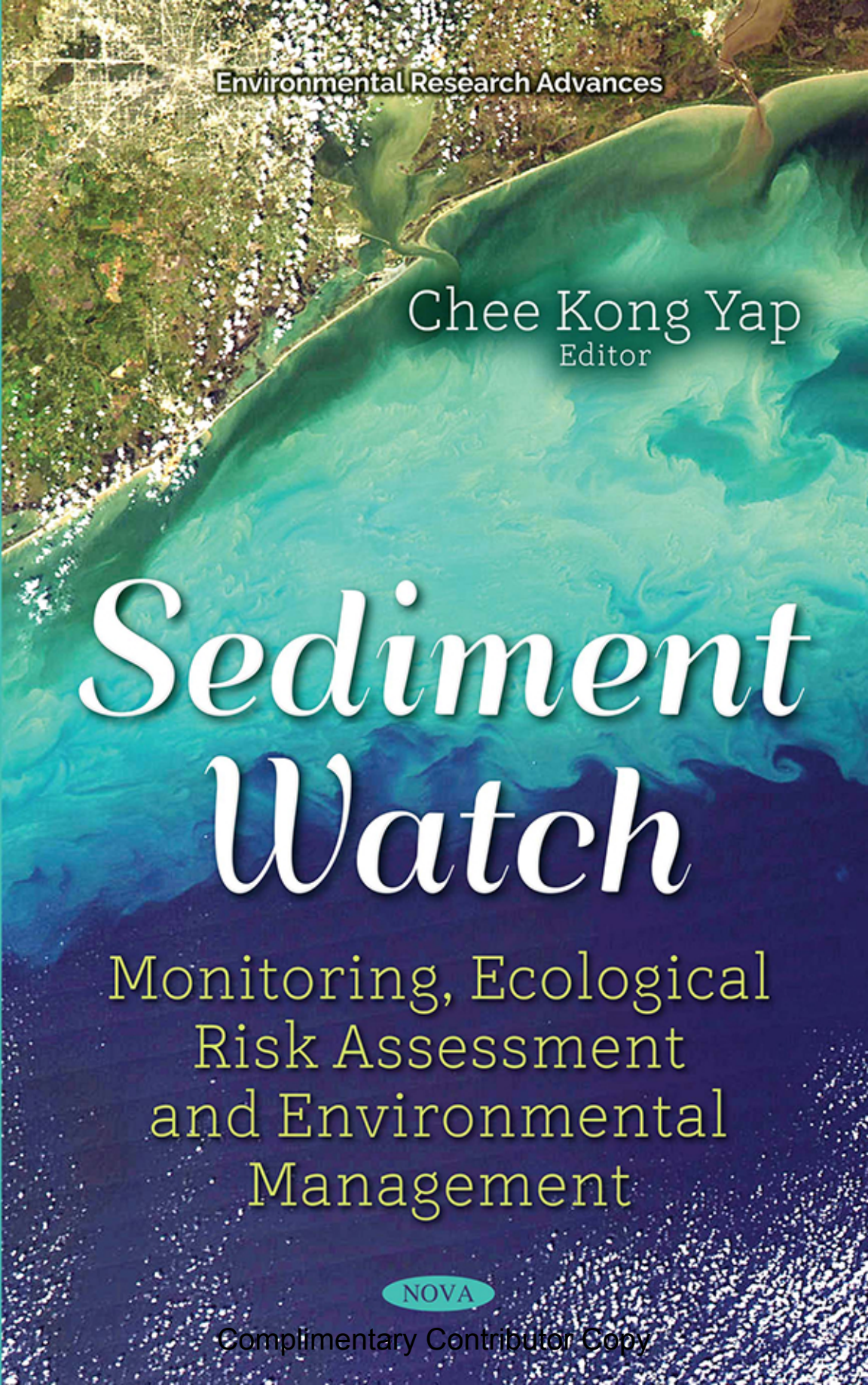

ENVIRONMENTAL RESEARCH ADVANCES

SEDIMENT WATCH

MONITORING, ECOLOGICAL RISK ASSESSMENT AND ENVIRONMENTAL MANAGEMENT

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MONITORING, ECOLOGICAL RISK ASSESSMENT AND ENVIRONMENTAL MANAGEMENT

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CONTENTS

PREFACE

The aim of this book is to provide the latest, if no the complete, of some updated information regarding the use of sediments for estimation of chemical pollution in the aquatic environment from three main perspectives namely, monitoring, ecological risk assessment and environmental management. All chapters in this book entails monitoring studies of pollutants/sedimentary characteristics (Chapter 3, 4, 6, 7, 8, 9, 10 and 11), especially heavy metals, continues to the application of the data for the ecological risk assessments (Chapters 2, 5, 6, 8, 9, and 10), and lastly, recommendations for possible environmental management (Chapters 1, 2, 4, 7, 8 and 10).

Chapter 1 reviewed 30 publications, published between 2015 and August 2017, the management of coastal environment focusing on the pollutants investigated in the sedimentary components of the resourceful area in the coasts. Three patterns have been identified: a) Chemical pollutants in the sediments are still widely reported in the literature, in at least 13 countries, b) Many chemical monitoring studies are mostly reported from China, and c) Lack of relationships of the pollutants between the humans and sediments. The authors concluded that the need for an effective coastal management by using Sediment Watch could be a solution, providing quantitative and qualitative monitoring data that can serve for the management of sustainable coastal resources. Prof. Hideo Okamura (Kobe University, Japan) and Prof Hiroya Harino (Kobe College, Japan) who co-

authored the paper have provided insightful ideas and comments to the quality improvement of this paper.

Chapter 2 presented the geochemical fractions of six heavy metals on surface sediments collected from drainages of Malacca Industrial area (MIA) and Malacca River. The authors found that four heavy metals were the metals most prevalent in the non-resistant fractions. Based on ecological risk assessment and geochemical fractions results, it can be concluded that three sites are polluted by heavy metals, with a high support of potential ecological risk index that two sites are categorized as 'considerable ecological risk'. Based on present findings, it is inferred and evidently shown that elevated levels of heavy metals in the drainages at MIA and Malacca River sediments was attributed to the untreated effluents.

Chapter 3 reviewed and compared scientific papers related to sedimentary characteristics (SC) of the tsunami sediments or deposits after the 2004 Indian Ocean and 2011 Tohoku-oki Tsunami (TOT). Two recommendations based on the present review are proposed. Firstly, monitoring of chemical organic and inorganic pollutants, and radioactive rare earth elements, should be studied in most coastal areas that are suspected to be inundated during tsunami events. Secondly, the documentation and checklists of natural food resources including their background levels of chemical pollutants, should be provided by conducting biological and ecological studies. Dr. Gen Kanaya (National Institute of Environmental Studies, Tsukuba, Japan) who co-authored the paper has revised and provided important additional information about TOT, for upgrading the quality of this manuscript.

Chapter 4 reviewed 14 ISI published papers on the metal contamination in sediments of the Persian Gulf that received impact from anthropogenic activities. Dr. Sharifinia stated that environmental management and monitoring of sediments is challenged with providing the basis for protection the environment against adverse anthropogenic impacts of pollution resulting from industrial and sewage discharges, aquaculture activities, oil pollution, and coastal modification. Altogether, findings from this chapter could be useful in providing more effective and targeted strategies for the better developmental management practices in the semi-

enclosed Persian Gulf. Dr. Moslem Sharifinia is the best researcher on Persian Gulf sediments who has published in high-ranked journals.

Chapter 5 presented the ecological risk assessment of heavy metals in the sediments collected, in 2007, from Sepang Besar River and Sepang Kecil River, that were previously a piggery farming area in early 1990s. Comparison with previous studies revealed that the result obtained from this study was generally lower than previously reported data for Cu, Ni, Pb and Zn. Only total Cd levels are higher than the metal level of established sediment quality guideline. Potential ecological risk index denoted 'minimal ecological risk (RI<150)' from the combination of Cd, Cu, Ni, Pb and Zn for both rivers. This indicates that the two rivers are not polluted by Cu, Ni, Pb and Zn. Although the two rivers are not receiving anthropogenic metals, the geochemical results indicated that the sediment is still dominated by non-resistant Zn.

Chapter 6 investigated the distribution and enrichment of six heavy metals in the surface marine sediments of coastal Sabah, Malaysia. Except for As, the enrichment factors are categorized as 'moderate enrichment' in some sampling sites, other metals are found to be 'no enrichment' at all sampling sites. The values of geoaccumulation index for all metals show 'unpolluted' at all five sampling sites. However, the values of modified degree of contamination of all sampling sites are found < 1.0, suggesting 'very low contamination' of the investigated metals in all sampling sites. Dr. Ahmadreza Ashraf is the best researcher on Sabah offshore sediments who has published in high-ranked journals.

Chapter 7 reported the concentrations of Cr, Co, Mn and Sc in the mangrove snail in associations of the above four metals with their habitat surface sediments. By using simple regression equation, it is found that the concentrations of Cr and Co in the soft tissues (ST) and shells of snails positively but weakly correlated with surface sediments. It is clearly seen that Mn levels in the ST and shells positively and strongly correlated with the surface sediments. For Sc concentrations, only ST showed positive and good correlation with surface sediments but almost no association in the case of shells. Therefore, the use of *C. obtusa* is a potential good biomonitor of Mn and Sc pollution in the mangrove ecosystem and for an effective

mangrove management in view of sustainable resources from the intertidal mangrove environment. Prof. Minoru Saito (Nihon University, Japan) who co-authored the paper has commented and revised this paper that helped to improve the paper.

Chapter 8 presented the ecological risk assessments of heavy metals in surface sediments collected from a rocky shore in Tanjung Harapan (TH). Based on the sediment quality guidelines, geoaccumulation index and enrichment factor, all metals in this study will not cause possible adverse effects or pollution to the surrounding. The Potential Ecological Risk Index (PERI) values for all metals in this study fell in the category of 'low ecological risk' at TH. However, PERI value at TH was found to be higher than most (7 out of 9 sampling sites) coastal sediments previously reported from Peninsular Malaysia. This indicated the impact of anthropogenic sources. The metal concentrations and ecological risk assessment of metals at TH are important for future reference in the effective coastal ecosystem management. Prof. Kazuhiro Toyoda (Hokkaido University) who co-authored the paper has provided perceptive comments and revised the whole paper that improved the paper substantially.

Chapter 9 investigated geographical spatial distribution, and the ecological and children's health risk assessments of Copper (Cu) aquatic ecosystem ranging from rivers, mangrove, estuaries and offshore areas were investigated using Cited Cu Data In The Sediments (CCDITS) from 100 randomly selected published papers in the literature. In general, three major patterns can be concluded based on the present review. Results show that overall sediments have a moderate to highly Cu enrichment level. This enrichment poses a high risk despite measured levels below sediment quality guidelines at most areas. All CCDITS are found below 1.0 for Hazard Quotient (HQ) while only 1% of the HQ values exceeded 1.0, indicating low chance of Cu non–carcinogenic effects in most areas. It is still recommended that regular monitoring of Cu pollution in the sediments of aquatic ecosystem needs to be conducted with a view of abating the risk of Cu exposure to children's health. All authors have given their useful comments or revisions on the improvement of the paper.

Chapter 10 presented the geochemical speciation and risk assessment of heavy metals in southwestern Taiwan coastal sediments. Dr. Hou-Chun Liu and Prof Chen-Feng You from National Cheng Kung University (Taiwan) have reviewed more than 11 studies and the heavy metal data were re-analyzed for enrichment factor and potential ecological risk index in order to evaluate the degree of heavy metal contamination and their potential ecological risk, respectively. By using statistical analyses on the collected dataset coupled with the sequential extraction procedure data, they concluded the re-analyzed dataset emphasizes the fact that the relative proportions of the geochemical fractions in the sediments are the indispensable factor influencing the heavy metal mobility and distribution in the marine sediments of southwestern Taiwan aquatic systems.

Chapter 11 presented the Neodymium (Nd) isotope compositions in the Fe-Mn hydroxides from two marine cores in west Pacific during the past 27 Ka. These cores, MD972143 and MD012403 were collected from the Benham Rise in the western Philippine Sea and southern Okinawa Trough, respectively. They show similar down core variations in εNd, both display about 5 ε units of variation during the past 27 Ka, εNd varies between -2.97 and 1.78 in the Benham Rise sediment core. For core MD012403, εNd values range between -10.2 to -7.8 and the range of εNd values of MD972143 are -3.0 to -1.8. They show similar down core variations in εNd, both display about 5 ε units of variation during the past 27 Ka.

I want to extend my gratitude to Universiti Putra Malaysia for granting me Sabbatical Leave that allowed me to have the time to prepare on this book. My academic visit to Japan has been a fruitful outcome because most of my book chapters have been commented and revised by the Japanese researchers and professors that ultimately have brought the quality of all the chapters to a greater height with their constructive comments. I have definitely learnt a lot from them, personally and academically. Lastly, Prof Chen-Feng You from National Cheng Kung University (Taiwan), and Dr. Moslem Sharifinia (Iranian National Institute for Oceanography and Atmospheric Science), who have supported this book by contributing chapters for book, are also highly appreciated. I want to thank Nova Science

Publishers for giving me this opportunity to become the editor for this book title.

Last but no the least, I want to thank my dearest wife and two lovely daughters who are always with me in the preparation of this book. They have been my primary source of support, courage and motivation to complete this book. I love you all.

We will always **M**iss the **S**now in **H**okkaido **U**niversity;
We will always **M**onitor the **S**ystem in **H**uman **U**niverse!
Let's do our part and pray for a healthier world.
Happy reading and good luck.

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Chapter 1

MANAGING SUSTAINABLE COASTAL ENVIRONMENTS BY SEDIMENT WATCH: A REVIEW

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ABSTRACT

In this review paper, the management of resourceful coastal environment is focused on the pollutants in the sedimentary components. However, the other two major components (social–economy) cannot be separated in this critical review of proposing Sediment Watch for the coastal environmental management. A total of 30 publications has been compiled for the chemical pollutants investigated in sediments published

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between 2015 and 2017. Based this short review, we can identify three patterns: a) Chemical pollutants in the sediments are still widely reported in the literature, in at least 13 countries, b) Many chemical monitoring studies are mostly reported from China, and c) Lack of relationships of the pollutants between the humans and sediments. The present review concluded that the need for an effective coastal management by using Sediment Watch can be a solution, providing quantitative monitoring data that can serve for the management of sustainable coastal resources.

Keywords: sediment management, monitoring, chemical pollutants

1. INTRODUCTION

Sediment is an indispensable abiotic part in any coastal environment (Bryan and Langston 1992). According to Corlay et al. (2003), coastal wetlands symbolize specific environments of great ecological value, and can be described as open bioenergetic systems of high quality due to the forceful interactions (sedimentary, gaseous, hydrological and biological) which take place there. Almost all coastal areas contain sedimentary particles, whether natural or artificially derived inputs. If there is absence of sediments in a coastal environment, a) What would be occurring to the natural resources such as fish, shellfish and mangrove ecosystem? b) What are the impacts to a country's economy? c) What would happen to the inhabitants or people of the coastal area? A simple logical answer to the above three questions could be 'All components will be suffering an intense stress before they eventually come to an end, if a foreign aid does not come on time.' Therefore, before the situation becomes worse, a proper management planning by the governing body should be implemented to decide the future fate of the coastal environment.

The management of coastal ecosystem involves three integrated components namely, social, economy and environment (De Oliveira et al. 2011). According to Chiau (1998), the coastal zone management aims to stabilize and optimize environmental protection and socio-economic growth. Apparently, these problems all involve economy, social and environmental perspectives.

The aim of this paper is to review published papers focusing on the pollutants in the sedimentary components of the resourceful coastal environment. This review was based on papers on chemical pollutants in sediments published between 2015 and 2017. Based on available and random selections of citations, we also review the management strategies and problems (such as social factors).

2. METHODOLOGY

In this review paper, keyword 'sediment management' was put to find the available papers based on Scopus database between 2015 and 2017 in August 2017. Out of the search, only abstracts with any chemical pollutants investigated in the sediments were selected. To reduce the biases, the first selection was based on the title of the paper with the relevant keywords regardless of the authors' name and from which country.

3. MONITORING OF POLLUTANTS IN SEDIMENTS

A review of different types of chemical pollutants in the sediment samples collected from different ecosystems and countries, is presented in Table 1. In general, the samples were collected for the determination of different chemical pollutants including persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Besides, inclusions of other chemicals are polycyclic aromatic hydrocarbons (PAHs), toxic metals, heavy and trace metals, nutrients (soluble reactive phosphorus and dissolved inorganic nitrogen), perfluoroalkyl acids (PFAAs) and perfluoroalkyl carboxylates (PFCAs). All of these chemical pollutants were reported in the papers published between 2015– August 2017 (Table 1). Based on 30 citations selected randomly as shown in Table 1, the countries (number of papers published) involved in the literature came from China (11), Korea (3), Malaysia (3), Australia (2), Persian Gulf (2), Ghana

(1), Democratic Republic of the Congo (1), Senegal (1), Pakistan (1), Morocco (1), Indonesia (1), Egypt (1) and Japan (1). Based this short review, we can identify three patterns:

a) Chemical pollutants in the sediments are still widely reported in the literature, in at least 13 countries.

The need of coastal management by using Sediment Watch is of urgency in view of the literature cited above. Sato and Mimura (1997) reviewed the coastal environmental problems in South and Southeast Asian countries, and proposed three main causes of environmental problems for the environmental management of coastal resources as follows: 1) Different coastal types have different physical and ecological characteristics and coastal environmental problems depend on these types of the coasts; 2) Coastal environmental problems are induced by the wrong use of coastal resources. Over–use and improper use of coastal resources give rise to deterioration of environment; 3) Problems related to environmental management can be divided into administrative system and management bodies. Management bodies do not have enough budget and human resources. Therefore, the need for an effective coastal management especially in South and Southeast Asian countries is essential.

According to Kroon et al. (2014), nearly 25% of the total global reef area were imperiled by agricultural pollution, with further increases in sediment and nutrient fluxes projected over the next 50 years. To protect the coral reef ecosystems, they proposed decline of agricultural pollution, decrease in fluxes of sediment and nutrients to coastal ecosystems. Hence, the need to control and regulate the agricultural pollution in the coastal area is necessary.

Table 1. Review of pollutants investigated in the sediment samples collected from different ecosystems and countries

No.	Area/Country	Trace metals, heavy metals and persistent organic pollutants investigated	Reference
1.	Kinshasa, Democratic Republic of the Congo	Toxic metals, and POPs including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs)	Kilunga et al. (2017)
2.	Beijing–Hangzhou Grand Canal, China	Cd, Cu, Ni, Pb, and Zn	Zhuang et al. (2016)
3.	Coastal Tema Harbour, Ghana	DDTs, HCHs, and PAHs	Botwe et al. (2017)
4.	Jiaozhou Bay catchment, China	Cu, Pb, Zn, Cr, Cd, and As	Xu et al. (2017)
5.	Bayan Lepas, Penang, Malaysia	Cd, Cr, Cu, Co, Fe, Pb, Ni, V, and Zn	Khodami et al. (2017)
6.	Sydney Harbour, Australia	Cu, Pb, and Zn	Birch (2017)
7.	Yalujiang Estuary, China	Nutrients (dissolved inorganic nitrogen and soluble reactive phosphorus) and trace elements (Hg, As, Pb, Cu, Cd, Cr, and Zn)	Li et al. (2017a)
8.	Suoxu River, China	Cd, Cr, Cu, Ni, Pb, and Zn	Jeelani et al. (2017)
9.	Dakar coast and Saint Louis estuary, Senegal	Trace metals	Diop et al. (2015)
10.	Liaohe Estuary, China	Heavy metals, PCBs, and OCPs	Li et al. (2017b)
11.	Haihe Basin, China	Cd	Tang et al. (2017)
12.	Northern part of the Persian Gulf, Iran	Cu, Zn, Pb, and Cd	Bastami et al. (2015)
13.	Brisbane River, Australia	Heavy metals	Duodu et al. (2016)
14.	Artificial lake An-Dong, Korea	Co, Ni, As, Cu, Zn, Cd, and Pb	Choi et al. (2015)
15.	Freshwater lakes in China	As, Cd, Cr, Cu. Hg, Ni, Pb, and Zn	Cheng et al. (2015)
16.	Le'an River, China	Cd, Cr, As, Hg, Pb, Cu, Zn, and Ni	Chen et al. (2016)
17.	Three Gorges Reservoir, China	Heavy metals Cd, Cu, Pb, and Zn	Bing et al. (2016)

Table 1. (Continued)

No.	Area/Country	Trace metals, heavy metals and persistent organic pollutants investigated	Reference
21.	Mahakam Delta, East Kalimantan, Indonesia	Heavy metals	Effendi et al. (2016)
18.	Red Sea. Egypt	Al, Zn, Cu, Ni, V, Pb, Cd, and Hg	El Nemrn et al. (2016)
19.	Estuaries in eastern China	As, Cd, Cr, Cu, Hg, Pb, and Zn	Bi et al. (2017)
20.	Liaohe River protected area, China	Cd, As, Cu, Ni, Pb, Cr, and Zn	Ke et al. (2017)
22.	South east coast of India	Trace metals	Kumar et al. (2017)
23.	Nador lagoon, Morocco	Heavy metals	Maanan et al. (2015)
24.	Chenab River, Pakistan	Mn, Zn, Pb, Cd, Co, Cu, and Pb	Hanif et al. (2016)
25.	Mand River delta, Persian Gulf	Cr, As, Ni, and Pb	Pourkerman et al. (2017)
26.	Ponds in Selangor, Peninsular Malaysia	Heavy metals	Yap et al. (2015)
27.	East Sea-Jung dumping site, Korea	Al, Fe, Mn, Li, Co, Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg	Song et al. (2015)
28.	Nakdong River Basin, Korea	Zn, Cu, Pb, As, and Cd	Chung et al. (2016)
29.	Mangrove area of west coast of Peninsular Malaysia, Malaysia	Toxic metals	Cheng and Yap (2015)
30.	Osaka Bay and coastal waters of Western Japan	Perfluoroalkyl acids (PFAAs) and perfluoroalkyl carboxylates (PFCAs)	Beškoski et al. (2017)

Based on a review by Sloan et al. (1994) on Indonesia's coastal environmental management, increasing the economic contribution of coastal resources in line with sustainable development is very important. The management problems in the coastal zones are complicated by fast population expansion worldwide (Chebo, 2009). Hence, the need to control and regulate the population expansion that caused the coastal hazards is important.

Sewage release is a main contribution of pollution in coastal environments. Municipal wastewaters can directly move into coastal environments transporting organic loads, nutrients and pathogen organisms (González-Fernández et al. 2010). Since coastal sediments can act as an

ultimate destiny of a variety of pollutants, environmental quality assessment in this matrix can help to identify pollution problems in the coastal areas. Consequently, the need to manage the coastal environment receiving sewage discharge cannot be ignored anymore.

b) Many chemical monitoring studies are mostly reported from China.

This indicated the aggravation of chemical pollution problems in China. According to a review by Sun et al. (2015), based on China's coastal wetlands, six major issues recently emerged in China's coastal wetland conservation have been identified; 1) the increasing hazards of pollution and anthropogenic activities, 2) the increasing unfavorable effects of pressurized factors on the functions of coastal ecosystem, 3) the increasing risks of sea-level rising and coastal erosion, 4) the inadequate funding for coastal wetlands conservation, 5) the defective management and legal system for coastal wetlands, and 6) the lacking education, research and international cooperation.

On the contrary, there were no papers published about trace metals and heavy metals in the sediments from Japan between 2015-2017. Particularly in Japan, recently, two unique pollutants, PFAAs and PFCAs, have been analyzed by Beškoski et al. (2017) who collected sediments from Ajifu Waterway in Osaka city, from Osaka Bay and Kagoshima Bay, Japan. They concluded sources from Keihanshin Metropolitan Area (Yodo River basin), and the dilution effect was the major factor that affected the variations in the patterns of PFAAs in Osaka Bay and coastal waters of Western Japan. Previously, an ecotoxicological study on the aquatic environment around Lake Kojima (Japan) was investigated by Okamura (1996). For ecotoxicity screening, Okamura (1996) collected surface water and sediment samples in 1993 from 16 sites. Harino et al. (2007) analyzed organotin compounds (OTs) in the sediment and mussels sampled from Otsuchi Bay (Japan). They also detected representative booster biocides in sediment from Otsuchi Bay, and found a higher concentration of triphenyltin (TPT) than tributyltin (TBT) in a small fishing port. Therefore, above studies indicated that the

sediments are important samples in their study to achieve their objective of study.

c) A lack of relationships of the pollutants between the humans and sediments.

Most of the monitoring studies in Table 1 do not include the ecological risk assessments (ERA) and human health risk assessments (HHRA) of the heavy metal exposure via dermal, ingestion and inhalation. Social factors have always been discussed and included for an effective coastal management besides environmental factors which is related to Sediment Watch, as shown in the following reviews.

