluted to 40 ml with double-distilled water (DDW). The diluted sample was filtered through Whatman No. 1 filter paper (size: medium) and the filtrate was stored in a cool room until metal determinations. An air-acetylene flame atomic absorption spectrophotometer (Model 800, PerkinElmer, Waltham, MA, USA) was used for Cu, Zn, Ni and Pb determinations. Atomic absorption spectroscopy (AAS) data are presented as μ g/g dry weight (DW). Standard solutions were prepared from a 1,000 mg/l stock solution of each metal (Titrisol, Merck, White House Station, NJ, USA). For quality control, all glassware and equipment used were acid-washed to avoid any possible contamination. The quality of the analytical procedures was checked with a Certified Reference Material (CRM) for Soil (PACS-2). The recovery of heavy metals in the CRM was within $\pm 10\%$ of the certified mean values. Data were analysed statistically using SPSS software (Chicago, IL, USA). Data was also compared

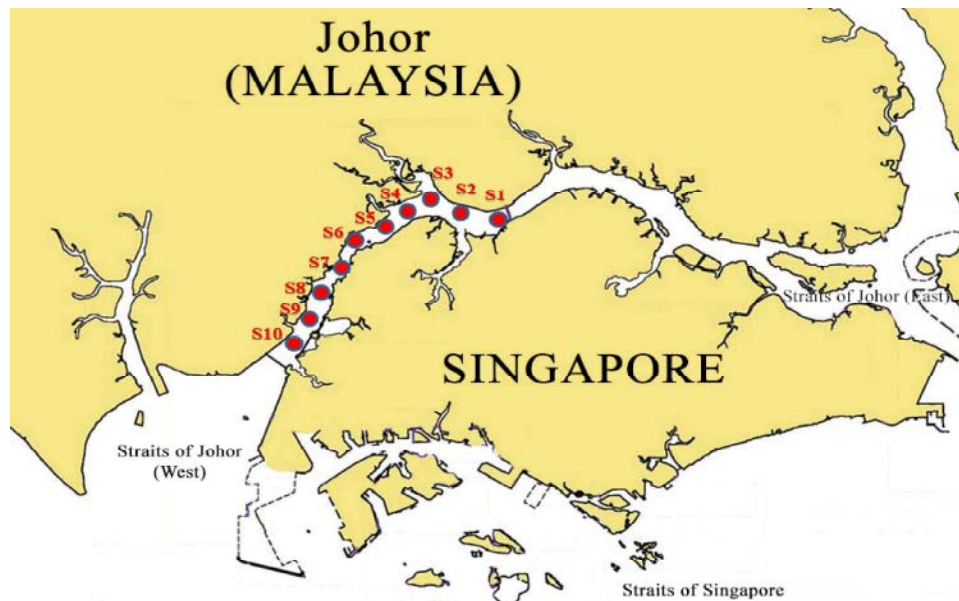


Fig. 1: Sampling stations (S1 until S10) along western part of the Straits of Johor.

with the Interim Sediment Quality Guideline (ISQG) for quick screening purposes. According to [13], ISQG-low is a threshold concentration by which below this concentration the frequency of adverse biological effects is expected to be very low. ISQG-high is intended to represent a concentration above which, adverse biological effects are expected to occur more frequently.

RESULTS AND DISCUSSION

In the present study, four heavy metals were measured in surface sediments, namely Cu, Zn, Ni and Pb. Among these metals, Zn ($111.7 \pm 78.8 \mu\text{g/g}$) had the highest concentration in sediments of the Johor Straits, followed by Pb ($28.4 \pm 30.0 \mu\text{g/g}$), Cu ($21.8 \pm 15.8 \mu\text{g/g}$) and Ni ($16.4 \pm 15.6 \mu\text{g/g}$). Concentration ranges of these metals are listed in Table 1. The metal concentrations reported in this study are within metal concentration ranges that have been reported around Peninsular Malaysia in previous studies. However, the metal concentrations in the Johor Straits were higher than those reported in previous studies [9, 10].