Based on a report to the Australian Parliament on the protection of the coastal environment (Crawford 1992), an extensive public inquiry by the parliamentary committee was followed. This resulted to its visiting various parts of the Australian coastline that held discussions from all sections of the community. This report did mention the social aspects in the coastal management plan but not specifically on sedimentary management. However, the coastal environment consists primarily of sedimentary components that become their abiotic factor or habitat of many living seafood resources from the coastal environment. Mani-Peres et al. (2016) evaluated the stakeholders' perceptions of a particular area in coastal zones. This can be helpful for recognizing the impacts of environment that happened previously, mainly in the deficiency of effective monitoring data. They concluded that the social factor was an important qualitative information and can be helpful for the establishment of management strategies and environmental impact assessment. Based on an interview survey among some of the stakeholders in the shrimp farms on the southwestern coast of Bangladesh, Paul and Røskaft (2013) reported eight negative impacts were treated as conflict generating factors. They found that the marginal farmers and the landless people were the two pioneer classes intensively concerned in these disagreements. Above both studies involved social factors in the management of coastal environment.

De Oliveira et al. (2011) investigated the natural and anthropogenic impacts on the characteristics of a macrotidal beach in northeastern Pará (Brazil). In this social perspective, the unregulated urban growth was the main contributor accountable for the erosion experienced in the northwestern part of the beach. The raise of population size had triggered bacterial contamination caused by the domestic sewage discharge which was untreated. One the recommendations by De Oliveira et al. (2011) was to improve the water supply quality and public sanitation system, and the recreational facilities. In Japan, the Guideline for Integrated Coastal Management (ICM) plans was issued in 2000 to promote planning and implementation of ICM (Wakita and Yagi, 2013). Wakita and Yagi (2013) clarified the reasons for the poor application by using a theoretical approach and a lack of a scheme that would provide national subsidies to local governments. They also stated that the diminished position of the coordinating national agency had hindered implementation of the Guideline. The major similarity in solving the problem as recommended between Brazil (De Oliveira et al. 2011) and Japan (Wakita and Yagi, 2013) was the social aspect that involved the managers, policy-makers and the governing body in power.

Based on the management of coastal area, all the citations above did mention the involvement of social aspect and its importance for an effective adaptive management in the said area. It is, therefore, the monitoring data should be interpreted for the understanding of public society. Reporting the baseline levels of pollutants is of paramount importance from monitoring point of view. However, without application of such chemical pollutant monitoring data to associate to human health, our monitoring study would probably be considered as not an intensified priority study. Therefore, it is recommended that both ERA and HHRA should be investigated in addition to the reports of monitoring data.

Basically, there are two pathways in which the metals in the sediments could reach humans. The schematic diagram of both direct and indirect pathways of metals in sediments potentially posing health risk is presented in Figure 1.

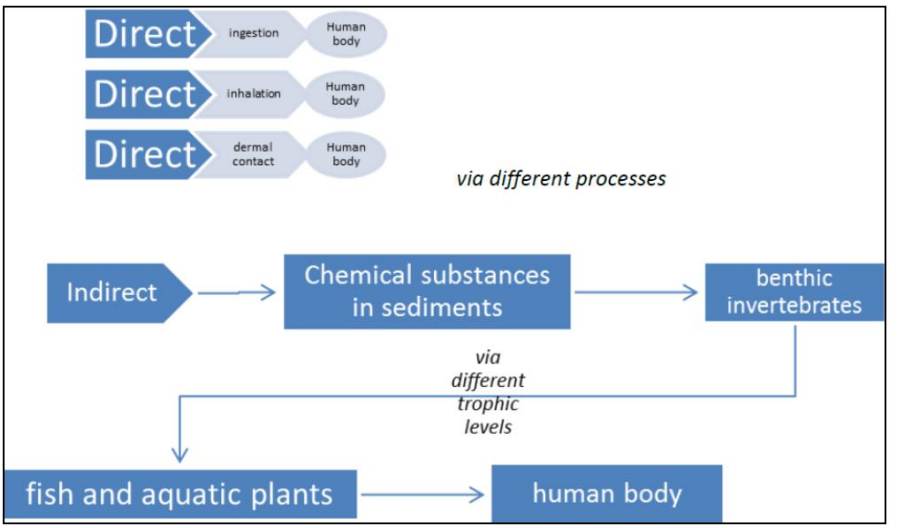

Figure 1. The schematic diagram of both direct and indirect pathways of metals in sediments potentially posing health risks.

Both direct and indirect pathways are probable to exhibit a role in registering the sediment-bound metals into human body (Perrodin et al. 2014). Despite this concern, there are limited studies focusing or investigating the impacts of sediment-bound metals to human health risk directly, judging from the current literature.

For direct pathway, the heavy metals bound to beach sand particles could enter human body by inhalation of the sand or dust particles and direct ingestion via hand-to-mouth action (Duggan and Inskip 1985). Therefore, this implies that the humans particularly children playing on the beaches could be potentially unprotected to these metal contaminants in the sands. This direct health risk of sediment-bound metals to human is recently reported by Zhu et al. (2016). Zhu et al. (2016) studied the health risk of trace metals in surface sediments from Qinhuangdao (China) which is a seashore tourist city and they found that there was no potential health risk of exposure to metals by routes of ingestion or inhalation.

For indirect pathway, there are many steps until the chemical substances in sediment reaches human body. Briefly, the chemical substances in sediment give an adverse effect for benthic organisms when they are highly

accumulated in benthic organisms. Then, the chemical substances remove to fish from benthic organisms by means of bio-accumulation. The human is exposed to the chemicals by consuming the fish containing harmful toxic chemical substances and these chemical substances give adverse effect on human body.

4. PROBLEMS AND CHALLENGES

In many monitoring studies, sediments are sometimes not collected instead of water samples. In the study of water quality, water samples are the target samples but not the sediments. Even though sediments have a great association with the water quality in the aquatic ecosystem, only the water samples are collected due to objective of the study and justification of the monitoring study.

Environmental sediment is only one the abiotic matrices found for the studies of various chemical pollutants in the coastal ecosystem. Some studies did analyze water and sediments for ecotoxicological studies. For instance, Okamura (1996) collected surface water and sediment samples for ecotoxicity screening. Li et al. (2017a) reported the heavy metal contamination in the seawater and sediment of Yalujiang Estuary.

Also, living organisms and habitat sediments were also sampled for the monitoring studies. Harino et al. (2007) collected sediment and mussels from Otsuchi Bay, for the measurements of organotin compounds (OTs) and representative booster biocides. Yap et al. (2002) sampled mussels *Perna viridis* and their surrounding surface sediments from the west coast of Peninsular Malaysia and analyzed for heavy metals in both samples. The snails *Telescopium telescopium* and their surrounding surface sediments were also collected to assess digestive caecum and tissue redistribution in gill of the snails by Yap et al. (2012). Jeelani et al. (2017) determined the trace metal levels in the plants and sediment from Suoxu River (China).

Li et al. (2017a) presented the baseline concentrations of polychlorinated biphenyls and organochlorine pesticides, and heavy metals in the sediments and marine organisms in Liaohe Estuary. Yap et al. (2015)

investigated heavy metal levels in fish tilapia and their habitat surface sediments while Cheng and Yap (2015) also measured the toxic metals in the mangrove snail and their habitat sediments too. Similarly, Bastami et al. (2015) reported the heavy metal levels in the sediments and mullet *Liza klunzingeri*.

According to Simons and Smith (2009), the data from the Texas National Coastal Assessment program provided a more complete assessment of water and sediment quality than the traditional report, with better spatial analysis. The monitoring of pollutants in the sediments is highly associated to Sediment Watch and the best part of the paper was the joint project by two different teams. They work together with the monitoring study that included sediment and water quality monitoring, and this could aid as a catalyst to a constant monitoring program.

Therefore, sediment sample is only one of the environmental matrices in the environmental monitoring study of chemical pollutants. The more biotic and abiotic samples will add to our understanding on a specific subject under investigation. Perhaps, the best answer why sediments are selected among other environmental samples is that the sediments are more persistent, less variable and more consistent in the aquatic environment (Bryan and Langston 1992). The sediments can be considered a sink for a variety of chemical pollutants such as heavy metals. Furthermore, although chemical substances in water and sediment samples are analyzed, some chemical substances in biological samples cannot be analyzed because of difficulty in the accuracy of analytical methods. Therefore, it is important to develop the integrated analytical methods (IAMs) for biological samples and water samples in line with Sediment Watch. If these IAMs can be established, Sediment Watch will become an excellent method to evaluate environmental problems.

5. MANAGEMENT OF CONTAMINATED SEDIMENTS

To manage the contaminated sediments, many issues and problems can be raised up. Leschine et al. (2003) stated that there was a clear pro-

environment and pro-development advocacy coalitions for the Puget Sound's contaminated sediment problem. The state's sediment management policy was highly dependent on the dilemma choice between political and economic preference. According to Nava et al. (2011), terrestrial and marine ecosystems are decreasing globally due to poorly planned resource use and environmental degradation. Therefore, Sediment Watch can be justified as an important environmental characterization in the management of contaminated sediments.

Pacheco et al. (2007) stated that an integrated technique of practical and interdisciplinary assessment is needed in the coastal management of the interactions between social-economic interests and the coastal environment. They reported that fishing, aquaculture, port activities, sediment mining, tourism and salt extraction all occurred in these ecosystems but are often in conflict with each other. To deal with sediments to manage the coastal environment is not highlighted in Pacheco et al. (2007)'s paper but the effect of sediment mining could have a good relationship with Sediment Watch.

6. CONCLUSION

Sediment Watch could be used as a management strategy in managing sustainable coastal environment. However, its success is challenged by the complication of society, economy policy and environmental involvement. Interestingly, there were no papers published about trace metals and heavy metals in sediments from Japan in the present search between 2015-2017. However, this should be interpreted with cautions. Firstly, the infamous Minamata disease caused by methyl-Hg contamination in 1960s was a very serious environmental and health problem in Japan. Never the least, nowadays, the current accepted rate on papers about heavy metal pollution in sediments from Japan in the international journals is low. This is because the heavy metal contamination in Japan is not as major as international contamination scenarios such as from China. Therefore, the editors of international journals would consider that these manuscripts do not contain

new findings or low in novelty. As a result, many such papers are published in minor Japanese journals.

Based on the present review of different areas and countries, provision of monitoring data of chemical pollutants in the sediments collected from a wide geographical area, is undoubtedly an essential research business in the past, present and future. Judging from the fact that Kilunga et al. (2017) reported the baseline data of toxic metals, and organic micro–pollutants, in sediments from tropical urban river, the trend of such monitoring studies using Sediment Watch would continue in future especially in developing countries such as China, other Asian and African nations. The lacking point is the ecological risk which is not fully assessed based on the present review. Its HHRA is also important to understand the degree of exposure to workers, in direct or indirect contact with the sedimentary components of the study sites at coastal area with public concerns. All in all, besides acting as baseline monitoring data for future reference, this review proposes Sediment Watch for the effective management of contaminated sediments in the coastal area around the world besides consideration of social-economic factors.

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Chapter 2

ECOLOGICAL RISK ASSESSMENTS OF HEAVY METALS IN POLLUTED DRAINAGE SEDIMENTS FROM THE MALACCA INDUSTRIAL AREA AND THE MALACCA RIVER, MALAYSIA

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ABSTRACT

The surface sediment of drainages of Malacca Industrial Area (MIA) and Malacca River were analysed for Cd, Cu, Fe, Ni, Pb, and Zn. The order of non-resistant (NR) of the metals was Zn (82.3%) > Cd (72.1%) > Ni (66.1%) > Cu (60.4%) > Pb (54.6%)> Fe (19.3%). This indicated that Cd, Ni, Pb, Cu and Zn were the most prevalent metals in the NR fractions. The ranges of total metal concentrations (mg/kg dry weight) were 1.88–7.01 for Cd, 18.9–1689 for Cu, 26.0–850 for Ni, 56.5–307 for Pb, and 75.4–312 for Zn while for Fe, it ranged from 1.76 to 6.15%. Based on ecological risk assessment and geochemical fractions, it was concluded that sites at 1 (drainage at Power Weld), 4 (Malacca River-2) and 7 (drainage at Omega) were polluted by heavy metals. Based on potential ecological risk index (PERI), sites 1 and 7 were also categorized as 'considerable ecological risk'. Therefore, it was evidently shown that elevated levels of heavy metals in the drainages at MIA and Malacca River sediment were most probably attributed to untreated (or incomplete treatment of) industrial effluents. Therefore, future mitigation of the heavy metal pollution at the study areas should be given priority in future sustainable developmental programs.

Keywords: Heavy metals; Geochemical fractions; Ecological risks; Drainage sediments

INTRODUCTION

Sediment is an important component of an aquatic ecosystem. It is not only the place where pollutants accumulated from the water body, but also as a secondary pollution source which has potential to impact the water quality as well as the biota of the ecosystem (Wang et al. 2011; Wong et al. 2017). The heavy metal contamination (HMC) in the river sediment has detrimental impact on the living organisms in the aquatic environment and poses a potential threat to human health (Wang et al. 2011). It is crucial that the risks posed by HMC to the environment to be characterized and regularly evaluated to ensure that the possible occurrence of future pollution can be discovered earlier and be rectified before it causes permanent damage to the ecosystem health.

Drainages are subjected to a large input of nutrients, heavy metals (HMs), and the enhancement of sedimentation due to human activities (Nsenga Kumwimba et al. 2016). However, the influence of different human activities and various types of land uses on the distribution and associated environmental risk of HMs in rivers, ditches/drainages in Malacca Industrial Area (MIA) and Malacca River (MR) remains largely unclear, which is needed for future water management.

One of the aspects of assessing the anthropogenic inputs of HM pollutants into an ecosystem is to analyse the geochemical speciation of HMs in the sediments. The analysis of HM speciation in sediments is normally achieved by sequential extraction procedure (SEP), which is an approach for investigating the different forms of HMs in sediment (Tessier et al. 1979; Badri and Aston 1983). Several SEPs have been developed to determine the metal distribution of water-soluble species and immobilized resistant forms in mineral lattices in operationally defined fractionation (Lopez-Sachez et al. 1996). Most of these methods are a derivative of the general technique proposed by Tessier et al. (1979).

Application of geochemical fractionations of HMs has been widely reported in the literature from various parts of the world such as from Kor River (Iran; Sheykhi and Moore 2016), Koumoundourou Lake (Greece; Hahladakis et al. 2016), Dan River (China; Meng et al. 2016), Golfe-Juan

coast (Mediterranean; Tiquio et al. 2017), Olifants River (South Africa; Moyo et al. 2015), Zabol (Iran; Javan et al. 2015), Lingdingyang Bay (South China; Cao et al. 2015), Yellow River (China; Ma et al. 2016), Sungai Buloh (Malaysia; Nemati et al. 2011) and Langat River (Malaysia; Wong et al. 2017).

Although the total concentrations of a metal in sediment does not necessarily indicate its mobility, availability, or toxicity (Lopez-Sachez et al. 1996), many of such monitoring data are still reportedly published in the literature. This obviously indicates that such concentrations of the metal in the sediments are still of relevancy from ecotoxicological and of public concerns. In this study, two approaches were deployed to assess ecological risks for HMs in the sediments.

The first approach was based on total metal concentrations are i) comparisons with sediment quality guidelines (SQGs), ii) geochemical pollution indexes (Igeo), and enrichment factor (EF), iii) contamination factor (Cf), potential risk of individual metal (Er) and potential ecological risk index (PERI), which are proposed by Hakanson (1980).

Originated from Long and Morgan (1990), the SQG is a tool to evaluate sediment chemical data in relation to possible adverse effects on aquatic biota. The SQGs were proposed to be used as benchmarks for evaluating sediment chemistry to identify situations that are potentially harmful to the aquatic organisms associated with bed-sediments. This would help set targets for long term aquatic ecosystem health sustainability management (CCME 1999).

These SQGs are developed for marine and estuarine ecosystems (Long et al. 1995; Long and MacDonald, 1998) via (a) the effect range low (ERL)/effect range median (ERM)/interim sediment quality value-low (ISQV-low) and (b) the threshold effect level (TEL)/probable effect level (PEL)/interim sediment quality value-high (ISQV-high) values. O'Connor (2004) has made a clarification that SQG's ERL is not a threshold chemical toxicity in sediment and there is no basis for the assumption of pollutant concentration above ERL that would increase the probability of toxicity. However, there are still multiple recent HM risk assessment studies that are employing ERL-ERM-based SQG (Long and Morgan 1990; Amin et al.

2009; Garcia et al. 2011; Muhammad Ali et al. 2015). Therefore, the ERL and ERM approach of risk assessment is still a reliable approach for HM risk assessment. In the present study, the HM levels in the sediment were compared in their SQGs with multiple approaches (ERL, ERM, TEL and PEL) to assess and deduce the possible environmental impact of the metal-contaminated sediments.

The second sub approach is the ecological risk assessment (ERA) by Hakanson (1980). This has been widely applied in several ERA-based studies. In Asian region, there were such reports from Khuzestan coastal waters, Iran (Madiseh et al. 2009), Northern Bohai and Yellow Seas, China (Luo et al. 2010), Dongjiang Harbor, China (Guo et al. 2010), Yangtze Estuary, China (Zhao et al. 2012), Lake Cıldır, Turkey (Kukrer et al. 2014), Ulsan Bay, Korea (Ra et al. 2014), and mangrove sediments of Peninsular Malaysia (Cheng and Yap 2015).

The second approach was based on metal geochemical fractions (GFs) in the sediment. Two values were calculated namely 1) ratio of non-resistant (NR) to resistant (R) fractions of HMs in the sediments (Yap 2010), and risk assessment code (RAC) (Perin et al. 1985).

The objectives of the present study were to estimate the ecological risk assessments based on 1) SQGs, 2) two geochemical pollution indexes, 3) PERI, 4) ratio of NR to R fractions of metals, and 5) the RAC.

2. MATERIALS AND METHODS

2.1. Sampling

The surface sediments (0-5cm) from 4 sites in the Malacca River (MR) and 6 sites in the drainages of Malacca Industrial Area (MIA), were collected on December 15th, 2006 (Figure 1). The site descriptions are presented in Table 1. The collected sediment samples were transferred into an acid-washed polyethylene bag and brought back to laboratory for temporary storage and analysis.

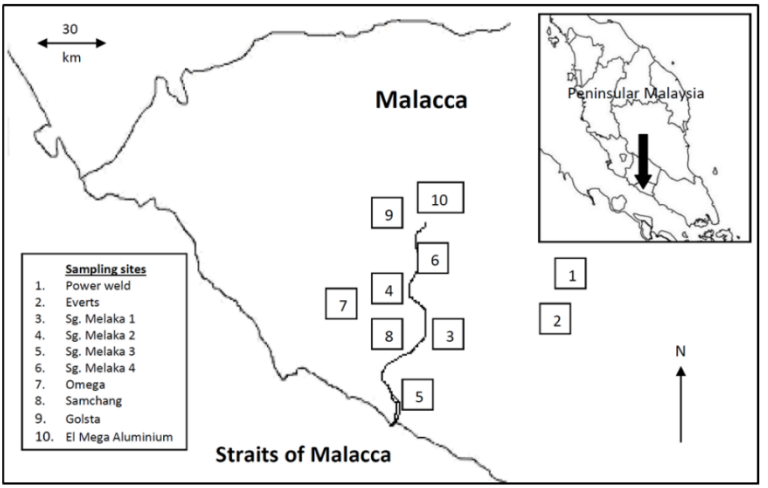

Figure 1. Map showing sampling sites in Malacca area.

Table 1. Site descriptions of surface sediments collected from the drainages in the Malacca Industrial Area, and Malacca River.

No.	Sites	Description of sampling site
1	Power Weld Sdn Bhd (PWeld) [drainage]	Electrode products.
2	Everts (M) Sdn Bhd (Everts) [drainage]	Balloon products.
3	Bt. Berendam Bridge at Malacca River (Malacca-1) [river]	Near an industrial area.
4	Tkg. India Bt. Berendam at Malacca River (Malacca-2) [river]	An industrial area, and residential area.
5	Hang Jebat Bridge at Malacca River (Malacca-3) [river]	An urban area, residential area, and tourism area.
6	Malim Bridge at Malacca River (Malacca-4) [river]	An industrial area, and residential area.
7	Omega Semiconductor Factory (Omega) [drainage]	Semiconductor products.
8	Samchang Precision Factor (Samchang) [drainage]	Semiconductor products.
9	Golsta Factory (Golsta) [drainage]	Chemical products.
10	El Mega Aluminium Factory (El Mega) [drainage]	Aluminium products.

Before the analysis, sediment samples were oven-dried at 60°C for at least 16 hours until constant dry weights. Thereafter, the dried sediment particles were sieved through a 63 µm stainless steel sieve. During the sieving process, the samples were also shaken vigorously to produce homogeneity.

2.2. Sample Digestion and Metal Analysis

The analyses of total concentrations of Cd, Cu, Fe, Ni, Pb and Zn in sediment samples were done based on direct aqua-regia method. About one gram of each dried and sieved sample was weighed and digested in a combination of concentrated HNO_3 (AnalaR grade, BDH 69%) and $HClO_4$ (AnalaR grade, BDH 60%), in the ratio of 4:1. The digestion was initially conducted at low temperature (40°C) for 1 hour and then the temperature was increased to 140°C for 3 hours until the samples were fully digested, with no brown fumes could be observed. The resulting solutions of the digestion were then diluted to a volume of 40ml by adding double distilled water. The samples were then filtered through filter papers (Whatman no. 1, pore size 11µm) and the filtrates were stored in acid-washed pill boxes until metal determination.

Modified sequential extraction procedure (SEP) from Badri and Aston (1983) and as used by Yap et al. (2002), was used to determine the geochemical fractions (GFs) of Cd, Cu, Fe, Ni, Pb and Zn in the sediments. This SEP could separate the metals in the sediment into four GFs namely (a) easily, free, leachable or exchangeable (EFLE; F1) fraction, (b) acid-reducible (AR; F2) fraction and (c) oxidizable-organic (OO; F3) fraction. The last fraction is a resistant (R; F4) fraction.

Flame Atomic Absorption Spectroscopy (FAAS; Perkin Elmer Model AAnalyst 800) was used to determine the concentrations of Cd, Cu, Fe, Ni, Pb and Zn. The data were presented in mg/kg dry weight (dw).

To ensure the accuracy and credibility of the measurements, some pre-caution steps were performed. During metal analysis, a quality control sample was routinely analysed to ensure the accuracy of the analysis. The metal recovery of the quality control samples was acceptable at 90-110%. All glassware and equipment used during sample processing and metal analysis were soaked in 10% HNO_3 to wash away the possible metal contaminant. For the quality control for SEP, the mathematical summation of all four fractions (EFLE + AR + OO + R) was compared to the result of direct aqua-regia digestion. The recoveries were acceptable at 90 to 105% for all six metals and their correlations were significant ($p<0.05$) with each

other. Certified Reference Materials (CRM) for Soil (International Atomic Energy Agency, Soil-5, Vienna, Austria) was used to assure the quality of direct aqua-regia method. The recoveries for all metals of the CRMs were found to be satisfactory (90-110%).

The statistical analysis of the data was carried out using Statsoft STATISTICA for Windows (Version 6.12). Pearson' correlation analysis was used to determine the correlation of variables among the samples at significance level of 0.05.

2.3. Data Treatment

2.3.1. Geoaccumulation Index (I_{geo})

The values of I_{geo} were calculated according to Muller (1969)'s formula:

$$I_{geo} = \log_2(C_n/(1.5 \times B_n)$$

where C_n is the total HM concentrations in the sediments and B_n is the "preindustrial reference values" (PRV; unit = mg/kg dw; Hakanson, 1980) which act as geochemical background values for each metal. The PRV for Cd, Cu Pb and Zn was 1.0, 50, 70 and 175, respectively (Hakanson, 1980). Owing to the absence of the PRV of Fe and Ni, they were referred to "upper continental crust" from Wedepohl (1995) and Rudnick and Gao (2003), in which the values were 3.09% and 47.0 mg/kg dw, respectively (Table 2).

To minimize the possible variation in background metal concentrations which might be contributed by lithogenic variations, a factor of 1.5 was introduced into the formula (Al-Haidarey et al. 2010; Binta Hasan 2013). It permits the content fluctuation of the metals in sediment and also some negligible anthropogenic influences (Loska et al. 1995). Muller (1969) has classified the resulting Igeo values into six classes according to the extent of the metal geo-accumulation.

2.3.2. Enrichment Factor (EF)

The EF in this study was determined using a formula defined by Buat-Menard and Chesselt (1979), with Fe as a normaliser:

$$EF= (C_n/C_{Fe})_{sample}/(C_n/C_{Fe})_{crust}$$

where $(C_n/C_{Fe})_{sample}$ is the metal to Fe ratio in the sediments; $(C_n/C_{Fe})_{crust}$ is the metal to Fe ratio in the earth crust which considered as pre-industrial unpolluted metal value of sediment.

The normalisation using Fe is necessary to correct for differences in sediment grain size and mineralogy (Schi and Weisberg 1999). The use of Fe as a normaliser was made since Fe is a major sorbent phase for HMs and is a quasiconservative tracer of the natural metal-bearing phases in fluvial and coastal sediments (Schiff and Weisberg 1999). According to Binta Hasan (2013), natural resources (98%) vastly dominated the input of Fe. In this expression, the normaliser (reference element) is assumed to have little variability of occurrence, and is present in trace concentration in the examined environment (Loska et al. 1995). The degrees of EF are categorized by Taylor (1964) and Birth (2003).

2.3.3. Ecological Risk Assessments

The contamination factor (C_f) was calculated to describe the contamination status of metals in the sediments (Hakanson 1980). C_f was calculated following a formula below:

$$C_f= C_{sed}/C_{ref}$$

where C_f is the contamination factor; C_{sed} is the mean metal concentration in the sediment; C_{ref} is the PRV of metals in the sediments. Hakanson (1980) has classified the C_f values into 4 categories.

According to Hakanson (1980), the potential risk for individual metal (E_r) can be calculated using a formula below:

$$E_r= TR \times C_f$$

where TR is the toxic-response factor for a metal (Table 2). Since the TR value for Fe was not available, the E_r for Fe was not calculated. C_f is the contamination factor for the same substance. The E_r for each metal was defined according to Hakanson (1980)'s standard.

The potential ecological risk index (PERI) was calculated as below:

$$PERI = \sum E_r$$

The PERI can be described according to categories suggested by Hakanson (1980).

3. RESULTS AND DISCUSSION

3.1. Total Concentrations of Heavy Metals

The minimum, maximum, average value and standard deviation of HMs distribution in the four GFs from all sites are presented in Table 1. The ranges of total metal concentrations (mg/kg dw) were 1.88–7.01 for Cd, 18.9–1689 for Cu, 26.0–850 for Ni, 56.5–307 for Pb, and 75.4–312 for Zn while for Fe, it ranged from 1.76–6.15%.

3.1.1. Sediment Quality Guidelines (SQGs)

The classification of SQGs along with its effects and comparative results are presented in Table 2. It is important to determine whether the total concentrations of HMs in sediments would pose a threat to aquatic life. In the present study, the sediment risk of each metal investigated is assessed by three sets of SQGs namely; 1) ERL and ERM by Long et al. (1995), 2) the lowest effect level (LEL) and severe effect level (SEL) by NYSDEC (1999), and 3) TEL and PEL by MacDonald et al. (1996, 2003). These three sets of numerical SQGs which were directly applied (without normalization) to assess the possible risks raised from the HM contamination in sediment of the study area.

Table 2. Comparisons between total heavy metal concentrations (mean, mg/kg dw; except for Fe in %) with those cited from sediment quality guidelines (SQGs) and reference values (RVs). The values of toxic-response factors, employed in this study are also presented

Site no.	Cd	Cu	Fe (%)	Ni	Pb	Zn	References
1	7.01	1673	3.91	129	94.9	312	This study
2	2.53	111	4.64	26.0	77.6	294	
3	1.88	195	3.70	44.7	74.4	174	
4	2.37	580	1.76	222	90.4	255	
5	2.32	139	2.03	35.20	87.60	194	
6	2.21	18.9	2.48	13.10	87.2	75.4	
7	2.80	1689	4.13	850	307	294	
8	3.21	203	4.15	167	132	301	
9	4.25	268	6.15	146	142	308	
10	4.19	102	3.81	65.9	56.5	232	
Malacca River and Malacca drainage area (Overall)	1.88 - 7.01	18.9-1689	1.76-6.15	26.0 - 850	56.5 - 307	75.4-312	This study
Mangrove area of Peninsular Malaysia	1.11-2.00	5.59-28.7	1.29-4.89	-	25.36-172.6	29.35-130.3	Cheng and Yap (2015)
SQGs	Cd	Cu	Fe (%)	Ni	Pb	Zn	
Effects range low (ERL)	1.20	34.0	-	-	46.7	150	Long et al. (1995)
Effects range median (ERM)	9.60	270	-	-	218	410	Long et al. (1995)
LEL	0.6	16	2	16	31	120	NYSDEC
SEL	9	110	4	50	110	270	NYSDEC
Threshold effect level (TEL)	0.68	18.7	-	-	30.2	124	MacDonald et al. (1996)
Probable effect level (PEL)	4.21	108.2	-	-	112.2	271	MacDonald et al. (1996)
RVs	Cd	Cu	Fe (%)	Ni	Pb	Zn	
Pre-industrial reference level	1.00	50.0	-	68.0*	70.0	175	Hakanson (1980)
Upper continental crust	0.098	25.0	-	44.0	17.0	71.0	Taylor and McLennan (1995)
Upper continental crust	0.102	14.3	3.09	18.6	17.0	52.0	Wedepohl (1995)
Upper continental crust	0.09	28.0	-	47.0	17.0	67.0	Rudnick and Gao (2003)
Toxic-response factor (*Tr*)	30.0	5.00	-	2.00	5.00	1.00	Hakanson (1980)

Note: All concentrations are presented in mg/kg dw except for Fe in % and *Tr* values are unitless.

For Cd, all sites were within the range of ERL-ERM. For Cu, sites 1, 4 and 7 exceeded the levels of the ERM while the remaining sites ranged between ERL-ERM except for site 6. For Pb, all sites exceeded ERL while site 7 exceeded the levels of the ERM and other sites fell within the acceptable ranges of ERL-ERM. For Zn, all sites fell within the ranges of ERL-ERM except for site 6 (below ERL), indicating that possible adverse

effects on aquatic biota. Therefore, in general, for ERL–ERM SQGs, most of the metals are within the limits of the ERL-ERM.

According to the present study findings, we concluded that Cd, Ni and Pb were of ecotoxicological concern in the study area and that might occasionally be associated with adverse biological effects. The ERL-ERM. The ERL represents the concentration below toxic effects are scarcely observed or predicted. While the ERM indicates that above which effects are generally or always observed. In the standard of ERL-ERM SQGs, three sites with Cu levels were found above ERM. This could be potential Cu threat to ecosystem. Since the design of these SQGs are originally aimed for North American region, the criteria of the guidelines were developed and validated by using only the data of toxicity assays in sediments of US coastal region only (Long and Morgan 1990). The SQGs should be used with caution during risk assessment effort (O'Connor 2004). Despite this concern, these SQG standards have been utilized in the interpretation of sediment data from various geographical regions (Birch and Taylor 2002).

When compared to the LEL–SEL SQGs, among the metals, Cd, Cu, Ni and Pb concentrations were exceeding LEL in all sites. For Cd, all sites fell within the range of LEL-SEL. For Cu, all sites exceeded SEL except for sites 6 and 10 that fell between LEL-SEL. For Fe, sites 2, 7, 8 and 9 exceeded SEL while other sites fell between the limits of the LEL-SEL except for site 4 within LEL. For Ni, sites 1, 4, 7, 8, 9 and 10 exceeded SEL while the remaining sites fell between LEL-SEL. For Pb, sites 7, 8 and 9 fell within the range of SEL while the rest of sites were between LEL-SEL. For Zn, all sites fell between the levels of the LEL-SEL except for site 6 (LEL).

According to Thompson et al. (2005), the LEL represents the contaminant concentration below which harmful effects on benthic invertebrates are not expected. The SEL represents the concentration above which harmful effects on benthic invertebrates are possibly occurred. About half of Ni and most of Pb exceeded SEL levels. Therefore, Cu, Ni, Fe and Pb concentrations in this study were likely to cause harmful effects on the benthic invertebrates, adversely affecting the health of the ecosystem. The concentrations of Cd and Zn exceeded LEL. This indicated that both metals would potentially cause harmful effects on the benthic invertebrates since

they were not exceeding SEL. However, they would still potentially cause occasional harmful effect on the benthic invertebrates as their concentrations were still above LEL.

It is interpreted that TEL as the concentrations, below which adverse biological effects would rarely occur. Hence, it is considered to provide a high level of protection for aquatic organisms. Similarly, PEL as the concentrations above adverse biological effects would frequently occur. Hence, it is considered to provide a lower level of protection for aquatic organisms. When compared to the TEL–PEL SQGs, 100% of the concentrations of Cd, Cu and Pb in the samples were above the TEL. For Cd, sites 1 and 9 exceeded the PEL while other sites fell between TEL-PEL. For Cu, all sites exceeded PEL except for site 10 which was between TEL-PEL. For Pb, sites 7, 8 and 9 exceeded PEL while the rest of sites fell between TEL-PEL. For Zn, all sites exceeded TEL except for site 6, while sites 1, 2, 7, 8 and 9 exceeded PEL and the rest of sites fell between TEL-PEL.

Therefore, Cd, Cu, Pb and Zn levels in the sediments might pose an ecological threat, as their concentrations might cause "frequent occurrence of adverse biological effect." While some sites with the similar four metals concentrations in MIA were "contaminated" with Cd, Cu, Pb and Zn, since their metal levels in sediments exceeded TEL. However, they were not above PEL levels, indicating they were not likely to cause "frequent adverse biological effect."

In comparison to reference values (RVs) (Table 2), the Cd levels of all sites exceeded the pre-industrial reference (PIR) level (Hakanson 1980), and the upper continental crust (UCC) values proposed by Taylor and McLennan (1995), Wedepohl (1995) and Rudnick and Gao (2003). For Cu, all sites exceeded the values of PIR and all the three UCC levels, except for site 6 that had a low Cu level and only exceeded UCC value by Wedepohl (1995). For Fe, sites 1, 2, 3, 7, 8, 9 and 10 exceeded the PIR and all UCC values by Wedepohl (1995), while the remaining sites were below the all RVs. For Ni, sites 1, 4, 7, 8 and 9 exceeded all the RVs while the remaining sites were below the PIR value but higher or below the three UCC values. For Pb, all sites exceeded all the RVs except for site 10 that was below the PIR but

higher than the three UCC values. For Zn, all sites exceeded all the RVs except for sites 3 and 6. However, all the above comparisons with the RVs only provided an overall status but not as specific as those in SQGs. Concentrations of some metals exceeded the PIR and UCC values, which were indicative of enrichment. It should be noted that the total concentration of a HM only reflects the amount stored in the system, and provides no information concerning availability.

3.1.2. Ecological Risk Assessments

Figure 2 shows the values of EF, I_{geo}, CF, ER and PERI of Cd, Cu, Ni, Pb and Zn in the surface sediments from all sampling sites, in which the reference values are based on Hakanson (1980). The overall statistics are summarized in Table 3.

Table 3. Overall statistics of enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF), ecological risk (ER) and potential ecological risk index (PERI) of heavy metals based on the surface sediments from the present study

	Ni				Pb				Cu			
	EF	Igeo	CF	ER	EF	Igeo	CF	ER	EF	Igeo	CF	ER
Min	0.24	-2.96	0.19	0.39	0.65	-0.89	0.81	4.04	0.47	-1.99	0.38	1.89
Max	9.36	3.06	12.5	25.0	3.28	1.55	4.39	21.9	26.4	4.49	33.8	169
Mean	2.21	-0.25	2.50	5.00	1.48	-0.04	1.64	8.21	8.89	1.65	9.96	49.8
SE	0.94	0.55	1.16	2.31	0.26	0.21	0.33	1.63	3.35	0.62	4.06	20.3
	Zn				Cd				PERI			
	EF	Igeo	CF	ER	EF	Igeo	CF	ER				
Min	0.54	-1.80	0.43	0.43	1.57	0.33	1.88	56.4	75.2			
Max	2.56	0.25	1.78	1.78	5.53	2.22	7.01	210	389			
Mean	1.26	-0.20	1.39	1.39	2.93	1.01	3.28	98.3	163			
SE	0.18	0.20	0.14	0.14	0.39	0.18	0.49	14.6	32.7			

Note: The reference values used in the present study were based on Hakanson (1980); SE= standard error.

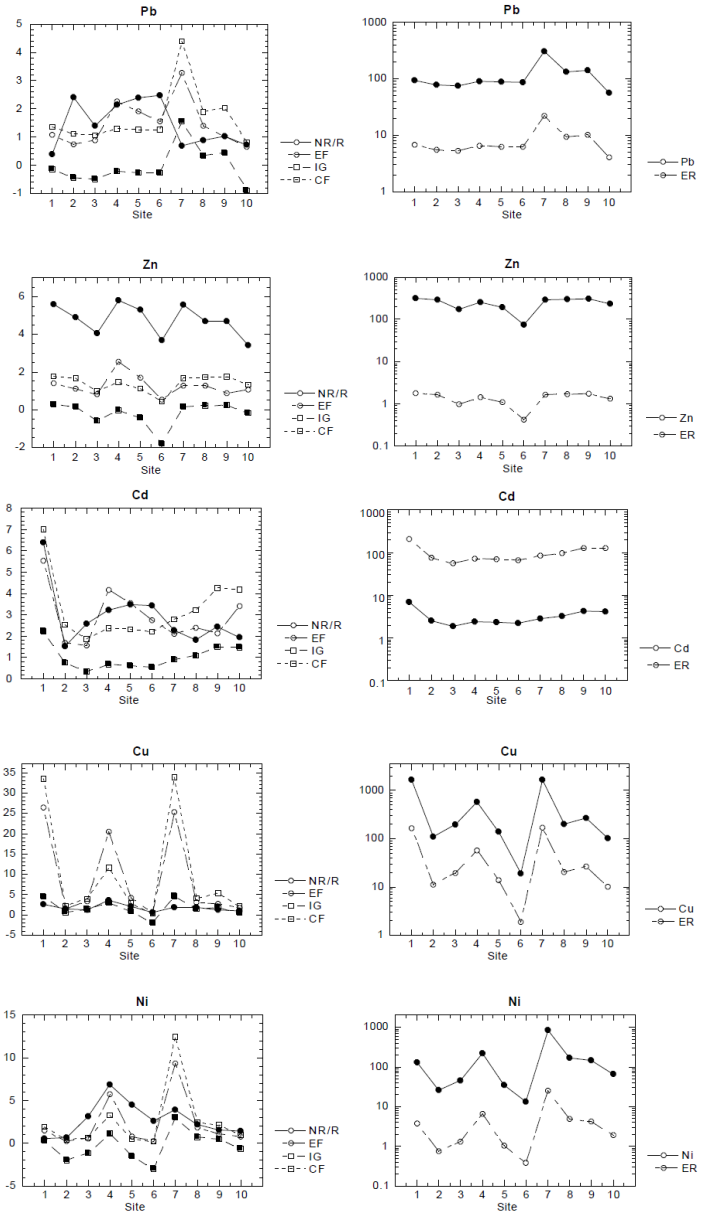

Figure 2. Ratios of non-resistant to resistant fractions (NR/R), values of enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (Cf), ecological risk (ER) and total concentration (metal) of heavy metals in the surface sediments from the present study. Note: Fe is not shown because ER cannot be calculated.

According to Sutherland (2000)'s categories, for Ni EF, sites 4 and 7 were categorized as 'significant enrichment', while the remaining sites were 'depletion to minimal enrichment'. For Cd EF, site 1 was categorised as 'significant enrichment', while sites 4, 5, 6, 7, 8, 9 and 10 were categorised as 'moderate enrichment' and sites 2 and 3 were categorised as ''depletion to minimal enrichment'. For Pb EF, sites 4 and 7 were categorized as 'moderate enrichment, while the remaining sites were 'depletion to minimal enrichment'. For Cu EF, sites 1, 4, and 7 were categorised as 'very high enrichment', while sites 3, 5, 8, and 9 were 'moderate enrichment' and the remaining sites were 'depletion to minimal enrichment'. For Zn EF, only site 4 was categorised as 'moderate enrichment' while the remaining sites were 'depletion to minimal enrichment'.

According to Muller (1969)'s categories, for Ni Igeo, sites 2, 3, 5, 6 and 10 were categorised as 'practically unpolluted', while sites 1, 8 and 9 were 'unpolluted to moderately polluted' and sites 4 was 'moderately polluted' while site 7 was 'strongly polluted'. For Pb Igeo, site 7 was 'moderately polluted, sites 8 and 9 were 'unpolluted to moderately polluted; while the remaining sites were 'practically unpolluted'. For Cu Igeo, sites 1 and 7 were 'strongly to very strongly polluted', site 4 was 'moderately to strongly polluted', sites 3, 8 and 9 were 'moderately polluted' while sites 2, 5 and 10 were 'unpolluted to moderately polluted' and site 6 was 'practically unpolluted'. For Zn Igeo, sites 1, 2, 7, 8 and 9 were 'unpolluted to moderately polluted', sites 3, 4, 5, 6 and 10 were 'practically unpolluted'. For Cd Igeo, site 1 was 'moderately to strongly polluted', sites 8, 9 and 10 were 'moderately polluted' while the remaining sites were 'unpolluted to moderately polluted'.

According to Hakanson (1980)'s categories, for Ni CF, sites 2, 3, 5, 6 and 10 were 'low contamination factor', sites 1, 8 and 9 were 'moderate contamination factor', site 4 was 'considerable contamination factor' while site 7 was 'very high contamination factor'. For Pb CF, site 10 was 'low contamination factor', sites 1, 2, 3, 4, 5, 6, 8 and 9 were 'moderate

contamination factor', while site 7 was 'considerable contamination factor'. For Cu CF, site 6 was 'low contamination factor', sites 2, 5, and 10 were 'moderate contamination factor', sites 3, 8 and 9 were 'considerable contamination factor' while sites 1, 4, and 7 were 'very high contamination factor'. For Zn CF, sites 3 and 6 were 'low contamination factor', while the remaining were categorized as 'moderate contamination factor'. For Cd CF, sites 2, 3, 4, 5, 6 and 7 were 'moderate contamination factor', sites 8, 9 and 10 were 'considerable contamination factor' while site 1 was 'very high contamination factor'.

According to Hakanson (1980)'s categories, the CR values for Ni, Pb and Zn at all sites were categorised as 'low potential ecological risk'. For Cu ER, all sites were categorized 'low potential ecological risk' except for sites 4 as 'moderate potential ecological risk' while sites 1 and 7 were 'high potential ecological risk'. For Cd ER, sites 2, 3, 4, 5, and 6 were 'moderate potential ecological risk' while sites 7, 8, 9 and 10 were 'considerable potential ecological risk' and site 1 was 'high potential ecological risk'.

For PERI based Cd, Cu, Ni, Pb and Zn, it was found that sites 2, 3, 4, 5, 6, 8 and 10 were categorized as 'low ecological risk', site 9 was 'moderate ecological risk' while sites 1 and 7 were 'considerable ecological risk' (Hakanson 1980). Wang et al. (2011) used the drainage river in North China as a study area with a selection of representative cross sections for measurement of HM pollution. They also determined the PERI based on the metals data in the sediment. Sheykhi and Moore (2016) investigated the speciation and environmental risk of nine metals in sediment samples collected from Kor River, Iran. "Individual contamination factor," "global contamination factor," and "Environmental Risk Index (ERI)" were used for their study. They revealed that the levels of As, Cr, Ni, Pb and Zn were mostly related to "Fe-Mn Oxide" fraction, "organic" fraction and "residual" fraction. However, Cd and Mo were predominantly accumulated in carbonate fraction.

3.2. Geochemical Fractionations of Heavy Metal Distributions

3.2.1. Metal Distribution

Distributions of four GFs of HMs in percentages of the surface drainage sediments collected from all sampling sites, are given in Figure 3. Table 4 shows the overall statistics of HM concentrations in the four GFs and their percentages of each fraction. The HMs associated with different GFs in the surface sediments collected from MIA and MR follow the following orders:

Cd:	F2	>	F4	>	F3	>	F1
Cu:	F3	>	F4	>	F1	>	F2
Fe:	F4	>	F3	>	F2	>	F1
Ni:	F3	>	F4	>	F2	>	F1
Pb:	F4	>	F3	>	F2	>	F1
Zn:	F2	>	F3	>	F1	>	F4

As shown in Figure 3, Cd was abundant in F2 fraction followed by F4, F3 and F1 fractions. The abundance of Cd in F2 fraction was an indication of the fact that the source was related to Fe-Mn oxides (F2) phase of the sediments collected from the present study. Besides the industrial discharge, the presence of Cd could also be as the result of road traffic, which has been described as an important source of Cd emission (Liu et al. 2012).

The F1 fractions were weakly bound metals that were associated to anthropogenic inputs. The metals in this fraction are chemically exchangeable and associated to carbonates in the sediment or soil. These metals could be easily mobilized by equilibrating themselves to aqueous phases, becoming bioavailable and causing environmental toxicity (Canuto et al. 2013). The metals associated with Fe-Mn oxides (F2) and organic matter (F3) are capable to regain their mobility and hence their bioavailability when the surrounding has becoming reducing and oxidizing (Canuto et al. 2013). The rest of the metals are mainly associated to detrital

and lattice origin or primary mineral phases. These metals form the F4 fraction. The metals in this fraction are characterized as strongly associated to soil minerals and hence, they are hardly mobilized and low in bioavailability. The abundance of Cd (72.1%) in NR fractions indicated that a significant amount of the Cd in the sediments may be of anthropogenic origin.

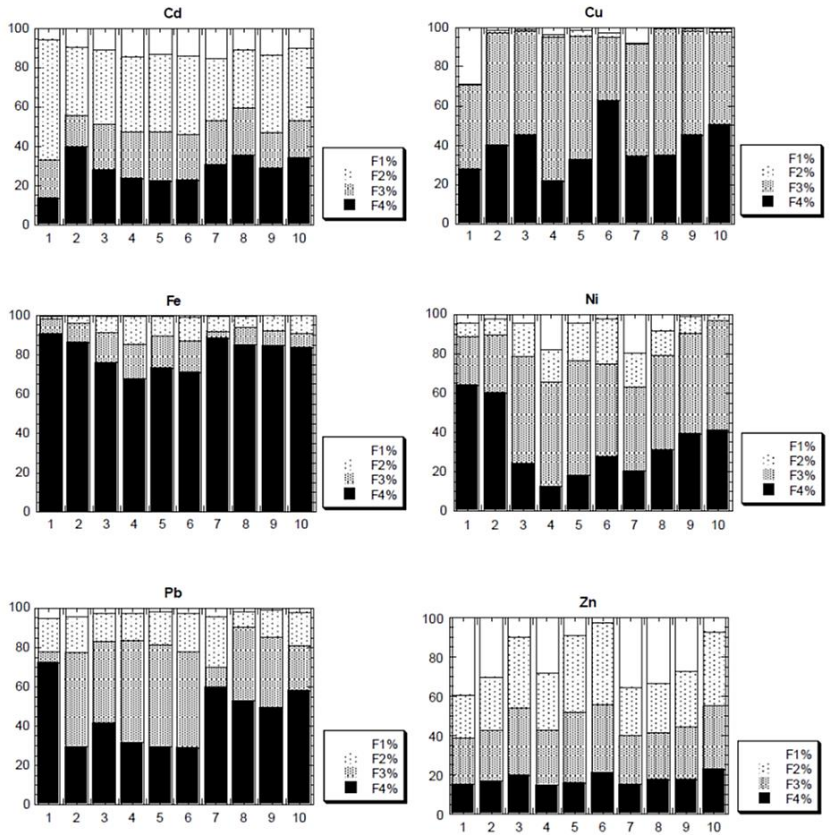

Figure 3. Distribution of four geochemical fractions of heavy metals in percentages, of the surface drainage sediments collected from all sampling sites in Malacca. F1=EFLE; F2= AR; F3= OO; F4= R.