Metal concentrations at the 10 sampling stations (S1 until S10) showed a decreasing trend, with higher metal concentrations at S1 and lower concentrations towards S10. Stations close to the Johor Causeway (stations S1, S2 and S3) had the highest metal concentrations and station S1 had the highest levels of all the heavy metals. This could be due to influx from Sungai Skudai and other developed areas of Johor Bahru city [14]. Sediments at S1 had several distinct features: they were black; they had a strong aroma due to the presence H_2S ; they were very porous; and they had a high percentage of water from the

surface to the bottom of the cores [10]. Semi-static water in areas near the Johor Causeway could increase the deposition of metals in sediments and prevent them from being transported to other areas. A similar phenomenon was observed in a previous study [15]. Additionally, the concentrations of heavy metals in sediments from S1 were significantly different from those in sediments from other sampling locations ($p < 0.05$). The anoxic features found in the surface sediments of stations S1, S2 and S3 along the Johor causeway generally suggest that severe contamination is occurring in the area [10]. Other stations farther from the causeway (S4 to S10) may be more impacted by seawater currents from the Strait of Malacca, especially during tidal events. Furthermore, the sediments at these stations may have more porous material, as previously proposed [10]. These stations are located close to Sungai Melayu and Sungai Pendas, which are relatively less developed areas [14]. Based on a previous study [9], locations in the western Johor Strait can be considered as having little to no enrichment of anthropogenic metals inputs. The western side of the Johor Straits is less polluted than the eastern side [16, 17]. Another study [18] reported a greater anthropogenic input of trace elements in surface sediment samples from the Pasir Gudang area than from sediments collected from other areas in the Straits of Malacca. However, the degree of heavy metal pollution depends upon the sampling area and the particular metal.

By comparing the data of the present study with the ISQG guideline [13], almost all sampling stations had metals concentrations below both ISQG-high and ISQG-low. However, only S1 had metal concentrations that exceeded ISQG-low but below ISQG-high for all metals. Sediments from S2, S3 and S4 exceeded ISQG-low for Ni.

Table 1: Concentration range of heavy metals ($\mu\text{g} \cdot \text{g}^{-1}$ dry weight) in Johor Straits of and other selected areas around Peninsular Malaysia

Location	Metal				Reference
	Ni	Cu	Zn	Pb	
Johor Straits (western part)	8.6-30.6	12.0-64.5	56.9-307.9	13.3-62.3	Present study (2015)
Johor Straits (western part)	2.8-24.7	2.0-37.5	29.4-225.3	8.7-66.1	[9]
Johor Straits (mean of eastern and western)	30.2	30.7	132.5	42.3	[10]
Pulau Tekong and Kranji (Singapore)	17.1-26.1	7.7-17.9	49.8-62.1	26.1-29.8	[20]
Sungei Buloh and Sungei Khatib Bongsu (Singapore)	7.4-11.6	7.0-32.00	51.2-120.2	12.2-30.9	[21]
Malaysian coast	-	1.7-8.2	13.8-42.4	6.1-27.5	[22]
Juru (Penang, Malaysia)	-	29	84	25	[23]
Sungai Puloh estuary (Selangor, Malaysia)	-	16.5-132.9	291.9-2584.3	0.6-1.6	[24]
Sungai Sepang Besar estuary (Selangor, Malaysia)	26.1	77.2	246.4	86.9	[25]
West coast of Peninsular Malaysia	-	<6.0	-	1.0-45.0	[26]
Moyan and Serpan (Sarawak, Malaysia)	-	180-274	-	-	[27]
Coastal areas of Peninsular Malaysia	2.4-36.3	1.6-150.8	23.7-609.2	7.9-93.1	[7]
ISQG-low	21	65	200	50	[13]
ISQG-high	52	279	410	220	[13]