Table 4. Overall concentrations (minimum to maximum, mean ± standard error (SE), mg/kg dry weight) of Cd, Cu, Fe, Ni, Pb and Zn in the four geochemical fractions and their percentages of each fraction, of the surface drainage sediments collected from all sampling sites in Malacca

Cd	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	0.19	5.91	0.65	29.3	0.30	16.1	0.39	13.5	60.2	1.51
Maximum	0.55	15.4	4.60	61.2	1.46	24.9	1.19	39.8	86.5	6.39
Mean	0.32	11.8	1.25	38.8	0.61	21.5	0.75	27.9	72.1	2.91
SE	0.03	0.90	0.38	2.73	0.10	0.97	0.09	2.42	2.42	0.44
Cu	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	0.61	0.36	0.41	0.18	6.85	31.9	13.5	21.8	37.1	0.59
Maximum	354	28.7	8.26	2.76	619	73.2	375	62.9	78.2	3.58
Mean	47.5	4.90	3.09	1.19	227	54.3	135	39.6	60.4	1.75
SE	35.1	2.74	0.84	0.27	69.7	3.70	39.4	3.78	3.78	0.28
Fe	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	0.70	0.00	369	1.04	1184	3.46	431	67.7	9.15	0.10
Maximum	259	0.85	3832	13.9	5093	17.7	43844	90.9	32.3	0.48
Mean	138	0.45	2545	7.84	3528	11.0	25247	80.7	19.3	0.25
SE	24.6	0.08	336	1.20	345	1.56	4088	2.54	2.54	0.04
Ni	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	0.13	0.14	1.81	3.10	6.68	24.9	4.01	12.7	36.1	0.57
Maximum	186	19.7	163	22.9	404	58.3	191	63.9	87.3	6.86
Mean	27.0	6.44	29.4	13.2	93.3	46.5	54.2	33.9	66.2	2.75
SE	18.4	2.18	15.5	2.00	37.8	3.53	17.8	5.47	5.47	0.62
Pb	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	0.77	1.03	6.22	8.06	3.43	5.47	17.6	28.8	27.8	0.38
Maximum	11.1	5.41	68.4	25.9	51.3	51.9	158	72.2	71.2	2.47
Mean	2.80	2.84	16.9	16.5	29.6	35.3	46.6	45.4	54.6	1.45
SE	0.95	0.44	5.82	1.46	4.68	5.38	13.8	4.87	4.87	0.26
Zn	F1	F1%	F2	F2%	F3	F3%	F4	F4%	NR%	NR/R
Minimum	2.07	2.61	32.9	21.8	27.5	23.5	16.90	14.7	77.3	3.41
Maximum	112	39.6	97.3	41.5	92.7	36.0	60.3	22.7	85.3	5.81
Mean	59.6	22.3	66.1	31.0	63.0	29.0	39.1	17.7	82.3	4.78
SE	13.9	4.30	5.09	2.20	5.32	1.52	4.07	0.87	0.87	0.26

Note: Non-resistant (NR)% = 100% -F4%.

For Cu, the F3 fraction was predominant (54.3% of the total content), followed by the F4, F1 and F2 fractions. Cu showed a greater content in the F3 fraction compared to the other metals. In polluted sites in site 1, Cu emission could be adsorbed by sediment particles exchange and specific

adsorption. Precipitation is also a major contributor on the retention of Cu in polluted sediments (Pagnanelli et al. 2004). With high occurrence of Cu in F3 fraction, organic matter in sediment from MIA was the most significant scavenger within NR fractions. Cu was easily associated to organic matters due to the easy formation of stable organic-Cu compounds with other organic substances (Stumn and Morgan 1981). Therefore, Cu is more easily adsorbed than other metals; the association of Cu^{2+} ions for soluble organic ligands may significantly elevate their mobility in the sediment (McLean and Bledsoe 1992). The present study revealed that the Cu NR percentages ranged were from 50% to 80%. Mat and Maah (1994) reported that about 56.5% of total Cu in sediment at Batu Kawan, a site close to Bukit Tambun near River Jejawi, was due to NR fraction of Cu. The primary sources of anthropogenic discharge of Cu included domestic wastewater, manufacturing processes, and the dumping of sewage sludge (Duc et al. 2013).

For the most abundant metal, Fe was dominated in the F4, followed by F3, F2 and F1 fractions. The dominance of Fe in R fraction indicated the Fe levels in the sediments were inert and poorly mobilized, suggesting they were mostly derived from natural origins (Cuong and Obbard 2006).

Therefore, there was low level of pollution of Fe in the studied region. Hence, the bioavailability potential of Fe was low and unlikely to be bioaccumulated into food chain. Several other studies have also agreed the dominance of Fe in F4 fraction (Ren-Ying et al. 2007; Passos et al. 2011). Natural mechanisms may impact the accumulation of Fe in the sediment (Gümgüm et al. 1994). The elevated level of Fe in the sediments (average 65 to 90% for all sampling sites) was found in Power Weld (90.9%). This is mainly due to the fact that Fe is the fourth most abundant element comprising 5% of earth crust weight. The leaching and weathering of parent rocks could attribute to R fraction in sediment (Cao et al. 2015).

Ni was mainly bound to the F3 and F4 fractions, followed by the F2 and F1 fractions. Anthropogenic factors contributed to the elevation of Ni concentrations in most sampling sites which ranged from 55 to 90% in NR fraction, especially in Malacca-2 (87.3%). This indicated the industrial discharges delivered by the drainages. Wong et al. (2017) found that urban

site and agricultural site were not necessarily having higher sediment Ni concentration. However, they found that the percentages of NR fractions were indeed higher in urban site and agricultural site, implying possible anthropogenic inputs.

Pb was found mainly in association with the F4 and F3, followed by the F2 and F1 fractions. Pb concentrations observed in the present study suggested NR fraction was slightly more compared to R fraction. It has been determined early that not only the effect of industrial wastes but also natural mechanism may affect high accumulation of this metal in sediments. The present study showed Pb levels ranged from 55 to 75% of NR fraction in which the highest percentage (71.2%) was found at Malacca-4. This indicated that anthropogenic Pb could have contributed to the elevation of total Pb concentration in the sediment in Malacca-4. Therefore, Cu, Ni and Pb exhibited high percentages (Cu: 54.3%; Ni: 46.5%; Pb: 35.3%) in the F3 fraction. This indicated that Cu, Ni and Pb were strongly complexed, and they were released following either degradation of organic matter, or oxidation of sulphides to sulphates or both (Passos et al. 2011).

Zn levels in the MIA were mainly accumulated in F2 and F3 fractions, followed by F1 and F4. Similar with the case of Cd, there was high accumulation of Zn in F2 fraction (>30%). Therefore, both Cd and Zn are strongly related to Mn and Fe oxides and hydroxides. The relation between HMs and Fe and Mn oxides and hydroxides in sediments have been reported to be associated with industrial effluents (Cao et al. 2015; Moyo et al. 2015; Sheykhi and Moore 2016). The F2 fraction associated metals were consistent with the emission of industrial wastes from various industries (Cao et al. 2015).

Metal geochemical fractionation plays a significant role in the toxicity and mobility nature of the metals emitted into river environment by natural or anthropogenic pathways (Yap et al. 2002; Canuto et al. 2013; Wong et al. 2017). GFs analysis is proven to be a competent method in identifying the possible origin of HMs (lithogenic or anthropogenic source) in a fixed region. The metals associated to anthropogenic origins are mainly concentrated in NR fractions. Lithogenic metals are predominantly

appearing in R fraction that are significantly harder to be extracted (Rubio et al. 2000; Passos et al. 2010).

As shown in Figure 3, F3 and F4 fractions constituted the largest proportion of metals in sediment from the present study. The metals in F1 and F2 fractions were less significant in comparison.

3.2.2. Ratio of Non-Resistant to Resistant Fractions

The ratios of NR/R for the 6 metals in all sites are presented in Figure 2 while the overall means are given in Table 4. Present study focuses on ratios NR/R fractions because this ratio has been suggested as a reliable indicator of metal pollution based on fractionation on the sediments (Yap 2010). For Cd, the NR/R ratios were >1.0, with the most distinct site 1 with 6.39, in which the NR was dominated by F2 (61.2%), while sites 4 and 5 exceeded 3.0. For Ni, site 4 had the highest ratio (6.86), followed by site 5 (4.49), sites 3 and 7 (>3.0), sites 6, 8, 9 and 10 (1–3), while sites 1 and 2 had NR/R ratios <1.0. For Pb, sites 2, 3, 4, 5, 6, and 9 (1.02–2.47) had the NR/R ratios >1.0 while sites 1, 7, 8 and 10 with NR/R ratios <1.0. For Cu, sites 1, 4 and 5 had higher NR/R ratios (2.07–3.58), followed by sites 2, 3, 7, 8 and 9 (1.19–1.89; ratios >1.0), while sites 5 and 10 had the NR/R ratios <1.0. For Zn, all sites were found to have NR/R ratios >1.0; 3.41–4.92, with sites 1, 4, 5 and 7 with ratios >5.0 (5.31–5.81). For Fe, all sites had NR/R ratios <1.0.

The geochemical speciation of metals in the sediments from the present study is comparable to numerous reported previous studies such as Meng et al. (2016) who studied the GFs in the sediments of Dan River drainage basin. Industrial and urban sewer, agriculture runoffs and estuarine discharges were found to be impacted the metal geochemical distribution in the sediments of Moroccan Atlantic shelf (Maanan et al. 2015). Hsu et al. (2016) also reported that the occurrence of organic matters in the sediments was associated with sewage discharges from traditional and semiconductor industries. Hahladakis et al. (2016) investigated the GFs of Ni, Cr, Pb, Zn, Cu and As in eight sediment samples from Elefsis Gulf (EG) and Koumoundourou Lake at Athens, Greece. Several ecological risk indicators have been applied in their study and they concluded that EG sediments were at a "moderate pollution level."

Tiquio et al. (2017) revealed a notable metal pollution spatial gradient on Golfe-Juan coast. They reported that the metal concentrations were affected by the geochemical nature of the sediment in addition to the distance to anthropogenic sources. Moyo et al. (2015) deployed four-step SEP to study the relationships of Cd, Co, Cr, Fe, Mn, Pb, Ti, and V with GFs in the sediments of Olifants, Klein Olifants, Wilge rivers and a tributary of the Olifants River. Five geochemical phases for Zn, Fe, Cd, Pb, Mn and Ni were extracted to investigate the metal concentrations and geochemical speciation of 180 sedimentary samples from Chahnimeh-1 reservoir, Iran (Javan et al. 2015). Cao et al. (2015) reported that the Cd in the Lingdingyang Bay was accumulated mainly in acid-soluble fraction in the sediments, suggesting high bioavailability and notable anthropogenic sources.

3.2.3. Risk Assessment Code (RAC)

The RAC values based on the SEP results are presented in Table 5. This RAC was originally established by Perin et al. (1985). It has since been widely utilized as a tool to assess metal pollution (Sundaray et al. 2011) and it is a scale aimed to measure the potential mobility and risk of HMs (Perin et al. 1985). In the present study, the determination of RAC was achieved by calculating the percentage of F1 fraction against the summation of all four fractions extracted. Perin et al. (2015) has categorized the risk of RAC into 5 categories: 1) no risk (RAC<1%), low risk (1≤RAC≤10%), medium risk (11≤RAC≤30%), high risk (31≤RAC≤50%), and very high risk (RAC>50%).

The percentages of F1 fractions of all sites are presented in Table 5. As F1 is considered RAC, their percentages are compared to the RAC categories as proposed by Perin et al. (1985). For Cd, sites 3, 4, 5, 6, 7 and 9 were categorised as ‘medium risk’, while the remaining sites were considered ‘low risk’. For Ni, sites 4 and 7 were categorized as ‘medium risk’ while the remaining sites were ‘low risk’ except for site 10 as ‘no risk’. For Pb, all sites were categorised as ‘low risk’. For Cu, only site 1 was categorized as ‘medium risk; while the remaining sites as ‘low risk’ except for sites 8, 9 and 10 as ‘no risk’. For Zn, sites 1, 2, 7 and 8 were categorised

as ‘high risk’ while sites 4 and 9 as ‘medium risk’ and sites 3, 5, 6, and 10 were ‘low risk’. For Fe, all sites were categorized as ‘no risk’. Therefore, Fe having less environmental risk was present mostly in R fraction from which it cannot be easily leached out and was under the ‘No risk’ category (<1%) in all sites. However, interpretation for Pb as ‘no risk’ should be interpreted with caution. Overall, HMs introduced by anthropogenic activities did not pose a considerable ecological risk to biota in term of the speciation. Therefore, there is no consistent pattern found for all the sites and each site has a specific metal ecological risk with different percentages of F1. This is difficult to make any correlations with any ERA as previously discussed.

Table 5. Percentages of easily, freely, leachable or exchangeable (EFLE) fraction as Risk Assessment Code

EFLE %	Cd	Ni	Pb	Cu	Zn	Fe
1.	5.91	4.25	5.41	28.72	39.6	0.39
2.	9.78	2.33	4.38	1.55	30.4	0.42
3.	11.0	4.38	2.53	1.04	9.74	0.49
4.	14.3	17.91	2.46	3.59	28.5	0.62
5.	13.3	4.28	1.75	1.59	9.18	0.59
6.	14.0	2.11	2.75	2.84	2.61	0.85
7.	15.4	19.7	4.19	8.08	35.3	0.53
8.	11.0	8.22	1.79	0.36	33.4	0.56
9.	13.5	1.06	1.03	0.44	27.2	0.02
10.	10.1	0.14	2.11	0.82	7.12	0.00
RAC category	Risk		Metal in carbonate and exchangeable fraction (%)			
1	No risk		<1			
2	Low risk		1–10			
3	Medium risk		11–30			
4	High risk		31–50			
5	Very high risk		>50			

Moyo et al. (2015) used RAC to the exchangeable fraction in sediments from the Olifants revealed that most of the metals posed a medium risk to aquatic life, except for Pb, which was classified into ‘high-risk’. Based on sediment samples collected from the Chahnimeh 1 reservoir, Javan et al. (2015) reported that major fraction for Pb and Zn occurred in the R phase

and fraction-bound hydrous Fe-Mn oxides. Their RAC showed 'moderate risk' for Pb and 'no risk' for Zn.

The GFs of metals have a definitive impact on the mobility and the potential toxicity of the pollutant (Maiz et al. 2000). Among the different GFs, F1 fraction is poorly retained and readily mobilized and regain bioavailability with aqueous phase (Rath et al. 2009). Therefore, this fraction is mostly impacted by anthropogenic activity.

It is evident from the data that the metals in the sediments are bound to different fractions with different strengths. RAC can be used to assess the availability of metals in sediments by applying a scale to the percentage of metals in the exchangeable and carbonate fractions (Singh et al. 2005). In the present study, the F1 fraction is considered as RAC. This is because of the F1 fraction was mostly introduced by anthropogenic activities and this fraction is typified by the adsorptive, exchangeable and bound to carbonate phases. They are weakly bonded metals that could equilibrate with the aqueous phase and thus become more rapidly bioavailable (Liu et al. 2008). Since F1 is the most easily leachable and exchangeable fraction, it is logically like the RAC. Similar studies conducted by Passos et al. (2010), who reported that the sediments in Poxim River (northeast Brazil) under the category of 'medium risk' for Cd, Cu, Ni, Pb, and Zn.

4. CONCLUSION

Based on the metal distribution in the sediments of MIA and MR, we concluded that sites 1 (drainage at Power Weld), 4 (Malacca River-2) and 7 (drainage at Omega) were polluted by HMs, and sites 1 and 7 were categorized as 'considerable ecological risk' under PERI values. Therefore, it was evidently shown that elevated levels of HMs in the drainages at MIA and MR sediment were most probably attributed to untreated (or incomplete treatment of) industrial effluents. This conclusion formed the basis for implementing appropriate policies to protect drainage and river sediment quality.

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Chapter 3

EFFECTS OF TSUNAMIS ON SEDIMENTARY CHARACTERISTICS AND CONTAMINATION LEVELS: A REVIEW OF THE 2004 AND 2011 GIANT EARTHQUAKES

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ABSTRACT

We reviewed papers on the sedimentary characteristics (SC) of the tsunami sediments and deposits after the 2004 Indian Ocean and 2011 Tohoku-oki Tsunamis. A greater number of publications have documented the SC than the contamination levels of tsunami sediments. This review makes two recommendations. First, chemical organic and inorganic

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pollutants, and radioactive rare earth elements should be monitored in coastal areas that might be inundated by tsunamis. Second, checklists of natural food resources, including their background levels of chemical pollutants, should be constructed in biological and ecological studies. Such basal information is very important for understanding the disaster-induced ecotoxicological impact of the chemical pollutants on the living biota in coastal ecosystems.

Keywords: contamination, tsunami sediments, chemical pollutants, sedimentary characteristics

1. INTRODUCTION

Tsunamis can cause sudden, drastic changes in coastal systems (Bryant et al. 1996; Scheffers and Kelletat 2003). These changes in coastal topography are due to erosion during the tsunami and the subsequent settlement of sediments (Bondevik et al. 1997). Processes occurring during a tsunami allow the complex deposition of sedimentary components (Paris et al. 2010). Kanaya et al. (2015b) and Sakuna et al. (2012) reported changes in sediment granulometry in coastal ecosystems caused by tsunami. Despite changes in the physical features of the affected site, a tsunami also causes massive intrusion of salt onto surface and ground waters, with ensuing detrimental effects on coastal organisms However, due to short period of time over which a tsunami occurs, it is difficult to assess the risks of tsunamis accurately (Ilayaraja and Krishnamurthy 2010).

In a review by Engel and Brückner (2011), onshore sedimentary data provided deep insights into the effects of extraordinary waves. To pre-evaluate local hazards, it was proposed that 'local and regional historical accounts on the effects of tsunamis' should be documented. Therefore, they proposed documenting the local and regional effects of tsunamis with a focus on research on the sedimentary environments.

This review paper compares the similarities and differences in findings of sedimentary characteristics and contamination levels pertaining to the 2004 Indian Ocean Tsunami (IOT) and 2011 Tohoku-oki Tsunami (TOT).

2. 2004 INDIAN OCEAN TSUNAMI (2004 IOT)

On the 26 December 2004, an earthquake triggered a large tsunami affecting countries in the Indian Ocean. This was the largest tsunami recorded in human history, and it killed approximately 300,000 of coastal residents. In addition to the damage caused by the impact of the wave, ensuing environmental problems included soil contamination due to the deposition of seawater and tsunami sediments, including contaminants from the wreckage of factories, petrol stations, etc. (Szczuciński et al. 2005). In addition to causing massive human casualties and property and infrastructure damage, the 2004 IOT caused environmental problems for many coastal and island nations in the Indian Ocean, primarily Thailand, India, Indonesia, Sri Lanka, The Maldives and the coastal regions of African (Srisutam and Wagner 2010).

A study of sedimentary deposits on the inner continental shelf of the Andaman Sea due to the 2004 IOT revealed their diagnostic sedimentological and geochemical properties (Sakuna et al. 2012). Extensive seafloor mapping was conducted that examined the sedimentary structures, chemical element composition, physical properties, particle size, and the activity of ^{210}Pb activity in three sediment cores.

The 2004 IOT had disastrous effects on the Khao Lak coast of Thailand. Satellite images and onshore deposits in this area indicated a huge massive transport, an indication of run-up and backwash of the seafloor caused by tsunami (Feldens et al. 2012).

Ilayaraja and Krishnamurthy (2010) collected 48 tsunamigenic surface sediment samples from different physical ecosystems on the coastline of the Andaman Sea islands. Sedimentological and granulometric analyses of these samples revealed tsunamigenic sediments having characteristics consistent with the depositional effects of earthquake-generated tsunamis.

Meshram et al. (2011) described the deformed soft sedimentary structure of Dive Agar Beach, in Srivardhan, India. In the affected area, 120-cm-thick sediments comprising undeformed sands were sharply cut by a 30-cm-thick mixture of beach sand and terrigenous sand. This was followed by complex

bedded structures and convolutions (8–15 cm) within a coarse sandy layer. They suggested that this may have resulted from the 2004 IOT.

Srisutam and Wagner (2010) collected 2004 IOT sediment samples from the Thai Andaman coast and used the wet-sieving method for grain-size analyses. The sediment samples were also compared with three deposits from coastal sub-environments. They reported erosion occurrence via a complex deposition process affecting swash zone, berm/dune, and inland zones in the study area.

Paris et al. (2010) investigated the sedimentary thickness and grain size of tsunami deposits at Western Banda Aceh (Indonesia) while Fujino et al. (2010) examined similar deposites in Southwestern Thailand. Goto et al. (2012a) collected samples from the lowlands of southwestern Thailand and compared them in terms of their sedimentary core structures. Similarly, Szczuciński (2012) observed the 2004 IOT deposits in 2005 and 2008 in the same area and found thin (of few cm) tsunami deposits that were well preserved, but with a disturbed sedimentary structure mainly due to bioturbation. Again, this was an outcome and backwash of the 2004 IOT.

3. 2011 TOHOKU-OKI TSUNAMI (2011 TOT)

On 11 March 2011, the Pacific coast of north eastern Japan was struck by huge tsunamis, with reported inundation depths of 20 m, generated by the M 9.0 Great East Japan Earthquake (reviewed by Kanaya et al. 2017). This 2011 TOT, also known as Great East Japan Earthquake, killed over 14,000 people massive destructions to the infrastructures, properties and the environments in many coastal areas, particularly in East Japan (reviewed by Okada et al. 2011). The huge resulting tsunami wrought massive destruction on the Pacific coast of Japan, including the coastline of Sendai.

The 2011 TOT scoured the sediments of tidal flats, salt marshes, and soft-bottom subtitle areas in the Tohoku region, and deposited huge amounts of allochthonous sediment. For example, the coastal sediment in the Sendai alluvial plain was removed and replaced by tsunami deposits consisting of drifting sea sands (Chagué-Goff et al. 2012; Pilarczyk et al. 2012; Richmond

et al. 2012; Szczuciński et al. 2012). The tsunami deposits associated with the 2011 TOT, especially on the Sendai Plain, have been analyzed in sedimentological studies (e.g., Jaffe et al. 2012) including in terms of the sedimentary characteristics (e.g., Pilarczyk et al. 2012; Kanaya et al. 2015a; Sugawara et al. 2014). Similar study have been reported on Sanriku coast (Naruse et al. 2012; Naiki et al. 2015; Kinoshita and Matsumasa 2016), Onagawa Bay (Abe et al. 2015, 2016; Seike et al. 2016), Kujukuri coastal plain (Matsumoto et al. 2016), coastal lowlands of Ibaraki and Chiba prefectures (Yamada and Fujino 2013), subtidal zone off Tohoku (Kitahashi et al. 2014; Toyofuku et al. 2014), and even the California coast, USA (Wilson et al. 2012) (see Table 1).

Sugawara et al. (2014) explored the characteristics of the marine materials deposited on the Sendai Plain, northeastern Japan, transported by the TOT tsunami, and differences between their inland extent and limit of inundation. Their simulation showed that the deposits were similar, in terms of thickness, compared with previous studies.

Matsumoto et al. (2016) reported on the sedimentary characteristics of the Hasunuma tsunami deposits on the Kujukuri coastal plain, Japan, resulting from the 2011 TOT. They concluded that most of the thick tsunami deposits were within 350 m from the coastline, but that distance extended to 1 km in the inundation area. Together with the pre-existing soil, the deposit reached an extent of 35 cm in thickness and mainly comprised a blend of fine to medium sands. To obtain a clearer picture of the sedimentary structures and variation in grain sizes, they categorized the deposits into several categories according to the number of inundation flows.

Seike et al. (2016) applied a more advanced approach using computed tomography scanning, X-ray radiography, and grain size analysis to examine the physical and biological changes in the sedimentary structures of seafloor deposits in Onagawa Bay, northeastern Japan, following the 2011 TOT. They revealed that the ability to preserve tsunami deposits at this site was compromised, mainly due to the rapid activity of burrowing animals.

Table 1. Review of sedimentary and contamination studies based on 2004 Indian Ocean Tsunami and 2011 Tohoku-oki Tsunami

No.	Area	Sediment characteristics investigated/ Findings	Reference
2004 Indian Ocean Tsunami			
1.	Andaman group of islands, Bay of Bengal, India	Sediment texture and granulometric studies. The tsunami sediments were mainly composed of boulders of corals and sand which determines the high-energy environment throughout the study area.	Ilayaraja and Krishnamurthy (2010)
2	Coastline of Khao Lak, Thailand	Seafloor morphology and geological features, as well as the sediment distribution and its inter-annual changes.	Feldens et al. (2012)
3.	Inner continental shelf offshore of Khao Lak, Andaman Sea, Thailand	Sedimentary structures, grain size composition (divided into mud, sand, gravels and pebbles), chemical elemental composition, physical properties and ^{210}Pb activity.	Sakuna et al. (2012)
4.	Dive Agar beach, west coast of India	A sequence of soft sediment deformation structures	Meshram et al. (2011)
5.	Lhok Nga, Western Banda Aceh, Sumatra, Indonesia	Grain size. sediment thickness.	Paris et al. (2007, 2010)
6.	Phang-nga Province, southwestern Thailand	Thickness and grain size of tsunami deposits.	Fujino et al. (2010)
7.	Thai Andaman coast.	Sediment characteristics.	Srisutam and Wagner (2010)
8.	Coastal Zone of Thailand	Mercury mobility and bioavailability by fractionation method [Contamination study]	Boszke et al. (2006)
9.	Coastal Zone of Thailand	Effects of rainy season on mobilization of contaminants from tsunami deposits [Contamination study]	Szczuciński et al. (2007)
10.	Kho Khao Island, Thailand.	Heavy minerals [Contamination study]	Jagodziński et al. (2009)
11.	Phuket island (around Patong Bay), and along the coastline between Khao Lak and Kho Khao Island, on the western coast of Thailand	Determination of salts contents in water-soluble fraction, and of Cd, Cu, Pb and Zn in the bioavailable fraction in tsunami sediments. [Contamination study]	Szczuciński et al. (2005)
12.	Thai Andaman Sea Coast	Iron speciation and major elements	Kozak and Niedzielski (2017)
13.	Southern Thailand	Geochemical fractions of heavy metals [Contamination study]	Kozak and Siepak (2009)

No.	Area	Sediment characteristics investigated/ Findings	Reference
2004 Indian Ocean Tsunami			
14.	Seagrass beds in Ranong, Andaman Sea, Thailand	Sediment grain size	Whanpetch et al. (2010)
2011 Tohoku-oki Tsunami			
1.	Onagawa Bay, Miyagi Prefecture, Japan	Physical and biogenic sedimentary structures of seafloor deposits.	Seike et al. (2016, 2017)
2.	Gamo Lagoon, Sendai Bay, Miyagi Prefecture, Japan	Silt-clay, total nitrogen, total organic carbon (TOC), acid-volatile insoluble sulfide, and hydrogen sulfide. Sediment in Gamo Lagoon became much coarser, organically poorer, and more oxidized after the tsunami; silt-clay and TOC sharply declined, while the redox potential values increased.	Kanaya et al. (2015a)
3.	Gamo Lagoon, Sendai Bay, Miyagi Prefecture, Japan	Grain size, polycyclic aromatic hydrocarbons, and *n*-alkanes in lagoon sediment. [Contamination study]	Kanaya et al. (2014)
4.	Hasunuma, a site on the Kujukuri coastal plain, Chiba Prefecture, Japan	Sedimentary characteristics and thickness.	Matsumoto et al. (2016)
5.	Sendai Plain, Miyagi Prefecture, Japan	Numerical modelling of sediment transport. Visualization of the onshore sediment transport indicated that the sediment transport was significantly affected by artificial topographic features. The flow speed and height varied across the topographic highs, and sediments were trapped on the seaward side of these highs.	Sugawara et al. (2014)
6.	Rikuzentakata City, Iwate Prefecture, Japan	Sedimentary features	Naruse et al. (2012)
7.	Coastal lowlands, Ibaraki and Chiba prefectures, Japan	Sedimentary characteristics	Yamada and Fujino (2013)
8.	Kesennuma Bay, Miyagi Prefecture, Japan	Analysis of sediment characteristics (silt-clay, TOC, Eh) and PAHs in the sediments. [Contamination study]	Kanaya et al. (2016)
9.	The tidelands of Tsugaruishi and Orikasa estuaries (Iwate Prefecture) and Gamou tideland (Miyagi Prefecture), Japan	Analysis of elemental concentrations in the tsunami sediments. [Contamination study]	Sera et al. (2012)

Table 1. (Continued)

No.	Area	Sediment characteristics investigated/ Findings	Reference
2011 Tohoku-oki Tsunami			
10.	Miyagi Prefecture, Japan	PAHs biodegradation potential from tsunami sediments [Contamination study]	Bacosa and Inoue (2015)
11.	Kanto to Tohoku coastal area, Japan	Concentrations of heavy metals in tsunami deposits [Contamination study]	Nakamura et al. (2016)
12.	Tohoku tsunami deposits in Sendai Plain, Miyagi Prefecture	Grain size and heavy minerals in tsunami deposits [Contamination study]	Jagodziński et al. (2012)
13.	Onagawa Bay, Miyagi Prefecture, Japan	Changes in grain size, total sulphide, and *n*-hexane extracts in subtidal sediment after the tsunami. [Contamination study]	Abe et al. (2015, 2016)
14.	Sendai Plain, Miyagi Prefecture, Japan	Grain size, organic content, ions, metals, and exchangeable metalloids (e.g., Cl, Na, SO_4, Br, As, Zn, Cu and Ni) of sediments in tsunami-inundated areas. [Contamination study]	Chagué-Goff et al. (2012)
15.	Sabusawa Island, Matsushima Bay, Miyagi Prefecture, Japan	Sedimentary features of various sizes of grains and clasts in inundated areas immediately after a tsunami	Goto et al. (2012b)
16.	1300 data from Sendai Plain, Miyagi Prefecture, Japan	Direct comparison of the sedimentation and erosion volumes as well as the tsunami hydrodynamic features (e.g., flow depth) and sediment thickness.	Goto et al. (2014)
17.	Kesennuma Bay, Miyagi Prefecture, Japan	Tsunami-induced reworking of sea bottom sediments around 10-15 m water depth area to thickness of a few meters, and forming of large dunes.	Haraguchi et al. (2013)
18.	Oi artificial tidal-flat, Tokyo Bay, Tokyo, Japan	Changes in sediment characteristics (grain size, redox condition, and sulfide content) by liquefaction.	Kanaya et al. (2015, 2017)
19.	Kanto to Tohoku coastal area in Japan	Heavy metals (As, Pb, Cd, and Cr) in tsunami deposits. [Contamination study]	Kawabe et al. (2012)
20.	Tsugaruishi, Orikasa, and Unosumai Estuaries, Iwate Prefecture, Japan	Sediment grain size in tidal-flats.	Kinoshita and Matsumasa (2016)
21.	landward slope of the Japan Trench (water depth, 120–5600 m), off Miyagi Prefecture, Japan	Sediment grain size	Kitahashi et al. (2014)
22.	Nine bays along the Sanriku Coast, Iwate Prefecture, Japan	Mud content, chemical oxygen demand (COD), and acid volatile sulfides (AVS)	Naiki et al. (2015)

No.	Area	Sediment characteristics investigated/ Findings	Reference
2011 Tohoku-oki Tsunami			
23.	Misawa coast, Aomori Prefecture, Japan	Thickness, facies, and structure of the tsunami deposit as well as its grain size and mineral assemblage	Nakamura et al. (2012)
24.	Off the Pacific coast of Tohoku	Polychlorinated biphenyls (PCBs) in deep-sea sediments [Contamination study]	Ohkouchi et al. (2016)
25.	Seven intertidal flats along the Kanto to Tohoku coastal area, Japan	PAHs in tidalflat sediments [Contamination study]	Onozato et al. (2016)
26.	Sendai Plain, Miyagi Prefecture, Japan	Stratigraphical, sedimentological, foraminiferal and geochemical characteristics of the tsunami deposit	Pilarczyk et al. (2012)
27.	Sendai Plain, Miyagi Prefecture, Japan	Erosion, deposition and associated landscape change by tsunami and tsunami-deposit	Richmond et al. (2012)
28.	Sendai, Miyagi Prefecture, and Odaka, Fukushima Prefecture, Japan	Marine-sourced biomarkers (e.g., short-chain *n*-alkanes, pristane, and phytane) in tsunami deposits	Shinozaki et al. (2015)
29.	Matsukawaura Lagoon, Fukushima Prefecture, Japan	Sediment grain size of lagoon sediment	Suzuki (2016)
30.	Seafloor, off Shimokita, Aomori Prefecture, Japan	Grain size, C/N ratio, carbon stable isotope ratio (^{13}C)	Toyofuku et al. (2014)
31.	Harbours in California coast, USA	Sediment scour and deposition	Wilson et al. (2012)

According to Kanaya et al. (2015a), there was a great difference in the sediment environment before and after tsunami in Gamo Lagoon. Most of the organic-rich and sulfidic mud were wiped off and replaced with sandy sediments around the lagoon. There was a significant depletion of silt-clay, total nitrogen and organic contents, acid-volatile insoluble sulfide (AViS), and hydrogen sulfide (H_2S), while the redox potential values in the sediments increased drastically. The loss of muddy sulfidic sediments was the most apparent environmental modification which was attributed to the shear stress under tsunami currents and massive sediment liquefaction during earthquake. Similar modifications in sediment grain size had also been reported from other intertidal zones in the Tohoku Region (Kinoshita and Matsumasa 2016; Suzuki 2016; see summarize in Kanaya et al. 2017).

All the above studies indicated that the sediment environment in the Tohoku Region had been altered substantially.

4. CONTAMINATION STUDIES

Forty-five papers examined the sedimentary characteristics resulting from tsunamis (see Table 1). However, only 15 papers focussed on the contamination of tsunami sediments. Catastrophes such as earthquake and tsunamis released many pollutants, including heavy metals, oils, and pyrogenic polyaromatic hydrocarbons (PAHs), into coastal waters (e.g., Szczuciński et al. 2007; Sera et al. 2012; Bacosa and Inoue 2015), which might pose an ecotoxicological threat to the biota of the affected locations.

4.1. 2004 Indian Ocean Tsunami

For 2004 IOT, there was limited publications on contaminant levels of tsunami deposits. Szczuciński et al. (2005) collected sediments deposits within 50 days of the 2004 IOT wave from the coast of Thailand. They found that the sediments had high levels of salt in the water-soluble fraction, heavy metals (Cd, Cu, Zn, Pb) in the bioavailable fraction, and As in the exchangeable fraction compared with reference samples. Thus, they demonstrated the potential for contaminants migration into ground waters and they food chain. Later, Szczuciński et al. (2007) studied the mobility of contaminants in tsunami deposits in respond to seasonal rain.

Jagodziński et al. (2009) studied the heavy mineral assemblages in onshore sandy deposits from the 2004 IOT on Kho Khao Island, southern Thailand. Minerals in the area included tourmalines, zircon, and opaque minerals. Higher mica levels and lower tourmaline levels distinguished the tsunami deposits from modern beach sediments and pre-tsunami soils.

Boszke et al. (2006) studied the mercury contents of sediments deposited in coastal areas of Thailand. They applied geochemical fractionation to make up for the insufficiency of the total mercury contents,

which was needed to assess the bioavailability and motility of this pollutant. They found that the majority of the mercury was attached to the least bioavailable compounds (sulphides, organomercury compounds and humic matter, accounting for 75%, 14%, and 9%, respectively). Water-soluble mercury (0.80%) and acid-soluble mercury (0.90%) fractions constituted the lowest proportions of total mercury. However, a higher content of highly toxic organomercury was detected in the fraction, although the overall mercury content was similar to that of the reference sample.

Kozak and Niedzielski (2017) studied the variations of chemical composition to the 2004 IOT related geological deposits in Thai Andaman Sea Coast from 2005 to 2008. They examined the Ca, Mg, Fe, Mn and Fe speciation of the acid-leachable fraction in the tsunami deposits and found that the directional changes in the chemical composition and Fe speciation were not in a similar trend. However, there was increased heavy metal concentrations in the acid-leachable fraction of the 2004 IOT tsunami deposits (Kozak and Siepak 2009).

4.2. 2011 Tohoku-oki Tsunami

Following the 2011 TOT, 11 papers on the contamination caused by the disaster were reviewed Sera et al. (2012) analyzed the elemental contents of tsunami sediments from the tideland estuaries of Tsugaruishi, Orikasa and Gamou. The concentrations of PAHs, *n*-alkane, and/or *n*-hexane extracts, in intertidal or subtidal sediments in several bays and tidal flats of the Tohoku Region, have been reported [Kanaya et al. (2014, 2016) for Gamo Lagoon and Kesennuma Bay, Abe et al. (2015, 2016) for Onagawa Bay; and Onozato et al. (2016) for seven intertidal flats in the Kanto to Tohoku area]. Ohkouchi et al. (2016) assessed the polychlorinated biphenyls (PCBs) contents in deep-sea sediments off the Pacific coast of Tohoku. Bacosa and Inoue (2015) reported the PAH biodegradation potential of tsunami sediments from the Miyagi area, while Chagué-Goff et al. (2012), Jagodziński et al. (2012), Kawabe et al. (2012), and Nakamura et al. (2016) documented the concentrations of heavy metals and heavy minerals in the Tohoku area.

Kanaya et al. (2016) assessed the ecological consequences of the fuel spills and the subsequent conflagration triggered by the TOT. The sediments collected from Kesennuma Bay (period 2011-2014) were found to contain elevated levels of PAHs, ranging from 18,023–89,197 μg/kg dry weight of the total PAHs content. They concluded that PAHs in the sediment were mainly from petrogenic sources (57 – 82%) for the inner bay, while the PAHs at other stations were of pyrogenic origins (55 – 86%). The PAHs contamination had also been studied by Other researchers also studied PAH contamination; for example, Bacosa and Inoue (2015) reported on the activities of communities of PAHs-degrading microbes in the tsunami sediments of Miyagi Prefecture.

Sera et al. (2012) collected samples of sludge generated by the massive 2011 TOT from three tidelands: the Gamou (Miyagi Pref.), the Tsugaruishi estuary (Iwate Pref.), the Orikasa estuary (Iwate Pref.) tidelands. Their main conclusion was that the tidelands were contaminated by heavy metals (As, Pb, Zn and Ba), with nearby beaches being contaminated to a lesser degree.

Nakamura et al. (2016) analyzed the 2011 TOT deposits along the Tohoku coast and found that the concentrations of Pb, As, and Cd were low, corresponding to a low ecotoxicological risks posed by these metals in the environment. Statistical analysis revealed a positive correlation between acid-leaching of the aforementioned metals and a dispersal pattern of water leaching. Digestion with HCl revealed that Pb and As in the tsunami deposits from the tsunami deposits appeared to be acid-extractable with 1 M HCl.

Jagodziński et al. (2012) analysed the 2011 TOT deposits for sedimentological and heavy mineral determination. They concluded that the main minerals in the deposits were orthopyroxenes, clinopyroxenes, amphiboles, limonites and opaque minerals. The heavy mineral concentrations and degree of accumulation of tsunami deposits in all collected samples were similar, such that they were difficult to identify based on heavy metal contents alone. However, their analyses successfully identified the origin of the lowermost portion (local origin) and upper portions (various origins) of the tsunami deposits, with no evident contribution from offshore sediments. Jagodziński et al. (2009) compared their results to those of a study of heavy minerals in 2004 IOT deposits and

found that the heavy minerals in tsunami deposits were mostly source-dependent and could serve as a useful supplementary tool in studies on tsunami deposits. Both studies by Jagodziński et al. (2009, 2012) supported the use of heavy mineral analyses for interpreting tsunami deposits.

5. CONCLUSION

This review on the sedimentary characteristics and contamination levels associated with 2004 IOT and 2011 TOT disasters provides a stimulus for future research and generates the following recommendations, First, chemical organic and inorganic pollutants, and radioactive elements such as rare earth elements (U and Th), should be studied in coastal areas that may be at risk of inundation during future tsunamis, where such baseline information is very important for comparing chemical pollutants before and after a tsunami. Second, since coastal areas are very productive, have high biodiversity and are characterized by mingling of the biota from fresh and marine ecosystems, natural food resources should be documented in biological, ecological and ecotoxicological studies. Such information would likely be important for understanding changes in biota after tsunamis.

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Chapter 4

ENVIRONMENTAL MANAGEMENT AND MONITORING OF SEDIMENTS IN THE PERSIAN GULF

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ABSTRACT

The contamination of the Persian Gulf sediments with metals resulted from anthropogenic activities is a serious threat to the ecosystem. Environmental management of sediments is challenged with providing the basis for protection the environment against adverse anthropogenic impacts of pollution such as industrial and sewage discharges, aquaculture activities, oil pollution, and coastal modifications. This chapter presents a review of studies (based on 14 peer-reviewed papers) carried out by the Iranian scientists and researchers in the Persian Gulf, and reflects their major results for use in international scientific communities. Altogether, findings from this chapter could be useful in providing more effective and targeted strategies for the better developmental management practices in the semi-enclosed Persian Gulf.

Keywords: sediment quality, monitoring methods, anthropogenic pressures, metal pollution, Persian Gulf

1. INTRODUCTION

Monitoring of Sediment Layers and Environmental Management (MOSLEM) in aquatic ecosystems is challenged with providing the basis for the protection of environment against adverse anthropogenic impacts of pollution such as industrial and sewage discharges, aquaculture activities, oil pollution, and coastal modifications (Yap et al. 2003, Apitz 2008, Akcil et al. 2015). Therefore, the aquatic sedimentary contamination and MOSLEM are important global environmental issues that national and international authorities are facing over the past two decades (Yap et al. 2002, Apitz 2008, Akcil et al. 2015). Anthropogenic activities in the marine ecosystems are expected to increase owing to the present and future global needs for marine resources, which will impose higher impacts and pressures on coastal and marine ecosystems (Halpern et al. 2008, Uusitalo et al. 2016). So, in aquatic ecosystems these activities play an imperative and significant role in the increase of high concentrations of pollutants (Tanner et al. 2000). In all the aquatic ecosystems, the fluctuations of contaminants in sediments are usually lower than water column (Gupta and Singh 2011, Akcil et al.

2015). Given that sediments act as both trace metal carriers and sink for pollutants, therefore, they reflect the amount of contamination from catchment inputs into the coastal and marine waters (Gupta and Singh 2011, Akcil et al. 2015).

Heavy metals are important pollutants in the coastal and marine environments owing to their abundance, bioaccumulation, persistence and non-degradability, inherent toxicity and ecological risks (Ye et al. 2012, Pejman et al. 2015, Jafarabadi et al. 2017, Sharifinia et al. 2018). These types of pollutants can be introduced to the aquatic ecosystems through a variety of sources (Figure 1). These pollutants can be bioaccumulated in food webs and would potentially poses a serious threat to humans and the environment. The most important cause for the sensitivity of aquatic ecosystems to pollution impacts could lie in the structure of their food webs (Mendoza-Carranza et al. 2016).

Due to special features of the Persian Gulf (i.e., shallow depth: 35-40 m, semi-closed environment, and an approximate area of 240 km^2) the period of its turnover is estimated to be between 3 to 5 years (Sheppard 1993, Banat et al. 1998, Pourang et al. 2005). Therefore, Sheppard (1993) stated that the resides of pollutants in the Persian Gulf are likely to take a significant period of time. Moreover, Pourang et al. (2005) argued that the impacts of contaminants on the Persian Gulf can be significant because of the above mentioned features such as shallow depths, limited circulation, high temperatures, and high salinities. Contamination from accumulation of metals in the Persian Gulf sediments is becoming a progressively dangerous and a serious threat to the safety of people that rely on marine resources such as food, fishing, and other purposes.

Over the last few decades, the coastal areas of the Persian Gulf have experienced significant socio-economic growth and industrial progresses. Anthropogenic pressures such as industrial wastewater and domestic sewage, dredging and reclamation, and pollution from oil and petroleum products played an important role in ecological processes of the Persian Gulf (Sheppard et al. 2010). Therefore, these man-made activities increase heavy metals accumulation in the Persian Gulf. Hence, the review from this chapter could be very important in providing more effective and targeted strategies

for the better developmental management practices in the semi-enclosed Persian Gulf. This chapter presents: (1) a review of studies (based on 14 ISI published papers) carried out by the Iranian scientists and researchers in this ecosystem, (2) strategies for observing and evaluation of coastal and marine sediments, and (3) some of physico-chemical approaches and methods for managing metals applied in the Persian Gulf.

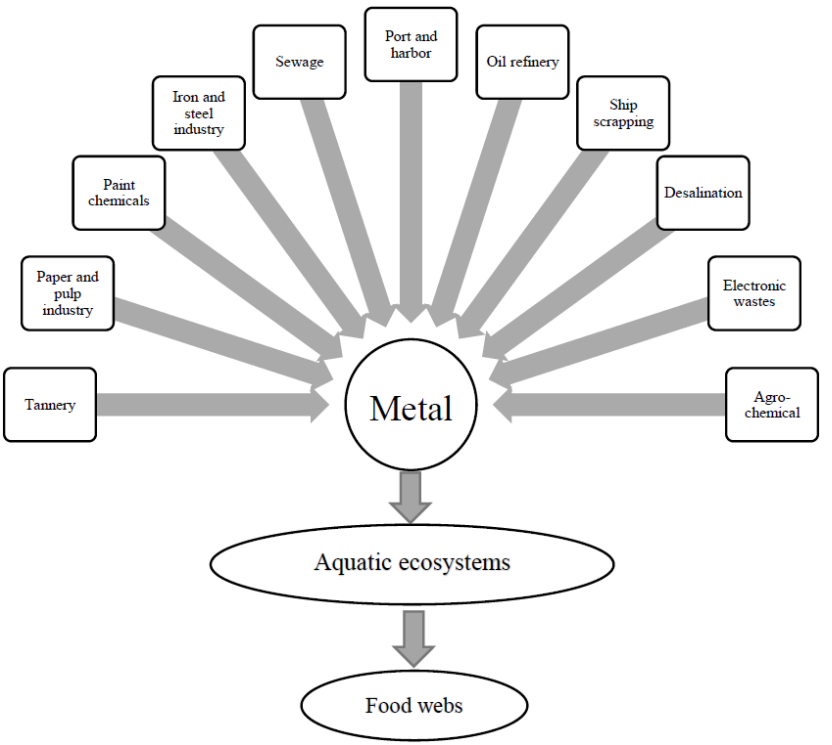

Figure 1. Sources of metals originating from human activities in aquatic environments (modified from Sharifuzzaman et al. (2016)).

2. Heavy Metals in the Persian Gulf Sediments

Organic and inorganic contaminants, mainly heavy metals, often comprise the pollution in the sediments. Heavy metals are toxic, persistent, and they cannot be decomposed, therefore, they are the underlying and

growing problems in managing water resources (Zoumis et al. 2001, Akcil et al. 2015). In coastal and marine environments, heavy metals are rapidly binding to suspended particles and deposited to the sea floor (Hedge et al. 2009). Consequently, the sediments of these aquatic ecosystems act as a reservoir for settle and accumulate of heavy metals (Ruilian et al. 2008). Salomons and Stigliani (1995) suggested that more than 99% of pollutants are stored in sediments, while less than 1% of them are dissolved in the water column.

In recent decades, various industrial pollution studies and risk assessment indicators have been used for evaluating heavy metals levels in coastal and marine sediments of the Persian Gulf (Karbassi 1998, Pourang et al. 2005, Bastami et al. 2015, Ghasemi et al. 2018, Sharifinia et al. 2018). For example, Karbassi (1998) investigated the levels of eleven heavy metal included Mn, Cd, V, Fe, Al, Ni, Zn, Cu, Pb, Co, and Ca in surface sediment of the Persian Gulf. They studied the chemical partitioning to explore the relationship between metals and various features of sediment. Later, they argued that the concentration of heavy metals (Co, Cd, Pb, and Ni) in the Persian Gulf sediments were related to anthropogenic activities.

Pourang et al. (2005) measured heavy metals levels in subtidal sediments of the Persian Gulf. This study showed that the concentrations of Pb, Cd, and Ni metals were remarkably upper than global standard ranges. Dehghan Madiseh et al. (2008) determined levels of heavy metals in sediments of several creeks in the coastal areas of the Persian Gulf based on BIO Production Index (BPI) and sedimentological toxic factors (S_t). Results from this study showed that the sediment of the studied creeks classified as "considerable ecological risk." An assessment of distribution patterns of metals contamination in intertidal sediments of coastal zones based on type regional development in the Persian Gulf was conducted by Kazemi et al. (2012). This study showed that human-made activities in each area can be a most important source of metals pollution in the Persian Gulf.

Abdollahi et al. (2013) assessed heavy metals and PAHs distribution and levels of its contamination in north part of the Persian Gulf sediments (Imam Khomeini Port). They found that the main cause of high levels of heavy metals and PAHs in the region was petrochemical industrial activities. It

should be noted that the PAHs and Hg concentrations were much higher than other areas. Pejman et al. (2017) investigated heavy metals fractionation and their potential risk assessment in sediments of Persian Gulf. They found that the Ni concentration was very considerable in carbonate and exchangeable fractions and, consequently, the potential risk of this metal would be much more than other studied metals. Based on risk assessment code, in comparison with other studied metals, Cd had the highest level of ecological risk.

Ecological risk assessment and distribution of heavy metals levels in sediments and coral reefs of the Persian Gulf was conducted by Jafarabadi et al. (2017). They indicated that the main causes for high levels of Hg and Cd metals are emerging hydrocarbon exploration, development of industrial activities, and oil refineries in the region. Based on hazard quotient index, they suggested that there is no adverse health effect through dermal exposure, and there is no carcinogenic and non-carcinogenic harm to human health. Sharifinia et al. (2018) investigated the ecological risk assessment of three subtropical estuaries and the impact of anthropogenic activities on these ecosystems during a one-year study period (2015-2016) using trace metals as pollution indices. Sediment samples were collected along the coastal waters of the Persian Gulf and Gulf of Oman following a gradient of contamination from the industrial wastewater and shrimp farming effluents to the less impacted stations. The sediments in the most stations in studied coastal ecosystems of Iran posed moderate or considerable ecological risk.

3. Strategies for Monitoring and Assessment of Coastal and Marine Sediments of the Persian Gulf

Lithogenic and anthropogenic sources are two main factors affecting the quality of the marine and coastal sediments of the Persian Gulf, as well as other marine ecosystems. Consequently, the heavy metal concentrations influenced by these main sources, which induce enriched metal levels into coastal and marine ecosystems by several ways, such as industrial

wastewater, river discharge, and deposition in the atmosphere (Kennish 1996, Sharifinia et al. 2018). When the amount of contaminants exceeds the standard level, they could pose harmful and toxic impacts on marine flora and fauna in the coastal and marine environments (Sany et al. 2014, Jafarabadi et al. 2017). Therefore, since 1980, many research projects have focused on monitoring and assessment of the aquatic environment quality and pollution. All of these works point out that the evaluation of coastal and marine environments need research strategies, guidelines, and indicators.