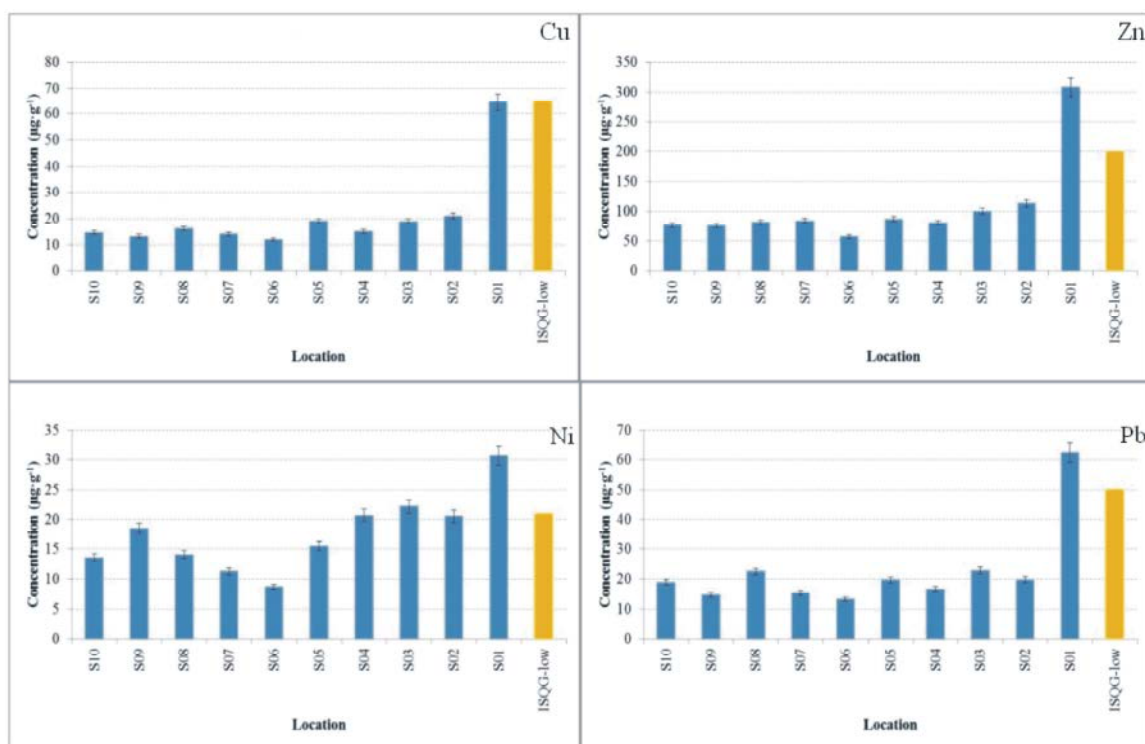


Fig. 2: Mean concentration ($\mu\text{g}\bullet\text{g}^{-1}\text{ dw}$) of selected metals in sediments collected from western part of Johor Straits

These findings suggest that some benthic communities in S1 could be affected by the present metal levels, while benthic communities in the S2, S3 and S4 areas could be affected by the Ni concentration in sediments. Further investigation using other statistical techniques (such as [19]) should be conducted to further estimate the extent of pollution impacts in the areas.

As noted, of all the metals, Zn exhibited the highest concentration in the surface sediments (Fig. 2b). The highly elevated Zn concentration at S1 near the causeway could be due to anthropogenic point- and non-point sources, such as agriculture-related activities, industrial activities (e.g., electrical and electronic factories), jetties, wastewaters and terrestrial transportation [7]. A similar finding was reported in a previous study [9], in which the concentration of Zn was the highest ($210.45\pm115.4\text{ }\mu\text{g/g}$) among all metals.