One of the main aspects of coastal and marine sediment assessment is the monitoring programs. These programs in the Persian Gulf include scientific research and abiotic and biotic data collection in different timescales (Bastami et al. 2015; Taherizadeh and Sharifinia 2015; Jafarabadi et al. 2017; Sharifinia et al. 2018). As a result, this information can be compared with baseline values and the natural background to define and make available information about the current status of the coastal and marine environments (Carr and Neary 2008). The monitoring and assessment of coastal and marine ecosystems should be described in the following information (Sheela et al. 2012; Jørgensen et al. 2016):

1	Explaining the condition of physico-chemical factors (e.g., quality of water, pollution sources, land use), morphometry (size, volume, depth, and area), conditions of geological and hydrological parameters (e.g., water balance, volume of water, and rate of flow), and transportation of sediment
2	Assessing the status and trends of environmental health/pollution in the coastal and marine ecosystems
3	Assessing the impact of different types of pollutants on marine environmental quality
4	Investigation and identification the relationship and interrelationship among all parameters
5	Determine the source of contamination and levels of their concentration
6	Assessing spatio-temporal trends using both historical data and collected data
7	Make available comprehensive monitoring data by indices and multivariate methods to make recommendations and references for management of decisions and policies in the future

In coastal and marine ecosystems, contaminants from organic and inorganic materials can accumulate in the sediments and, therefore, sediment acts as a high-capacity storage area for metals and play an important role in the transfer of metals (Akcil et al. 2015; Sharifinia et al. 2018). Overall, for comprehensive evaluation of sediment quality, concentrations and the effect of pollutants, specific chemical compounds, sediment natural parameters, and the native biological assemblages should be considered. Therefore, in order to monitor the aquatic ecosystems, the combination of physico-chemical and biological factors would be necessary (Lehr et al. 2005; Sharifinia et al. 2016).

The first step in evaluating coastal and marine sediment quality is physical variables analysis. Consequently, this information is important to examine and understand the pollutants effects on benthic assemblages, fate, bio-availability, and pollutants transportation in sediments. Physical variables are analyzed based on measuring factors such as particular size, total solid, specific gravity, and pH. In comparison to natural conditions, the chemical methods can be used to evaluation the particular level of pollutants in sediments (Sany et al. 2014). These methods may provide useful information about specific levels of pollutants that can lead to bio-accumulation and toxicity. In chemical approach, the actual data compares with locations that comprising insignificant pollutant concentration. This approach is useful, particularly, in samples collected from deeper sediment layers at a given station, since these materials are derived from the same catchment area and typically similar in composition of its substrate. However, normalization with respect to grain size distribution is necessary (Calmano and Förstner 2012). Table 1 provides a summary of the some of physico-chemical methods applied in the Persian Gulf.

Table 1. Some of physico-chemical methods applied in the Persian Gulf (Bastami et al. 2015; Jafarabadi et al. 2017; Ghasemi et al. 2018; Sharifinia et al. 2018)

Algorithm	Description
$\mathrm{CF} = \frac{\mathrm{C_H}}{\mathrm{C}_B}$	n: number of heavy metals CF: contaminant factor C_H: heavy metal concentration C_B: heavy metal background reference value (Zn = 64, Cu = 26, Pb = 10, Cd = 0.16)
$\mathrm{CD} = \sum_{\mathrm{i}=1}^{\mathrm{i}=n} CF$	CD: sum of the contaminant factor (CF)
$\mathrm{PLI} = (\mathrm{C}F_1 \times \mathrm{C}F_2 \times \mathrm{C}F_3 \times \ldots \times \mathrm{C}F_n)^{1/n}$	CF: contaminant factor
$\mathrm{PERI} = \sum_{I=1}^{n}(\mathrm{T}_r \times \mathrm{CF})$	Tr: toxicity coefficient (Zn = 1, Cu = Pb = 5, Cd = 30)
$\mathrm{I_{geo}} = \log_2\left(\frac{\mathrm{C_n}}{1.5 \times \mathrm{B_n}}\right)$	Cn: the measured metal concentration (n) in the sample Bn: the geochemical background of metal concentration (n) The factor 1.5: applied to minimize the possible variations effects in the background values

Table 2. Reasons for choosing macrobenthic species for biological evaluation in coastal and marine sediments (Pearson and Rosenberg 1978; Borja et al. 2003)

1	They can indicate the impact of natural and anthropogenic pressures because of low mobility.
2	The changes in macrobenthic species is expectable because of the presence or absence of them are not affected by tidal flux and diurnal cycles.
3	Macrobenthic species categorized based on their resistance and sensitivity to various conditions.
4	They play an important ecological role in recycling of nutrients.
5	There are clear foreseeable trends of benthic species reaction to changes in marine quality.

In the benthic zone of coastal and marine ecosystems, biological assessment of sediment can be conducted using surveys and other direct measurements of resident biological organisms such as macroinvertebrates. The aim of this method is to evaluate the potential effects of the action on species and determine whether any such species are likely to be harmfully affected by the action. Because of several aspects that are listed in Table 2, macrobenthic assemblages are valuable biotic indices for monitoring the quality of coastal and marine sediments. This method has been successfully applied in the Persian Gulf by many researchers to assess the health or pollution status of coastal and estuaries see floor using biotic indices such as AMBI, BENTIX, alpha and beta diversity (Mooraki et al. 2009; Shokat et al. 2010; Taherizadeh and Sharifinia 2015).

4. Persian Gulf Metal Pollution Management

Most of the regions seriously endangered by the increasing metal pollution are the shallow coastal zones of marginal seas in the catchment areas of heavily populated and highly industrialized regions (Förstner and Wittmann 2012). In contrast to dispersion processes, which seemingly take place on an unrestricted scale in the oceans, the material exchange of the Persian Gulf seems to be rather restricted. Pollution resulted from heavy metals in marine ecosystems is a problem of global concern, requires global control and prevention strategies (Mansour 2014). The Persian Gulf characteristics as a semi-enclosed and shallow ecosystem that is imperiled to severe man-made pressures make it vulnerable to pollution from heavy metals. Therefore, there is a pressing need and immediate attention to metal pollution management in the Persian Gulf in the future.

Figure 2 shows the suggested classification of heavy metal management strategies in the Persian Gulf. These strategies are including two actions: immediate and long-term programs. The immediate measures comprise: (1) preparing quality guidelines, standards, and baselines, (2) applying current environmental regulations and laws at the national and international levels, and (3) implementation of comprehensive environmental monitoring

programs. The long-term actions comprise: (1) implementation of Environmental Impact Assessment (EIA) in the region, and (2) provide the necessary fields for scientific research and applying modern technological methods (Naser 2013).

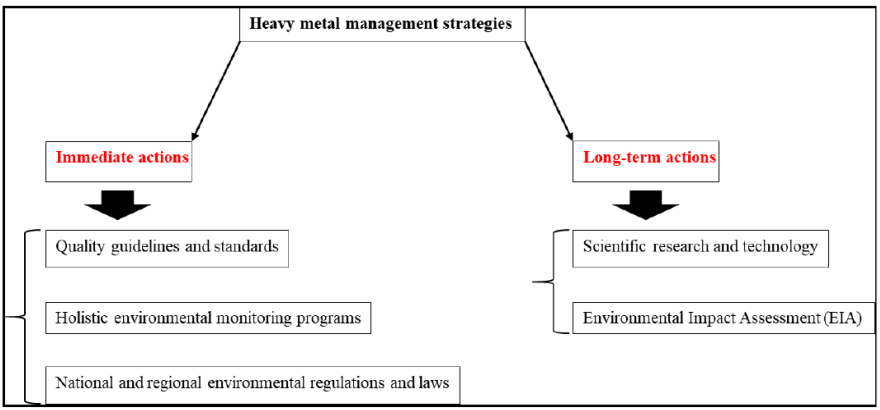

Figure 2. Heavy metal management strategies in the Persian Gulf.

CONCLUSION

In the present chapter, we have concerned ourselves with pollution from heavy metals in sediments of the Persian Gulf, and found that, a series of metals have become accumulated in estuarine and coastal area sediments. This review shows that in urbanized and industrialized areas, the accumulation of heavy metals can be related to anthropogenic activities. Moreover, analyses of heavy metals in sediments of the Persian Gulf provide a low-cost approach to evaluate the levels of anthropogenic changes and act as a metal pollution stress indicator. In this type of evaluation, the data obtained almost at a low-cost and relatively easy approach. Therefore, these methods make available the pollutant framework on which more accurate and focused multidisciplinary research can be the basis for comprehensive regional and national environmental monitoring programs.

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Chapter 5

ECOLOGICAL RISK ASSESSMENT OF HEAVY METALS IN SURFACE MANGROVE SEDIMENTS COLLECTED FROM THE SEPANG RIVER ESTUARY, PENINSULAR MALAYSIA

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ABSTRACT

Sepang Besar River (SBR) and Sepang Kecil River (SKR) were previously known as piggery farming areas in the early 1990s. These rivers are known to be highly contaminated with Zn and Cu as they received effluents from the piggery farming. Besides that, domestic wastes, boating and fish farming effluents were also common in these rivers banks. In this study, the surface sediments collected from SBR and SKR in 2007 were analysed for its Cd, Cu, Fe, Ni, Pb and Zn concentrations. The present study revealed that the levels of these heavy metals were lower compared to the previous reports from similar areas (except of Cd concentrations). Only total Cd levels were higher than the metal level of established sediment quality guideline. Potential ecological risk index denoted 'minimal ecological risk (RI < 150)' from the combination of Cd, Cu, Ni, Pb and Zn of both rivers. This indicated that the two rivers were not significantly polluted by Cu, Ni, Pb and Zn. Geochemical studies revealed that 78% of 'non-resistant' fractions for Zn in the nine sampling sites of both rivers were higher than 'resistant' fractions. Although these two rivers were not receiving anthropogenic metals, the sediment was still dominated by non-resistant Zn.

Keywords: heavy metal Sediment sequential extraction, sediment quality guidelines

1. INTRODUCTION

The proliferation of anthropogenic activities has contributed to various extent of metal contamination to the environment (Wong et al. 2017). As the main sink of the heavy metal contaminant, the sediment in the mangrove areas is the logical focus in the ecological assessment of heavy metal pollution (Filgueiras et al. 2004). Therefore, multiple independent studies were carried out to investigate the possible heavy metal pollution in several regions such as in Leizhou Peninsula, China (Liu et al. 2015), conserved mangrove ecosystem, India (Chowdhury and Maiti, 2016), the western coast of the Peninsular Malaysia (Cheng and Yap 2015), and mangrove sediments of the Tanzania coast (Rumisha et al. 2016). Application of sediments to assess the anthropogenic influence on the aquatic ecosystem has proven to

be useful tool in ecotoxicological studies. Transports and settlements of heavy metals are highly influenced by the surrounding sediments and environmental settings (Salomons et al. 1987). Identification of the spatial and temporal sources of anthropogenic heavy metals contamination can be determined via assessing the heavy metals levels in the sediment (Yuan et al. 2014; El-Amier et al. 2017). Sediment is the main sink of the anthropogenic metals (Filgueiras et al. 2004). These heavy metals are persistent in the marine ecosystem and only low concentrations of these metals may runoff into the coastal water (Fang et al. 2005; Nemati et al. 2011).

Since sediments can be potential reserve for the heavy metals as well as other pollutants, the sediment can be a sustaining source of contaminants that disperse to the surrounding ecosystem (Salomons et al. 1987; Sin et al. 2001; Filgueiras et al. 2004). The accumulated concentrations in the sediments are risked becoming a secondary of heavy metal source to the surrounding aquatic ecosystem (Sin et al. 2001). However, various physico-chemical variables have proven to influence the metals' bioavailability in the sediment.

Total metal concentration has received some arguments as it does not necessarily provide sufficient insight on the bioavailability and the source of the metal. The geochemical speciation or fractionation pattern of a particular metal detects its mobility and bioavailability (Sundaray et al. 2011). An alteration in the distribution of each geochemical fraction could be due to the mineralization in the basin as well as the anthropogenic inputs of heavy metals in the region (Alves et al. 2007; Wong et al. 2017). Therefore, incorporation of metal geochemical speciation in the analysis is crucial for assessing the risk caused by heavy metal pollution (Sundaray et al. 2011). This analysis can be performed by sequential extraction technique (Tessier and Campbell 1987). The deployment of this procedure in the assessment of metal speciation in soil or sediment has been widely reported since its introduction in 1980s (Badri and Aston 1983; Calmano and Froster 1983; Panda et al. 1995; Galvez-Cloutier and Dubé 1998; Tokalioglu et al. 2000; Yap et al. 2002b). In the last decade, Najamuddin et al. (2016) studied heavy metal geochemical speciation from tropical estuary surface sediment in

Jeneberang River, Indonesia. While in China, the intertidal sediment in Donghai Island was investigated by Zhang et al. (2016) for geochemical speciation of Cd and Pb. This approach has been also utilized by Chowdhury and Maiti (2016) for determination of the amplitude of heavy metal contamination in Sundarbans Biosphere Reserve, India.

According to Martin and Whitfield (1983), approximately 90% of particulate matters in rivers would eventually settle in estuarine and coastal areas. Metal pollutants released into the environment would likely to be adsorbed onto particulate matter in water and are eventually sedimented to the bottom of the rivers. Therefore, the regional heavy metal pollution status can be revealed based on the accumulation and distribution of heavy metals in the coastal sediment. The comparatively high and stable concentration of contaminants in the sediment improved analytical effectiveness compared to dissolved and suspended particulate phases in the water current (Hanson et al. 1993). Thus, sediment monitoring provides critical facts on the coastal marine heavy metal pollution.

The Sepang Besar River was reported to be highly polluted with Cu and Zn as it received effluents from pig farm (Ismail and Ramli 1997). Ismail and Rosniza (1997) reported that the polluted Sepang Besar River had Cu concentration as high as 670 mg/kg dry weight due to pig farm effluents. This alarming level is certainly of much public concern due to the metal itself is potential to pose undesirable hazardous impacts on the biota of the ecosystem. Due to the Japanese Encephalitis (JE) outbreak in 1999, pig farming activity was halted (Yap et al. 2007).

In Malaysia, geochemical fractionations of heavy metals were reported in river sediment (Ismail and Rosniza 1997; Wong et al. 2017) and coastal sediment (Yap et al. 2002b). Previous studies by Ismail and Ramli (1997), Saed et al. (2002, 2004) and Yap et al. (2003) showed that the non-resistant fraction for Zn and Cu were not dominant in Sepang River. These studies suggested that metal inputs to Sepang Besar River were still occupied by anthropogenic origins (Yap et al. 2007). The objectives of the present study are to 1) determine the concentrations of Cd, Cu, Fe, Ni, Pb and Zn in the surface sediments in the estuaries of Sepang Besar River (SBR) and Sepang Kecil River (SKR), 2) determine the geochemical speciation of the six heavy

metals in the mangrove sediment of both rivers to identify the sources of contamination, and 3) estimate the ecological risk assessments of the sediments samples.

2. MATERIALS AND METHODS

2.1. Sampling

The sediment samples from SBR and SKR were collected on 1st December 2007. Six (6) and three (3) strategic sites from SBR and SKR were selected, respectively (Figure 1 and Table 1). Triplicate samples of the surface sediments were sampled using Ekman grab and plastic hand scoops. Thereafter, the collected samples were transported back to laboratory for further analysis.

Table 1. Site descriptions and GPS of sampling sites from Sepang Besar River (SBR) and Sepang Kecil River (SKR). All samples were collected on 1 December 2007

Sampling site no.	Location	Latitude	Longitude	Description of sampling site
1	SBR 1	02˚ 36.653’ N	101˚ 42.345’E	Prawns hatchery area and water was muddy
2	SBR 2	02˚ 36.980’N	101˚ 42.819’E	Mangrove area
3	SBR 3	02˚ 36.260’ N	101˚ 42.133’E	A Jetty area, fishing hatchery and water was muddy
4	SBR 4	02˚ 36.102’ N	101˚ 42.337’E	Mangrove area at side of river and water was muddy
5	SBR 5	02˚ 35.933’ N	101˚ 42.826’E	Estuarine area, not far from sea and water was muddy
6	SBR 6	02˚ 36.042’ N	101˚ 42.461’E	Clear water and mangrove area at the estuary
7	SKR 1	02˚ 37.198’ N	101˚ 41.235’E	River water was muddy
8	SKR 2	02˚ 37.201’ N	101˚ 41.239’E	River was stagnant and water was muddy
9	SKR 3	02˚ 36.890’ N	101˚ 41.026’E	River water was muddy

In the laboratory, the samples were dried at 60°C until constant weight (Yap et al. 2002a). Then, the dried sediments were grounded and sifted through a 63 µm siever, which were heavily associated with metals (Tam and Wong 2000). Homogeneity of sediment grains was carried out using vigorous shakier during the sifting process (Yap et al. 2002a). The sifted sediments were stored in new and clean plastic bags for further analysis.

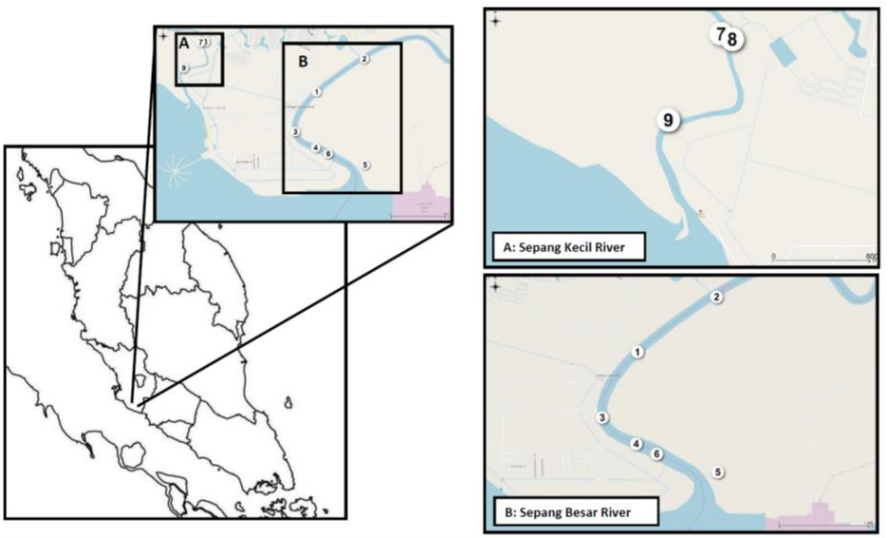

Figure 1. The sampling map of the mangrove estuary sediments at Sepang Kecil River (A) and Sepang Besar River (B). (The maps were generated using QGIS Desktop version 2.18.13).

2.2. Sample Treatment

The digestions of sediments were divided into two (2) methods which were measurement of 1) total metal concentrations by using direct aqua-regia digestion, and 2) speciation into four geochemical fractions using the modified sequential extraction technique (Tessier et al. 1979; Yap et al. 2002a).

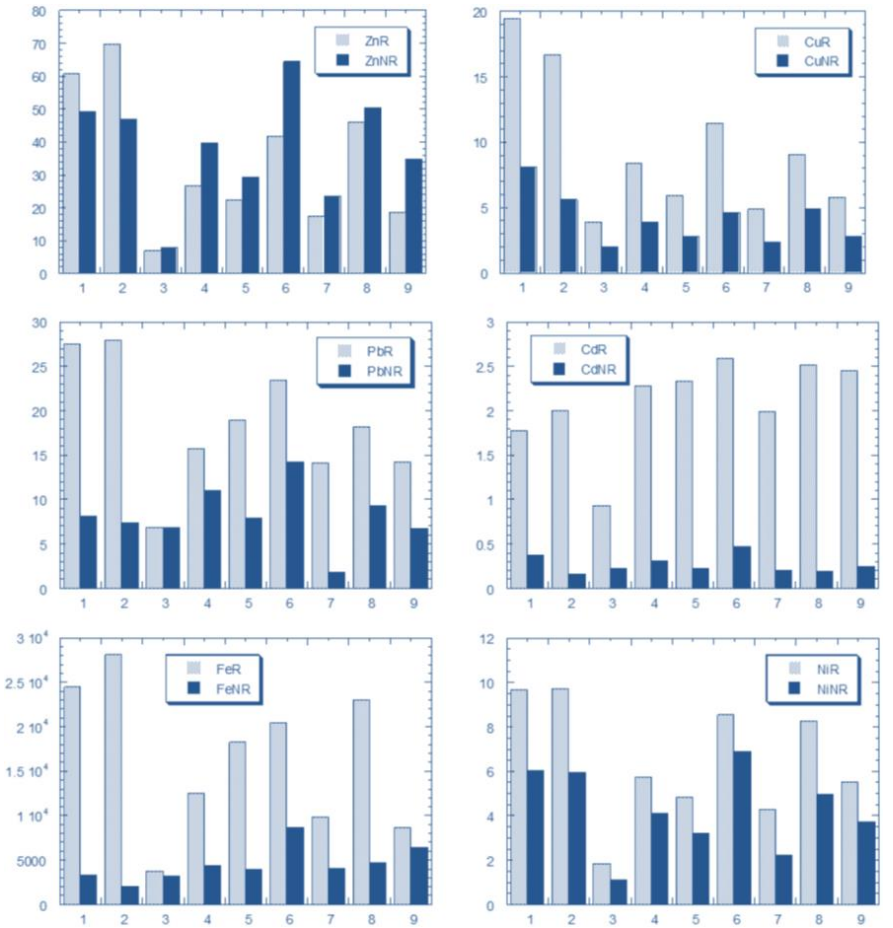

Figure 2. The concentration (mg/kg dry weight) of sediment non-resistant (NR) and resistant (R) fractions of Cd, Cu, Fe, Pb, Ni and Zn from Sepang Besar River-SBR (Site 1 to 6) and Sepang Kecil River-SKR (Site 7 to 9). (X-axis = metal concentrations in mg/kg dry weight; Y- axis = sampling site number).

For direct aqua-regia digestion, about 1.00 g of dried sediments was inserted into acid-washed digestion tube. The digestion reagent of aqua-regia consisted of 10mL of a combination solution of AnalaR grade 69% HNO_3 and 60% $HClO_4$ in the ratio of 4:1 (Yap et al. 2002b). The samples were digested for 4 hours (40°C at the first hour and 140°C for the subsequent three hours).

For geochemical speciation analysis, the heavy metals in the sediments were sequentially extracted based on the modified sequential extraction technique (SET) (Badri and Aston 1983; Tessier and Campbell 1987). The SET consisted of four fractions, namely 1) easily, freely, leachable or exchangeable (EFLE); 2) acid-reducible (AR); 3) oxidisable-organics (OO); and lastly 4) resistant (R). The extraction of first fraction (EFLE) involved addition of 50mL of 1.0 M ammonium acetate (NH_4CH_3COO) at pH 7 and shaken for 3 hours at room temperature. The AR fraction was extracted by addition of 50 mL hydroxyl ammonium chloride ($NH_2OH.HCL$) at pH 2 and shaken for 3 hours at room temperature. The third fraction (OO), was involved initial oxidization with 15mL of 30% hydrogen peroxide in water bath at 90-95°C followed by addition of 50mL ammonium acetate (NH_4CH_3COO) at pH 2 and shaken again for 3 hours. All agitation needed for the extraction of the first three fractions was conducted using orbital shaker (model GYROMAX 722) agitated at 1600rpm. The fourth fraction (R), was commenced according to the aforementioned direct aqua-regia method.

After the aqua-regia digestion, the resulting digestates were diluted to 40mL using double distilled water (DDW) and filtered through Whatman No. 1 filter paper (11µm). The filtrates were kept at 4°C until further metal analysis. Before proceeding to next SET extraction, the residue was rinsed with 20mL of DDW. For first three fractions, the extraction reagents were filtered out by Whatman no 1 filter paper and the filtrate was acidified by HCl and analysed for its metal content. Between each fraction, the residue was weighed before next fraction extraction was carried out. For each fraction, a procedural blank was prepared for quality control purpose (Yap et al. 2002a).

2.3. Metal Determination

The digestates were analysed using the Air Acetylene flame Atomic Absorption Spectrophotometer (FAAS) Perkin Elmer to determine the concentrations of the six metals. To ensure the accuracy of the reading, a

quality control sample was routinely analysed during the metal analysis. Standard solutions (1000mg/L stock solution) that were used to calibration of FAAS and as quality control samples during analysis, were supplied by Merck Titrisol.

2.4. Quality Assurance

To prevent contamination from occurring, all glassware and non-metallic equipment used were washed with 5% HNO_3. Metallic apparatus was washed thoroughly with detergent (DECON 90). These apparatuses were rinsed with distilled water before use.

To ensure the accuracy of sequence extraction procedure, the mathematical summation of four extracted fractions was compared with that found by using the aqua-regia digestion. The recovery of this procedure was acceptable at 90-105% for all metals and their correlation was significant ($p < 0.05$). Standard Reference Material (SRM) for Soil (Soil-5, International Atomic Energy Agency Vienna, Austria) was used as standard material to ensure the aqua regia digestion process was free of contamination. The CRM was treated and digested along with other samples. The recovery of the metals was acceptable at 90-110%.

2.5. Statistical Analysis

The data from the data conversion were transformed into graphs using IBM SPSS Statistics for Window (Version 15). The significance of the levels of heavy metals between each sampling sites was checked by one-way analysis of variance (ANOVA). The correlation between the two variables was determined using Spearman's correlation analysis at 0.05 significance level.

2.5.1. Data Treatment

Geo-Accumulation Index

The values of geo-accumulation index (Igeo) were determined according the formula proposed by Muller (1969), as follow:

$$Igeo = Log_2 (C_n/1.5 \times B_n)$$

where C_n is the heavy metal concentrations of the sediments and B_n is the preindustrial reference values (mg/kg dw) namely 1.0, 50, 68, 70 and 175 for Cd, Cu, Ni, Pb and Zn (Hakanson 1980), respectively (Table 2). The preindustrial reference value represents the background value for each value. The background value for Fe (3.09%) was obtained from upper continental crust (UCC; Wedepohl 1995). These background values have been summarized in Table 2. In this formula, a factor of 1.5 was introduced to reduce the effect of possible lithogenic fluctuation in the background values of the sediments (Al-Haidarey et al. 2010; Hasan et al. 2013). It has also permitted content fluctuations of a target pollutant in the environment as well as minute anthropogenic impacts (Loska et al. 1997). The interpretation of Igeo was based on the classification proposed by Muller (1969) (Table 3).

Table 2. Background concentrations (mg/kg dry weight except indicated as %) of reference values for of heavy metals used in the present study. *Ni from average shale (Turekian and Wedepohl 1961) cited in Zheng et al. (2010). **Fe background from upper continental crust (UCC) (Wedepohl, 1995)

	Ni*	Pb	Cu	Zn	Cd	Fe (%)**
Preindustrial reference level (Hakanson, 1980)	68.0	70.0	50.0	175	1.00	3.09
Factor of toxic response (Hakanson, 1980)	2.00	5.00	5.00	1.00	30.0	NA
UCC (Wedepohl, 1995)	18.6	17.0	14.3	52.0	0.102	3.09

Table 3. Interpretation standards of A) Geo-accumulation index (I_{geo}) (Muller, 1969; Gonzáles-Macías et al. 2006; Wong et al. 2017); B) Enrichment factor (Sutherland, 2000); C) Contamination factor (C_f^i) (Hakanson 2000); D) Risk index for individual metal (Er) (Hakanson, 2000); E) Potential Ecological Risk Index (PERI) (Hakanson 2000)

A)	Geo-accumulation index, Igeo	Interpretation
	Igeo < 0	practically unpolluted
	0 < Igeo < 1	unpolluted to moderately polluted
	1 < Igeo < 2	moderately polluted
	2 < Igeo < 3	moderately to strongly polluted
	3 < Igeo < 4	strongly polluted
	4 < Igeo < 5	strongly to very strongly polluted
	Igeo > 5	very strongly polluted
B)	Enrichment factor, EF	Interpretation
	EF < 2	depletion of mineral enrichment
	2 ≤ EF < 5	moderate enrichment
	5 ≤ EF < 20	significant enrichment
	20 ≤ EF < 40	very high enrichment
	EF > 40	extremely high enrichment
C)	Contamination factor, CF	Interpretation
	CF < 1	low contamination factor
	1 ≤ CF < 3	moderate contamination factor
	3 ≤ CF < 6	considerable contamination factor
	CF ≥ 6	very high contamination factor
D)	Risk index for individual metal, Er	Interpretation
	ER < 40	low potential ecological risk
	40 ≤ ER < 80	moderate potential ecological risk
	80 ≤ ER < 160	considerable potential ecological risk
	160 ≤ ER < 320	high potential ecological risk
	ER ≥ 320	very high potential ecological risk
E)	Potential ecological risk index, PERI	Interpretation
	PERI < 150	low ecological risk
	150 ≤ PERI < 300	moderate ecological risk
	300 ≤ PERI < 600	considerable ecological risk
	PERI ≥ 600	very high ecological risk

Enrichment Factor

The Enrichment Factor (EF) was calculated based on Buat-Menerd and Chesselt (1979)'s formula:

$$EF = (C_n/C_{Fe})_{sample}/(C_n/C_{Fe})_{crust}$$

where (C_n/C_{Fe}) sample is the ratio between a metal (n) to Fe in the sediments; (C_n/C_{Fe}) crust is the ratio of the metal (n) to Fe in the earth crust which would refer as the background value of sediment in this study (Table 2).

Fe was selected as a normalizer for EF calculation to correct the possible variations may be caused by sediment mineralogy and particle size distribution (Schi and Weisberg 1999). The is because the input of Fe has been vastly dominated by those by natural origin (98%) (Tippie 1984; Hasan et al. 2013). Moreover, Fe is a major metal sorbent and a viable tracer of the natural metal-containing substances in river and coastal sediments, making it suitable to be used as a normalizer in the determination of EF (Schi and Weisberg 1999). The degrees of EF were categorized based on the suggestion by Sutherland (2000) (Table 3).

Ecological Risk Assessment by Risk Index of Individual Metal (ER) and Potential Ecological Risk Index (PERI)

The objective of the calculation of contamination factor (CF) was to estimate the contamination of pollutant in an aquatic ecosystem (Hakanson 1980). In this study, the CF was calculated using a formula below:

$$CF = C_D/C_R$$

where CF = contamination factor; C_D = mean metal concentration in the sediment; C_R = preindustrial reference values (PRV) of each metal (Table 2). The interpretation of CF was done as Hakanson (1980) recommendation (Table 3).

The potential risk index for an individual metal was calculated according to formula below (Hakanson 1980):

$$ER = T_r \times CF$$

where T_r = toxic-response factor, as preseted in Table 2 for each metal investigated (Hakanson 1980; Xu et al. 2008). Due to the absence of T_r value for Fe, ER for Fe was not calculated. CF = contamination factor. The ER for this study was interpreted according to Hakanson (1980) recommendation (Table 3).

The mathematical summation of each ER forms potential ecological risk index (PERI) (Hakanson 1980):

$$PERI = \Sigma ER$$

where ER = potential risk of individual metal. The PERI was interpreted according to Hakanson (1980) recommendation (Table 3).

3. RESULTS AND DISCUSSION

3.1. Heavy Metals in Sediments

Table 4 shows the concentrations of Cd, Cu, Fe, Ni, Pb and Zn in the surface sediment samples collected from SBR and SKR. Overall, the concentrations (mg/kg dry weight (dw)) varied among the heavy metals. In SBR, the concentrations were 3.68–4.44 for Cd, 5.23–22.7 for Cu, 7086–32489 for Fe, 3.54–13.9 for Ni, 18.9–41.3 for Pb and 18.1–88.3 for Zn. Meanwhile, for SKR, the metal concentrations were 3.57–4.24 for Cd, 7.96–13.5 for Cu, 11079–21444 for Fe, 20.0–32.5 for Pb, 6.85–12.8 for Ni and 52.3–98.9 for Zn.

The areas around SBR and SKR were in the vicinity of pig farming in the past, and the piggery activities had been largely ceased as Japanese Encephalitis (JE) dealt a heavy blow to the piggery industry in the region. The Pre-JE reference of the metal concentrations survey in this region was conducted by Saed et al. (2002) in which their study was conducted before shutting down the pig farming business due to epidemics. Saed et al. (2002) revealed that Cu and Zn concentration (mg/kg dw) in the two samplings sites near to the estuaries of SBR and SKR, were between 0.50–0.70 for Cd, 100–

150 for Cu,15–25 for Pb, and 110–220 for Zn. These two sampling sites were closest the present sampling sites as indicated in the sampling map. In comparison to the present study, the ranges of metal concentrations (mg/kg dw) in SBR were 1.15–2.60 for Cd, 5.23–22.7 for Cu, 18.9–41.3 for Pb and 18.1–88.3 for Zn. Therefore comparatively, the levels of Cu and Zn in sediment collected in 2007 were significantly below in comparison to previous reported values (Saed et al. 2002) before the closing pig farms based on the sediments collected in 1998. This showed the decrement of the two important elements acting as growth catalyst in the feeds for the piggery husbandry at Bukit Pelanduk. However, present Cd and Pb levels were slightly above than the values reported by Saed et al. (2002).

Based on sediment samples collected in 1996 at SKR, previous study by Ismail and Ramli (1997) reported the high concentrations of Cu, Pb and Zn in surface sediment and gastropods collected in the vicinity to the pig farming areas. However, they also detected about 100-folds decrement of metal concentrations towards the river mouth. The range concentrations of trace metals (mg/kg dw) in sediment studied were 4–670 for Cu, 4–550 for Zn, 3.4–46.5 for Pb and 0.1–2.1 for Cd. The geochemical speciation analysis on the surface sediments also revealed that 60 to 70% of the Cu, Zn and Pb in the sediments were originated from land-based piggery slurry (Saed et al. 2002, 2004).

In the present study, there was an elevation of Zn and Cu in the sediment near site 6 (Figure 1 and Table 4) located at SBR. This elevated levels were caused by pig farming effluents discharged to the rivers. There were several studies which suggested that pig farm effluents was a potential contribution to the elevation of sediment Cu and Zn concentrations at other Malaysian rivers (Devi 1986; Arzul and Maguer 1980; Ismail and Ramli 1997). Devi (1986) reported that Cu and Zn were commonly added into the pigs' fodder to prevent parasites infestation. The introduction of high concentration of Cu and Zn into pig's diet could also act as a growth promoter (López Alonso et al. 2000). In pig diet, dietary concentration of 150-250 mg/kg of $CuSO_4$ and 2500-3000 mg/kg of $ZnSO_4$ have known to be able to promote growth without jeopardizing livestocks to any toxicity risk (Brumm 1998). As highlighted earlier in this study, the activities in the pig farm were the most

probable contributor to the elevation of Cu and Zn in the sediment at the region. Another study also revealed that pig slurry could induce pollution of Cd, Cu and Zn (Bernal et al. 1992). Several other findings were also in coincidence and suggested that frequent utilization of pig slurries could result in the accumulation of Cu and Zn in the soil (Moral et al. 2008; Comas et al. 2014; Zhang et al. 2014; Benedet et al. 2016).

For the SKR, Saed et al. (2002) reported the two sampling sites closest in concentrations (mg/kg dw) at the present study as: 2–3 for Cd, 45–50 for Cu, 6–8 for Pb, and 80–90 for Zn. In comparison to the present study, the Cd, Cu, Pb and Zn concentration ranges (mg/kg dw) in Saed et al. (2002) at SKR were 2.19–2.70, 7.96–13.5, 20.0–32.5, and 52.3–98.9, respectively. Therefore, Cd and Zn levels were comparable between the two periods of samplings while Cu was significantly lower in our 2007 samples, than that of the 1998 samples. However, present Pb levels were significantly higher than those reported by Saed et al. (2002). Coincidently, higher levels of Pb in both estuaries of SBR and SKR in 2007 samples than 1998 samples could be due to sources of land-based and sea-based human activities.

3.2. Geochemical Speciation Analysis of Sediments

The concentrations and percentages of NR and R fractions in the metals are presented in Tables 4 and 5, respectively. For SBR, the ranges of percentages (%) of R fractions were 80.8–92.2 for Cd, 65.3–74.7 for Cu, 54.1–93.2 for Fe, 55.5–62.1 for Ni, 49.9–79.1 for Pb, and 39.3–59.96 for Zn. The percentages of ranges of NR fractions were 7.83–19.1 for Cd, 25.3–34.6 for Cu, 6.78–45.9 for Fe, 37.9–44.5 for Ni, 20.9–50.1 for Pb, and 40.1–60.7 for Zn.

For SKR, the ranges of percentages of R fractions in all metals of this study were 90.9–92.9 for Cd, 64.9–67.6 for Cu, 57.7–83.0 for Fe, 59.8–65.7 for Ni, 66.1–88.4 for Pb, and 34.8–47.7 for Zn. The ranges of NR fractions were 7.04–9.13 for Cd, 32.4–35.2 for Cu, 16.9–42.3 for Fe, 34.4–40.2 for Ni, 11.6–33.9 for Pb, and Zn: 52.3–65.2 for Zn.

Table 4. Mean concentrations (mg/kg dry weight) of Cd, Cu, Fe, Ni, Pb, and Zn of four geochemical fractions in the surface sediments at Sepang Besar River -SBR (Site 1 to 6) and Sepang River Kecil-SKR (Site 7 to 9)

Site	Zn						Cd						Pb					
SBR	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4
1	82.1	110	0.94	14.2	34.1	60.7	3.81	2.15	0.31	0.05	0.01	1.78	25.6	35.6	0.71	1.02	6.38	27.5
2	80.1	116	0.65	9.35	36.7	69.7	4.41	2.17	0.11	0.04	0.01	2.00	26.3	35.3	0.63	1.33	5.41	28.0
3	18.1	14.7	1.45	3.58	2.70	6.96	4.34	1.15	0.18	0.03	0.01	0.93	19.0	13.7	0.82	3.13	2.90	6.83
4	74.8	66.5	1.53	15.8	22.5	26.6	4.44	2.60	0.27	0.03	0.01	2.28	28.3	26.8	1.93	1.69	7.38	15.8
5	64.9	51.7	1.25	13.5	14.5	22.4	4.42	2.56	0.18	0.04	0.01	2.33	29.1	26.8	1.20	1.20	5.45	19.0
6	88.3	106	1.55	19.1	43.8	41.7	3.68	3.07	0.43	0.03	0.01	2.59	41.3	37.7	1.72	1.39	11.1	23.5
Min	18.1	14.7	0.65	3.58	2.70	6.96	3.68	1.15	0.11	0.03	0.01	0.93	19.0	13.7	0.63	1.02	2.90	6.83
Max	88.3	116	1.55	19.1	43.8	69.7	4.44	3.07	0.43	0.05	0.01	2.59	41.3	37.7	1.93	3.13	11.1	28.0
Mean	68.1	77.6	1.23	12.6	25.7	38.0	4.18	2.28	0.25	0.04	0.01	1.99	28.3	29.3	1.17	1.63	6.44	20.1
SE	10.5	16.5	0.15	2.22	6.28	9.78	0.14	0.27	0.05	0.00	0.00	0.24	2.98	3.67	0.22	0.31	1.12	3.29
SKR	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4
7	52.3	41.1	2.65	12.9	8.12	17.5	3.57	2.19	0.18	0.01	0.01	1.99	32.5	16.0	0.80	0.57	0.47	14.2
8	99.0	96.5	0.70	13.2	36.6	46.0	4.15	2.70	0.10	0.08	0.01	2.51	23.4	27.5	1.25	0.30	7.78	18.2
9	57.4	53.5	2.12	15.8	16.9	18.6	4.24	2.69	0.16	0.07	0.01	2.45	20.0	21.1	0.40	0.83	5.56	14.2
Min	52.3	41.1	0.70	12.9	8.12	17.5	3.57	2.19	0.10	0.01	0.01	1.99	20.0	16.0	0.40	0.30	0.47	14.2
Max	99.0	96.5	2.65	15.8	36.6	46.0	4.24	2.70	0.18	0.08	0.01	2.51	32.5	27.5	1.25	0.83	7.78	18.2
Mean	69.6	63.7	1.82	14.0	20.5	27.4	3.99	2.53	0.15	0.05	0.01	2.32	25.3	21.5	0.82	0.57	4.60	15.5
SE	14.8	16.8	0.58	0.93	8.42	9.34	0.21	0.17	0.02	0.02	0.00	0.16	3.72	3.34	0.25	0.15	2.16	1.34

Table 4. (Continued)

Site	Fe						Cu						Ni					
SBR	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4
1	25512	27808	119	1016	2197	24475	22.7	27.5	0.19	0.38	7.54	19.4	13.1	15.7	0.27	0.25	5.51	9.68
2	25823	30177	101	750	1196	28130	17.1	22.3	0.13	0.32	5.18	16.7	13.9	15.7	0.47	0.32	5.14	9.74
3	7086	6950	470	733	1987	3760	5.23	5.89	0.04	0.32	1.68	3.85	3.54	2.98	0.47	0.25	0.41	1.85
4	17012	16968	249	835	3325	12560	11.5	12.3	0.03	0.24	3.60	8.40	9.90	9.82	0.39	0.14	3.57	5.72
5	13564	22140	199	1102	2599	18241	9.00	8.69	0.01	0.14	2.62	5.92	8.49	8.06	0.35	0.25	2.61	4.84
6	32489	29071	816	1451	6380	20424	15.3	16.1	0.05	0.13	4.47	11.5	16.1	15.4	0.53	0.28	6.06	8.54
Min	7086	6950	101	733	1196	3760	5.23	5.89	0.01	0.13	1.68	3.85	3.54	2.98	0.27	0.14	0.41	1.85
Max	32489	30177	816	1451	6380	28130	22.7	27.5	0.19	0.38	7.54	19.4	16.1	15.7	0.53	0.32	6.06	9.74
Mean	20248	22186	326	981	2947	17932	13.5	15.5	0.07	0.26	4.18	11.0	10.8	11.3	0.41	0.25	3.88	6.73
SE	3817	3662	112	112	744	3572	2.54	3.37	0.03	0.04	0.84	2.50	1.84	2.14	0.04	0.02	0.87	1.28
SKR	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4	Total	SUM	F1	F2	F3	F4
7	11080	13824	1148	990	1910	9776	7.96	7.27	0.11	0.14	2.14	4.88	6.85	6.55	0.21	0.54	1.50	4.30
8	21444	27688	932	1010	2754	22992	13.5	13.9	0.16	0.10	4.63	9.04	12.8	13.3	0.31	0.36	4.30	8.28
9	11520	15094	1785	1109	3486	8715	8.81	8.58	0.13	0.01	2.65	5.80	8.82	9.25	0.11	0.30	3.30	5.53
Min	11080	13824	932	990	1910	8715	7.96	7.27	0.11	0.01	2.14	4.88	6.85	6.55	0.11	0.30	1.50	4.30
Max	21444	27688	1785	1109	3486	22992	13.5	13.9	0.16	0.14	4.63	9.04	12.8	13.3	0.31	0.54	4.30	8.28
Mean	14681	18869	1288	1036	2717	13828	10.1	9.93	0.13	0.08	3.14	6.57	9.47	9.69	0.21	0.40	3.03	6.04
SE	3384	4425	256	36.8	455	4592	1.72	2.04	0.01	0.04	0.76	1.26	1.73	1.95	0.06	0.07	0.82	1.18

Note: F1 = Easily, freely, leachable or exchangeable; F2 = acid-reducible; F3 = oxidisable-organic; F4- resistant; SUM = summation of F1, F2, F3 and F4. Total = total concentration using direct aqua-regia method. Min = minimum; Max = maximum; SE = standard error.

The total metals have been always criticized that it does not necessarily provide an accurate insight on the bioavailability of the metals and which was due to man-induced activities (anthropogenic activities). The mobilization capacity and bioavailability of heavy metals were determined by their presence in different geochemical fractions (Nemati et al. 2011).

The EFLE fraction comprised of only a small fraction, for all six metals, in the sediments of SBR and SKR. The EFLE fraction was generally easily leachable by water. Hence, low EFLE fraction in this study would imply that poor bioavailability of these metals in the sediment could not be easily leached out by water. Even though, EFLE fraction only represented low percentage compared to other fractions, this fraction still cannot be ignored as the metals due to the leachability from sediment even at pH 7. Therefore, the metals in this fraction should be concerned for their potential bioavailability (Jenne and Luoma 1977). The bioavailability could be lowered with the association of the metals with hydrous iron, manganese oxide or on soil particles (Jenne and Luoma 1977). Although marine sediment is a major sink for ionic heavy metals in seawater (Lyons and Fitzgerald 1980), there was a possibility of the remobilization of sediment-bound metals under the alteration of the surrounding physico-chemical conditions leading to the release of ionic heavy metals to the interstitial water and overlying seawater.

All investigated metals in this study except Zn recorded low levels in the AR fraction. Organisms-mediated organic substance decomposition can cause reduction in the sediment (Calmano and Frostner 1983). The metals within this fraction are known to bind with oxides, hydroxides and possibly carbonates of Fe and Mn. Fe and Mn oxides could bind with trace metals with high efficiencies due to the high scavenging efficiencies of these compounds toward trace metals. However, the remobilization of metals in AR fraction was possible under anoxic condition due to the thermodynamic instability of Fe and Mn oxides under this condition (Tokalioglu et al. 2000). The remobilization of the metal would imply the increase of bioavailability of these metals. Therefore, the low AR fraction metals (with the exception of Zn) could due to relatively lower anthropogenic metal emission in the region and also due to the possibility of the oxygen-depletion condition

experienced by the sediment. However due to the fact of the lower EFLE percentage within all fraction, the potential amount of AR fraction metals would be limited.

Among the metals, Zn showed the highest level of OO fractions which was almost similar to the Zn levels of R fraction in the two rivers. Besides that, Cu, Pb, Ni and Fe also showed higher percentage of OO fraction among the NR fraction. OO fraction was related with various organic materials in sediment (Tokalioglu et al. 2000). The distribution, transportation and chemical transformation of metal species in ecosystem have been heavily shaped by the dissolved organic matters in the sediment (Singer 1997). The appearance of organic phase in the sediments could impact the mobility of metals in ecosystem from several perspectives, physical transportation of particulate organic matters would be one of them (Singer 1977). The association of metals with sediment organic matters could be in the form of insoluble organic complexes or peptized colloidal species (Lee 1975). Disintegration of organic matters would occur under oxidizing condition resulting in leaching of soluble metals into water phase. The result implied that Cu, Fe, Ni and Pb in SBR and SKR had a high affinity to humic matters. Humic matters in the sediment or soil is a group of chemically active organic matters that tend to form stable complexes and metal sulphites particles with heavy metals (Forstner and Whittman 1981; Tokalioglu et al. 2000). The result implicated that metals occurred the area were mainly associated with the occurrence of organic matters in the sediment, contributing to its abundance in OO fraction. Several different previous studies indicated that Cu in the soil may complexes with organic substances in the sediment (Tessier et al. 1979; Badri and Aston 1983; Mat and Maah 1994a; Mat and Maah 1994b). The other metals that were abundant in this fraction might share similar environmental fate. Among all metals, Cd comprised the lowest proportion in OO fraction among all NR fractions.

In this study, at least half of the Fe was belonging to R fraction (54.1–93.2%). The proportioning of Fe among the four geochemical fractions indicated that lithogenic Fe comprised around half of the Fe concentrations in sediment in the region. The geochemical fractions distribution of Fe was also shared by other metals analysed except for Zn. The R fraction of Cd

(>80%) showed a marked difference when compared to NR fraction of Cd in all the two rivers. The metals in R fraction were incorporated within the silicate matters in crystal lattice in the sediment (Badri and Aston 1983). The strong association between metals with the silicate matters in the sediment contributed to its low bioavailability. The abundance of these metals (except for Zn) implied that the metal inputs in the study region were not dominated by anthropogenic sources, indicating low pollution level. Metals in the R fraction had been identified as natural lithogenic source. Therefore, the ecotoxicological concern of the metals in this fraction was low.