As for Pb, possible anthropogenic sources of Pb include the manufacture and use of batteries, cables, alloys and chemicals, as well as leaded-fuel products and the semiconductor industry and related industrial activities [7]. Furthermore, a previous study reported that

intensive dredging, reclamation; construction and shipping activities may also contribute to the resuspension and bioavailability of metal-containing particulate matter, especially in the Ponggol estuary of Singapore (east of the Johor Strait) [28]. Resuspended sediments could increase the possibility of pollutants to be released into water column [28]. Once this event occurs, it will make the pollutants available for bioaccumulation into biological tissues of aquatic biota and transported in the existing food web in the area [29, 30]. Yet, greater industrial development was reported on the eastern side of the causeway [10]. Such anthropogenic activities may elevate the Pb concentration as well. Consequently, the Pb concentration ($28.4\pm30.0\text{ }\mu\text{g/g}$) was highest at station S1 (Fig. 2d) and it exhibited the second highest concentration, after Zn, of all the metals. Because S1 is located close to the Johor Causeway, accumulations of Pb are likely to be high. This is due to exhaust emissions from the large volume of vehicles and the use of lead-containing gasoline that has been sold in Malaysia and Singapore in the past [10]. The results showed lower Pb concentrations than those reported in previous studies [9, 10] ($42.3\pm11.0\text{ }\mu\text{g/g}$ and $52.52\pm28.41\text{ }\mu\text{g/g}$, respectively).

The findings regarding the other heavy metals studied (Cu and Ni) were similar to those for Zn and Pb (Fig. 2a and Fig. 2c), as station S1 had elevated heavy metal concentrations compared with the other stations. Based on a previous study [14], the accumulation of Cu in *Perna viridis* was higher in a location near the Skudai River compared with the western side of the Johor Straits. Furthermore, urban and industrial developments along the coastal areas, river and estuary, transportation, agriculture, aquaculture etc. are the main factors that result in the deposition of anthropogenic metals into the sea. This may increase the Ni concentration as well. A previous study reported that more than 50% of the Ni and Cu in the surface sediment samples originated from anthropogenic sources, which were said to enter via riverine inputs, non-points sources (runoff from land) and direct point sources (discharges) [9]. Additionally, atmospheric deposition also plays a role in contributing to heavy metal pollution, as a previous study showed that it was the main pathway for metal input into the ocean [31]. Overall, most of the highest metal concentrations in this study were recorded at station S1, which is situated along the Johor Causeway and the Skudai River. Stations S4 to S10 accumulated lower concentrations of heavy metals. Therefore, it can be generally stated that the western side of the Johor Straits is less polluted than the eastern side (near the Johor Causeway). These results are in good agreement with those from previous studies [9, 16, 17, 32].

CONCLUSION

The concentrations of heavy metals in sediments of the Johor Straits are higher in areas close to the Johor Causeway because of high metals inputs from surrounding developed areas and low water currents. Increasing metal concentrations in sediments, after a comparison with results from previous studies, demonstrate the continuous input of metals from point and non-point sources. A monitoring program should be conducted for effective management and mitigation of heavy metals in the future.

ACKNOWLEDGEMENT

This study was jointly supported by the special Fundamental Research Grant Scheme (FRGS) (Reference No. KPT.P.(S)400-7/2/29-4(65)) for matching fund research

between JSPS Asian CORE Program and Universiti Putra Malaysia (UPM) and FRGS (Reference No. FRGS/1/2014/STWN01/UPM/02/4) from the Ministry of Education Malaysia.

REFERENCES

1. Barlas, N., N. Akbulut and M. Aydogan, 2005. Assessment of heavy metal residues in the sediment and water samples of Uluabat Lake, Turkey. *Bulletin of Environmental Contamination and Toxicology*, 74(2): 286-293.
2. Mitra, A., R. Chowdhury and K. Banerjee, 2012. Concentrations of some heavy metals in commercially important finfish and shellfish of the River Ganga. *Environmental Monitoring and Assessment*, 184(4): 2219-2230.
3. Sow, A.Y., A. Ismail and S.Z. Zulkifli, 2013. Geofractionation of heavy metals and application of indices for pollution prediction in paddy field soil of Tumpat, Malaysia. *Environmental Science and Pollution Research*, 20(12): 8964-8973.
4. Apitz, S.E., J.W. Davis and K. Finkelstein, 2005. Assessing and managing contaminated sediments: Part I. Developing an effective investigation and risk evaluation strategy. *Integrated Environmental Assessment and Management*, 1(1): 2-8.
5. Ismail, A. and A. Safahieh, 2005. Copper and zinc in intertidal surface sediment and *Telescopium telescopium* from Lukut River, Malaysia. *Coastal Marine Science*, 29(2): 111-115.
6. Wan, E.C.K. and F. Mohamat-Yusuff, 2014. Contamination of trace elements (Cu, Pb, Cr) in Kong Ko Laut, Johor, Malaysia. In *From Sources to Solution*, Eds., A.Z. Aris, T.H. Tengku Ismail, R. Harun, A.M. Abdullah and M.Y. Ishak. Singapore: Springer, pp: 567-572.
7. Zulkifli, S.Z., F. Mohamat-Yusuff, T. Arai, A. Ismail and N. Miyazaki, 2010. An assessment of selected trace elements in intertidal surface sediments collected from the Peninsular Malaysia. *Environmental Monitoring and Assessment*, 169(1-4): 457-472.
8. Bryan, G.W. and W.J. Langston, 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution*, 76(2): 89-131.

9. Zulkifli, S.Z., A. Ismail, F. Mohamat-Yusuff, T. Arai and N. Miyazaki, 2010. Johor Strait as a hotspot for trace elements contamination in Peninsular Malaysia. *Bulletin of Environmental Contamination and Toxicology*, 84(5): 568-573.
10. Wood, A.K.H., Z. Ahmad, N.A.M. Shazili, R. Yaakob and R. Carpenter, 1997. Geochemistry of sediments in Johor Strait between Malaysia and Singapore. *Continental Shelf Research*, 17(10): 1207-1228.
11. Ismail, A., 1993. Heavy metal concentrations in sediments of Bintulu, Malaysia. *Marine Pollution Bulletin*, 26(12): 706-707.
12. Ismail, A. and R. Ramli, 1997. Trace metals in sediments and molluscs from an estuary receiving pig farms effluent. *Environmental Technology*, 18(5): 509-515.
13. ANZECC/ARMCANZ, 2000. Australian and New Zealand guidelines for fresh and marine water quality. Canberra: Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand (ANZECC and ARMCANZ), pp: 314.
14. Azman, S., B.C.W. Chiang, R. Ismail, J. Jaafar and M.I.M. Said, 2012. Effect of land use on coastal water and *Perna viridis* at Johor Straits, Malaysia. *International Journal of Environmental Science and Development*, 3(3): 237-239.
15. Simms, P.H., E.K. Yanful, L. St-Arnaud and B. Aubé, 2000. A laboratory evaluation of metal release and transport in flooded pre-oxidized mine tailings. *Applied Geochemistry*, 15(9): 1245-1263.
16. Bayen, S., G.O. Thomas, H.K. Lee and J.P. Obbard, 2004. Organochlorine pesticides and heavy metals in green mussel, *Perna viridis* in Singapore. *Water, Air and Soil Pollution*, 155(1-4): 103-116.
17. Yap, C.K., M.S. Choh, F.B. Edward, A. Ismail and S.G. Tan, 2006. Comparison of heavy metal concentrations in surface sediment of Tanjung Piai wetland with other sites receiving anthropogenic inputs along the south western coast of Peninsular Malaysia. *Wetland Science*, 4(1): 48-57.
18. Ismail, A., 2008. A need for monitoring of heavy metals and organotin compounds in the east coast of Johor, In *Research and information series of Malaysian coast of Malaysia marine ecosystem*, Eds., M. Che Abdul Rahim, M.A. Masri, C.K. Zaidi and A. Norhayati. Bangi: Marine Ecosystem Research Centre UKM, pp: 163-176.
19. Al-Badaii, F. and M. Shuhaimi-Othman, 2014. Heavy metals and water quality assessment using multivariate statistical techniques and water quality index of the Semenyih River, Peninsular Malaysia. *Iranica Journal of Energy and Environment*, 5(2): 132-145.
20. Cuong, D.T. and J.P. Obbard, 2006. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Applied Geochemistry*, 21(8): 1335-1346.
21. Cuong, D.T., S. Bayen, O. Wurl, K. Subramanian, K.K. Shing Wong, N. Sivasothi and J.P. Obbard, 2005. Heavy metal contamination in mangrove habitats of Singapore. *Marine Pollution Bulletin*, 50(12): 1732-1738.
22. Ismail, A., N.R. Jusoh and I. Ghani, 1995. Trace metal concentrations in marine prawns off the Malaysian coast. *Marine Pollution Bulletin*, 31(1): 108-110.
23. Lim, P.E. and M.Y. Kiu, 1995. Determination and speciation of heavy metals in sediments of the Juru River, Penang, Malaysia. *Environmental Monitoring and Assessment*, 35(2): 85-95.
24. Ismail, A., M.A. Badri and M.N. Ramlan, 1993. The background levels of heavy metals concentrations in sediments from the west coast of Peninsular Malaysia. *Science of the Total Environment*, 134(S1): 315-323.
25. Udechukwu, B.E., A. Ismail, S.Z. Zulkifli and H. Omar, 2015. Distribution, mobility and pollution assessment of Cd, Cu, Ni, Pb, Zn and Fe in intertidal surface sediments of Sg. Puloh mangrove estuary, Malaysia. *Environmental Science and Pollution Research*, 22(6): 4242-4255.
26. Ramsie, S.A., S.Z. Zulkifli, F. Mohamat-Yusuf and A. Ismail, 2014. Geochemical fractionations of heavy metals in sediments of Sepang Besar River, Malaysia. *Acta Biologica Malaysiana*, 3(1): 1-9.
27. Kanakaraju, D., F. Ibrahim and M.N. Berseli, 2008. Comparative study of heavy metal concentrations in razor clam (*Solen regularis*) in Moyan and Serpan, Sarawak. *Global Journal of Environmental Research*, 2(2): 87-91.
28. Nayar, S., B.P.L. Goh and L.M. Chou, 2004. Environmental impact of heavy metals from dredged and resuspended sediments on phytoplankton and bacteria assessed in in situ mesocosms. *Ecotoxicology and Environmental Safety*, 59(3): 349-369.

29. Zulkifli, S.Z., F. Mohamat-Yusuff, A. Ismail and N. Miyazaki, 2012. Food preference of the giant mudskipper *Periophthalmodon schlosseri* (Teleostei: Gobiidae). Knowledge and Management of Aquatic Ecosystems, 405: 07.
30. Zulkifli, S.Z., F. Mohamat-Yusuff, A. Mukhtar, A. Ismail and N. Miyazaki, 2014. Determination of food web in intertidal mudflat of tropical mangrove ecosystem using stable isotope markers: A preliminary study. Life Science Journal, 11(3): 427-431.
31. Zhang, X., G. Zhuang, J. Guo, K. Yin and P. Zhang, 2007. Characterization of aerosol over the Northern South China Sea during two cruises in 2003. Atmospheric Environment, 41(36): 7821-7836.
32. Said, M.I.M., S. Sabri, S. Azman, K. Muda, 2013. Arsenic, cadmium and copper in gastropod *Strombus canarium* in western part of Johor Straits. World Applied Sciences Journal, 23(6): 734-739.