Table 5. Percentages (%) of Cd, Cu, Ni Pb and Zn in the four geochemical fractions of the surface sediments at Sepang Besar River-SBR (St. 1 to 6) and Sepang Kecil River (SKR, St. 7 to 9)

Zn						Cu					
SBR	F1	F2	F3	F4	NR	SBR	F1	F2	F3	F4	NR
1	0.86	12.9	31.0	55.2	44.8	1	0.69	1.38	27.4	70.6	29.4
2	0.56	8.03	31.5	59.9	40.1	2	0.58	1.43	23.2	74.7	25.3
3	9.87	24.4	18.4	47.4	52.6	3	0.68	5.43	28.5	65.4	34.6
4	2.30	23.8	33.9	40.1	59.9	4	0.24	1.95	29.3	68.4	31.6
5	2.42	26.1	28.1	43.3	56.7	5	0.12	1.61	30.2	68.1	31.9
6	1.46	18.0	41.3	39.3	60.7	6	0.31	0.81	27.7	71.1	28.9
Min	0.56	8.03	18.4	39.3	40.1	Min	0.12	0.81	23.2	65.4	25.3
Max	9.87	26.1	41.3	59.9	60.7	Max	0.69	5.43	30.2	74.7	34.6
Mean	2.91	18.9	30.7	47.5	52.5	Mean	0.44	2.10	27.7	69.7	30.3
SE	1.88	20.9	31.3	45.4	54.7	SE	0.44	1.52	28.1	69.5	30.5
SKR	F1	F2	F3	F4	NR	SKR	F1	F2	F3	F4	NR
7	6.44	31.3	19.8	42.5	57.5	7	1.51	1.93	29.4	67.1	32.9
8	0.73	13.7	37.9	47.7	52.3	8	1.15	0.72	33.2	64.9	35.2
9	3.97	29.6	31.7	34.8	65.2	9	1.52	0.12	30.9	67.6	32.4
Min	0.73	13.7	19.8	34.8	52.3	Min	1.15	0.12	29.4	64.9	32.4
Max	6.44	31.3	37.9	47.7	65.2	Max	1.52	1.93	33.2	67.6	35.2
Mean	3.71	24.8	29.8	41.7	58.3	Mean	1.39	0.92	31.18	66.5	33.5
SE	1.65	5.61	5.33	3.74	3.74	SE	0.12	0.53	1.10	0.85	0.85
Fe						Pb					
SBR	F1	F2	F3	F4	NR	SBR	F1	F2	F3	F4	NR
1	0.43	3.65	7.90	88.0	12.0	1	1.99	2.86	17.9	77.2	22.8
2	0.33	2.49	3.96	93.2	6.78	2	1.78	3.77	15.3	79.1	20.9
3	6.76	10.6	28.6	54.1	45.9	3	5.99	22.9	21.2	49.9	50.1
4	1.47	4.92	19.6	74.0	26.0	4	7.21	6.32	27.6	58.9	41.1
5	0.90	4.98	11.7	82.4	17.6	5	4.47	4.47	20.3	70.7	29.3

Zn						Cu					
SBR	F1	F2	F3	F4	NR	SBR	F1	F2	F3	F4	NR
6	2.81	4.99	22.0	70.3	29.7	6	4.56	3.69	29.5	62.2	37.8
Min	0.33	2.49	3.96	54.1	6.78	Min	1.78	2.86	15.3	49.9	20.9
Max	6.76	10.6	28.6	93.2	45.9	Max	7.21	22.9	29.5	79.1	50.1
Mean	2.12	5.26	15.6	77.0	23.0	Mean	4.33	7.33	22.0	66.4	33.7
SE	1.00	1.13	3.81	5.75	5.75	SE	0.88	3.15	2.25	4.63	4.63
SKR	F1	F2	F3	F4	NR	SKR	F1	F2	F3	F4	NR
7	8.30	7.16	13.8	70.7	29.3	7	5.00	3.56	2.94	88.4	11.6
8	3.37	3.65	9.95	83.0	17.0	8	4.54	1.09	28.3	66.1	33.9
9	11.8	7.34	23.1	57.7	42.3	9	1.90	3.94	26.4	67.7	32.4
Min	3.37	3.65	9.95	57.7	17.0	Min	1.90	1.09	2.94	66.1	11.6
Max	11.8	7.34	23.1	83.0	42.3	Max	5.00	3.94	28.3	88.4	33.9
Mean	7.83	6.05	15.6	70.5	29.5	Mean	3.81	2.86	19.2	74.1	25.9
SE	2.45	1.20	3.90	7.30	7.30	SE	0.97	0.89	8.15	7.20	7.20
Cd						Ni					
SBR	F1	F2	F3	F4	NR	SBR	F1	F2	F3	F4	NR
1	14.4	2.33	0.47	82.8	17.2	1	1.72	1.59	35.1	61.6	38.4
2	5.07	1.84	0.46	92.2	7.83	2	3.00	2.04	32.8	62.1	37.9
3	15.7	2.61	0.87	80.9	19.1	3	15.8	8.39	13.8	62.1	37.9
4	10.4	1.15	0.38	87.7	12.3	4	3.97	1.43	36.4	58.3	41.8
5	7.03	1.56	0.39	91.0	8.98	5	4.34	3.10	32.4	60.1	40.0
6	14.0	0.98	0.33	84.4	15.6	6	3.44	1.82	39.4	55.5	44.5
Min	5.07	0.98	0.33	80.9	7.83	Min	1.72	1.43	13.8	55.5	37.9
Max	15.7	2.61	0.87	92.2	19.1	Max	15.8	8.39	39.4	62.1	44.5
Mean	11.1	1.75	0.48	86.5	13.5	Mean	5.37	3.06	31.6	59.9	40.1
SE	1.77	0.26	0.08	1.86	1.86	SE	2.11	1.09	3.72	1.08	1.08
SKR	F1	F2	F3	F4	NR	SKR	F1	F2	F3	F4	NR
7	8.22	0.46	0.46	90.9	9.13	7	3.21	8.24	22.9	65.7	34.4
8	3.70	2.96	0.37	93.0	7.04	8	2.34	2.71	32.4	62.4	37.6
9	5.95	2.60	0.37	91.1	8.92	9	1.19	3.24	35.7	59.8	40.2
Min	3.70	0.46	0.37	90.9	7.04	Min	1.19	2.71	22.9	59.8	34.4
Max	8.22	2.96	0.46	93.0	9.13	Max	3.21	8.24	35.7	65.7	40.2
Mean	5.96	2.01	0.40	91.6	8.36	Mean	2.25	4.73	30.3	62.6	37.4
SE	1.30	0.78	0.03	0.66	0.66	SE	0.58	1.76	3.83	1.70	1.70

Note: F1 = Easily, freely, leachable or exchangeable; F2 = acid-reducible; F3 = oxidisable-organic; F4 - resistant; SUM = summation of F1, F2, F3 and F4. Nonresistant = summation of F1, F2 and F3. Total = total concentration using direct aqua-regia method. Min = minimum; Max = maximum; SE = standard error.

Since 1999 JE outbreak, pig farming activity was largely halted (Yap et al. 2007). Three years after the shutting down of pig farming (2003), sampling study was conducted. The latter study by Yap et al. (2007) reported that the total concentration of Zn and Cu (mg/kg dry weight) ranged from

34.5 to 420.6 for Zn and 2.88 to 161 for Cu which showed lower ranges of Zn and Cu with the maximum metal concentrations found being lower that before the cessation of the piggery activities. The decline of Zn and Cu concentrations might be due to stoppage of dumping of animal wastes in the SBR.

3.3. Geochemical Indexes

Table 6 depicted the EF and Igeo values of five metals (Cd, Cu, Ni, Pb and Zn) in this study. The Ni EF values for SBR and SKR are 0.23–0.28 and 0.27–0.35, respectively. The Pb EF values for SBR and SKR were 0.44–1.18, and 0.48–1.29, respectively. The Cu EF values for SBR and SKR were 0.29–0.55 and 0.39–0.47, respectively. The Zn EF values for SBR and SKR were 0.45–0.84, 0.81–0.88, respectively. The Cd EF values for SBR and SKR were 2.60–5.83, 3.89—7.20, respectively. Based on the classification by Sutherland (2000), all EF values for Cu, Ni, Pb and Zn were belonged to lack or minimal enrichment (EF < 2) category. For Cd, present values fell between $2 \leq EF < 5$ and hence categorized as 'moderate enrichment' except for site SBR-5 which fell into 'significant enrichment' category.

Table 6. Enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF) and ecological risk (ER) of heavy metals based on the surface sediments at Sepang Besar River-SBR (St. 1 to 6) and Sepang River Kecil-SKR (St. 7 to 9)

No.	Ni EF	Igeo	CF	ER	Pb EF	Igeo	CF	ER	Cu EF	Igeo	CF	ER
1	0.23	-2.96	0.19	0.39	0.44	-2.04	0.37	1.83	0.55	-1.72	0.45	2.27
2	0.24	-2.88	0.20	0.41	0.45	-2.00	0.38	1.88	0.41	-2.13	0.34	1.71
3	0.23	-4.85	0.05	0.10	1.18	-2.47	0.27	1.36	0.46	-3.84	0.10	0.52
4	0.26	-3.36	0.15	0.29	0.73	-1.89	0.40	2.02	0.42	-2.71	0.23	1.15
5	0.28	-3.59	0.12	0.25	0.95	-1.85	0.42	2.08	0.41	-3.06	0.18	0.90
6	0.23	-2.66	0.24	0.47	0.56	-1.35	0.59	2.95	0.29	-2.30	0.31	1.53
Min	0.23	-4.85	0.05	0.10	0.44	-2.47	0.27	1.36	0.29	-3.84	0.10	0.52
Max	0.28	-2.66	0.24	0.47	1.18	-1.35	0.59	2.95	0.55	-1.72	0.45	2.27
Mean	0.25	-3.38	0.16	0.32	0.72	-1.93	0.41	2.02	0.42	-2.63	0.27	1.35

No.	Ni EF	Igeo	CF	ER	Pb EF	Igeo	CF	ER	Cu EF	Igeo	CF	ER
SE	0.01	0.32	0.03	0.05	0.12	0.15	0.04	0.21	0.03	0.31	0.05	0.25
7	0.28	-3.90	0.10	0.20	1.29	-1.69	0.46	2.32	0.44	-3.24	0.16	0.80
8	0.27	-3.00	0.19	0.38	0.48	-2.16	0.33	1.67	0.39	-2.48	0.27	1.35
9	0.35	-3.53	0.13	0.26	0.77	-2.39	0.29	1.43	0.47	-3.09	0.18	0.88
Min	0.27	-3.90	0.10	0.20	0.48	-2.39	0.29	1.43	0.39	-3.24	0.16	0.80
Max	0.35	-3.00	0.19	0.38	1.29	-1.69	0.46	2.32	0.47	-2.48	0.27	1.35
Mean	0.30	-3.48	0.14	0.28	0.85	-2.08	0.36	1.81	0.43	-2.94	0.20	1.01
SE	0.03	0.26	0.03	0.05	0.24	0.21	0.05	0.27	0.02	0.23	0.03	0.17

No.	Zn EF	Igeo	CF	ER	Cd EF	Igeo	CF	ER	RI
1	0.57	-1.68	0.47	0.47	2.60	0.52	2.15	64.5	69.5
2	0.55	-1.71	0.46	0.46	2.60	0.53	2.17	65.1	69.6
3	0.45	-3.86	0.10	0.10	5.01	-0.38	1.15	34.5	36.6
4	0.78	-1.81	0.43	0.43	4.72	0.79	2.60	78.0	81.9
5	0.84	-2.02	0.37	0.37	5.83	0.77	2.56	76.8	80.4
6	0.48	-1.57	0.50	0.50	2.92	1.03	3.07	92.1	97.6
Min	0.45	-3.86	0.10	0.10	2.60	-0.38	1.15	34.5	36.6
Max	0.84	-1.57	0.50	0.50	5.83	1.03	3.07	92.1	97.6
Mean	0.61	-2.11	0.39	0.39	3.95	0.54	2.28	68.5	72.6
SE	0.07	0.36	0.06	0.06	0.58	0.20	0.27	7.96	8.34
7	0.83	-2.33	0.30	0.30	6.11	0.55	2.19	65.7	69.3
8	0.81	-1.41	0.57	0.57	3.89	0.85	2.70	81.0	85.0
9	0.88	-2.19	0.33	0.33	7.22	0.84	2.69	80.7	83.6
Min	0.81	-2.33	0.30	0.30	3.89	0.55	2.19	65.7	69.3
Max	0.88	-1.41	0.57	0.57	7.22	0.85	2.70	81.0	85.0
Mean	0.84	-1.98	0.40	0.40	5.74	0.75	2.53	75.8	79.3
SE	0.02	0.29	0.09	0.09	0.98	0.10	0.17	5.05	5.00

The Cd Igeo values for SBR and SKR were -0.38 to 1.03, and 0.55 to 0.85, respectively. The Zn Igeo values for SBR and SKR were -3.86 to -1.57, and -2.33 to -1.41, respectively. The Ni Igeo values for SBR and SKR were -4.85 to -2.66, and -3.90 to -3.00, respectively. The Pb Igeo values for SBR and SKR were -2.47 to -1.35, -2.39 to -1.69, respectively. The Cu Igeo values for SBR and SKR were -3.84 to -1.72, and -3.24 to -2.48, respectively. According to Muller (1969), all values for Cu, Ni, Pb and Zn fell in the category of 'unpolluted' (Igeo ≤ 0). For Cd, it was categorized as 'unpolluted to mildly polluted' ($0 <$ Igeo ≤ 1) while SBR-6 fell in the category of 'mildly polluted' ($1 <$ Igeo ≤ 2). Costa-Böddeker et al. (2017) surveyed Thi Vai Estuary and Can Gio Mangrove Forest (Vietnam) for its

heavy metal pollution and found that levels of Co, Cu and Zn in their region were categorized as 'low contamination' while Cr and Ni were in 'moderate contamination.' Interestingly, despite some of their sites were belong to highly industrialized region, the metal concentrations for their study was found to be lower than expected. They proposed a hypothesis that the metal distribution was affected by dilution effect, erosion rates and hydrodynamics of the region. These natural occurring events might also impact on the heavy metal pollution in local ecosystems.

3.4. Ecological Risk Assessments

The values of CF, ER and PERI of the surface sediments in SBR and SKR are presented in Table 6. The ranges of Zn CF values for SBR and SKR were 0.10–0.50, and 0.30–0.57, respectively. The ranges of Cd CF values for SBR and SKR were 1.15–3.07, and 2.19–2.70, respectively. The ranges of Ni CF values for SBR and SKR were 0.05–0.24, and 0.10–0.19, respectively. The ranges of Pb CF values for SBR and SKR were 0.27–0.59, and 0.29–0.46, respectively. The ranges of Cu CF values for SBR and SKR 0.10–0.45, and 0.16–0.27, respectively. The CF values for Ni, Pb, Cu and Zn were categorized as 'low contamination' ($CF \leq 1$) (Hakanson, 1980). For Cd, the SBR values fell in the category of 'mild contamination' ($1 < Cf \leq 3$) while the SKR was within the category for 'considerable contamination' ($3 < CF \leq 6$). Costa-Böddeker et al. (2017) also found that the CF values of his study fell in the category of 'mild to considerable pollution' for Ni.

The ranges of Zn ER values for SBR and SKR were 0.10–0.50, and 0.30–0.57, respectively. The ranges of Cd ER values for SBR and SKR were 34.50–92.10, and 65.70–81.00, respectively. The ranges of Ni ER values for SBR and SKR were 0.10–0.47, and 0.20–0.38, respectively. The ranges of Pb ER values for SBR and SKR were 1.36–2.95, and 1.43–2.32, respectively. The ranges of Cu ER values for SBR and SKR were 0.52–2.27, and 0.80–1.35, respectively. According to Hakanson (1980)'s classification, the ER values of As, Cu, Cr, Hg, Pb and Zn were below 40, falling into the category of 'minimal potential ecological risk' (< 40) for these metals, while

the ER values of Cd fell in the category of 'mild potential ecological risk' ($40 \leq ER < 80$). Lastly, the ranges of PERI values for SBR and SKR were 36.59–97.55, and 69.32–84.96, respectively. These PERI values denoted 'minimal ecological risk ($RI < 150$)' from the combination of all the five metals (Hakanson 1980).

4. CONCLUSION

When compared to previous studies, SBR and SKR recorded a general reduction in the total heavy metal concentrations of Cu, Ni, Pb and Zn. The present study findings were slightly higher compared to those reported from several Malaysian studies. Based on established sediment quality, all these rivers were polluted by Cd, while the levels of Cu, Ni, Pb and Zn were within all the reported ranges.

All metals in this study except Zn showed higher R fractions than NR fractions for both rivers, indicating that the two rivers were not receiving anthropogenic metals because the sediment was still dominated by R fractions of Cd, Cu, Fe, Ni and Pb. By using Sediment Watch, the increasing metal levels in the two rivers, whether of anthropogenic or natural, can be addressed properly.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

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Chapter 6

LOW ENRICHMENT OF HEAVY METALS IN SURFACE (CORE-TOP) SEDIMENTS OF OFFSHORE SABAH COASTAL WATERS: A RELIEF OR NEED FOR STRICTER REGULATION?

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ABSTRACT

A study was carried out on the distribution and enrichment of heavy metals (As, Cd, Cr, Cu, Ni, and Pb) in the surface marine sediments of offshore Sabah, Malaysia. Twenty-five surface (core-top) marine sediments were sampled from three coastal regions of Sabah (three sites from South China Sea, one site each from Sulu and Sulawesi Sea) and analyzed for heavy metals by using an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The enrichment factor (EF), geoaccumulation index (Igeo) and the modified degree of contamination (mC_d) were used to calculate the anthropogenic and pollution status of the metals in the samples. Except for As, the EF values were categorized as 'moderate enrichment' in some sampling sites, other metals were found to be 'no enrichment' at all sampling sites. The values of Igeo for all metals showed 'unpolluted' at all five sampling sites. However, the values of mC_d of all sampling sites were found < 1.0, denoting 'very low contamination' of the investigated metals in the sampling sites of this study. The present findings were a relief to the public since there is not ecotoxicological risks of the heavy metals to the living resources from the offshore coastal Sabah. However, the governing body should keep on monitoring the toxic chemicals and implement a stricter regulation in order to maintain the current pristine condition of the offshore Sabah coastal waters.

Keywords: heavy metals; geochemical indexes; marine sediments; offshore Sabah coastal waters

1. INTRODUCTION

Industrialization and urbanization in coastal regions are the main factors of environmental pollution where anthropogenic inputs are the main contribution of marine sedimentary contamination (El Nemr et al., 2016). Among the significant global environmental problems occurring nowadays, the common heavy metal contamination of the aquatic ecosystems cannot be ruled out (Gao and Chen 2012). Due to the recalcitrant nature of heavy metals, they are regarded as major pollutants in the natural environment. According to Gan et al., (2013) and Ip et al., (2007), coastal sediments are the primary sources of pollutants such as heavy metals. The heavy metals found in marine sediments were a result of natural processes including

weathering, erosion, and volcanic eruptions (Shang et al., 2015) and anthropogenic activities such as mismanagement of waste discharges during industrial and agricultural processes. Other sources of heavy metal enrichment in the sediments were contributed by domestic sewage, boating activities (Chatterjee et al., 2007), mining, and refining (Shang et al., 2015). The elevated concentrations of heavy metals in the contaminated sediments could potentially elicit hazardous effects on benthic fauna and other aquatic organisms as evidenced in many reported studies (Hill et al., 2013; Roberts 2012). Heavy metal pollution in sediments might have severe health hazards effects on humans, invertebrates, and fish (Boyd 2010; Martín et al., 2015). In Malaysia, Wood et al., (2004) had studied the geological and diagenesis, and transportation of coastal sediments around in the Island of Penang, while Rezaee et al., (2011) provided data of heavy metal distribution and enrichment around the sediments collected from South China Sea. While there is considerable numbers of heavy metal studies reported from Malaysia, the study of heavy metals in the offshore Sabah coastal waters is still lacking.

In this study, the distribution and enrichment of six heavy metals, namely As, Cd, Cr, Cu, Ni and Pb in the surface (core-top) marine sediments of offshore Sabah coastal waters were determined by an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) technique.. The main objective of this study was to evaluate the status of the above six heavy metals in the marine sediments of offshore Sabah coastal waters, based on enrichment factor (EF), geoaccumulation index (I_{geo}), and modified degree of contamination (mC_d).

2. MATERIALS AND METHODS

2.1. Sampling

The core-top (surface 0-2 cm) sediments were sampled in August 2004 by using the standard corer sampler at the five stations of coastal Sabah Malaysia (Figure 1). The stations, based on the Global Positioning System

(GPS) were divided into three regions, namely the South China Sea (SB01 (06° 00.0' N, 115° 00.0' E), SB02 (06° 32.7' N, 115° 53.9'E), and SB03 (07° 24.68' N, 116° 46.91' E)), Sulu Sea (SB04 (05° 49.88' N, 118° 41.89' E)), and Sulawesi Sea (SB05 (04° 44.87' N, 118° 38.77' E)).

This sampling trip involved a team of workers from the Malaysian Nuclear Agency, Universiti Putra Malaysia (UPM), and school of Oceanography, University of Washington (Wood 2001). The sediments were collected at a sea depth of between 49 and 109 m from all the three regions of the offshore Sabah coastal waters by using a box corer of 20 cm×30 cm cross-sectional areas. The samples were later refrigerated (-5°C) until further analysis (Ashraf et al., 2016, 2017).

Figure 1. Map showing the sampling stations in the offshore Sabah coastal waters (Ashraf et al., 2017).

2.2. Sample Preparation for Metal Analysis

About 0.50 g of dried and powdery core-top sediment samples from each sampling site were weighed and digested in a combination of nitric acid (analytical research grade) and perchloric acid (analytical research grade), in a ratio of 4:1 (Yap and Pang 2011).

All sediment samples and procedural blanks were digested at 40°C for the first hour and consequently increased to 140°C for three hours. Digested samples were left to cool, and later diluted to 40 ml with double distilled water and eventually filtered by using Whatman No. 1, into acid-washed polyethylene pillboxes until further analysis. The prepared samples were analyzed by using ICP-MS techniquefor the determination of As, Cd, Cr, Cu, Ni, Pb and Fe.

2.3. Quality Assurance and Quality Control

For quality control purposes, duplicate samples, procedural blanks and the certified reference materials namely IAEA-SL-1 had been utilized. In addition to that, daily routine check on the energy calibration of the gamma spectroscopy system was conducted to ensure the accuracy of the instrument. The recoveries of metals between measured and certified values of CRM were being between 86.8 and 121% (Table 1).

2.4. Ecological Risk Assessments

2.4.1. Enrichment Factor (EF)

The calculation of normalized EF to reflect the metal concentrations above unpolluted background levels is a common method to evaluate the anthropogenic effect of metals on sediments (Abrahim et al., 2007). The EF approach normalized the measured heavy metal concentrations with the Fe of the present study. In the present work, the EF was calculatedbased on the following formula:

$$EF= (M_x/M_{ref})_{sample}/(M_x/M_{ref})_{average\ shale} \quad (1)$$

where $M_x/M_{ref})_{sample}$ represents the ratio of the measured metal concentrations in the sediment sample to the normalizing Fe, while $(M_x/M_{ref})_{average\ shale}$ represents the metal concentrations of an appropriate

background or baseline reference material such as average shale. The background or baseline reference used were (mg/kg dry weight except for those indicated as %) 4.72%, 13.0, 0.22, 90.0, 39.0, 68.0, and 23.0 for Fe, As, Cd, Cr, Cu, Ni, and Pb, respectively (Forstner and Salomons 1984; Turekian and Wedepohl 1961).

The EF values were interpreted based on the five categories of metal enrichment as suggested by Sutherland (2000). These five categories of metal enrichment were: EF< 2, denoting a depletion to minor degree of enrichment; 2 <EF< 5, denoting medium degree of enrichment; 5 <EF< 20, denoting significant degree of enrichment; 20 <EF< 40, denoting very high degree of enrichment and; EF> 40, denoting extreme degree of enriched enrichment.

Table 1. Comparisons of metal concentrations (mean ± SD, mg/kg dry weight) between measured and certified values of the certified reference materials (IAEA SL-1) by using ICP-MS technique

Elements	Certified values	Measured values	Recovery (%)
As	27.6 ± 2.90	30.2 ± 3.10	109
Cd	0.26 ± 0.05	0.30 ± 0.04	102
Cr	104 ± 9.00	90.4 ± 2.80	86.8
Cu	30.0 ± 6.00	30.3 ± 4.40	101
Ni	44.9 ± 8.50	53.4 ± 2.30	119
Pb	37.7 ± 7.40	45.7 ± 5.80	121
Fe	6.74 ± 0.170	5.77 ± 0.30	117

In general, if the EF value equals one or less than one, the major source of heavy metals in the sediments is of crustal or marine environmental origin. On the other hand, if the EF value becomes much greater than one, the major source of heavy metals is contributed by anthropogenic inputs.

2.4.2. Geoaccumulation Index

Another prominent method of assessing the enrichment of metal concentrations above background or baseline concentrations is by using Igeo indexes (Muller 1969). The approach estimates the degree of metal contamination based on seven enrichment categories (Abrahim et al., 2007). The following formula was used to calculate the index:

$$Igeo = \log_2 (M_n/1.5 \times B_n) \quad (2)$$

where M_n represents the concentration of the metal of the present sediment samples; B_n represents the background (average shale) or pristine value of the metal (Forstner and Salomons 1984; Turekian and Wedepohl 1961); 1.5 serves as a factor to reduce variations of the background values due to lithologic disparity in the sediments (Stoffers et al., 1986).

2.4.3. Modified Degree of Contamination (mC_d)

Lastly, the contamination factor (CF) was determined based on the comparison to a baseline pristine reference metal level. The following formula was used to calculate the CF value:

$$CF = M_{sample}/M_{background} \quad (3)$$

where M_{sample} and $M_{background}$ represent the mean concentrations of the heavy metals in the present sediments samples and the average shale values, respectively (Forstner and Salomons 1984; Turekian and Wedepohl 1961).

Furthermore, the summation of all metal CF values demonstrates the overall degree (Hakanson 1980) of sediment contamination (C_d) by using the following formula:

$$C_d = \sum CF \quad (4)$$

The C_d supplies the degree of the overall pollution in surface layers of a specific core or sampling location. The modified and generalized version of

the Eq. (4) for the calculation of the overall degree of pollution is exhibited by Eq. (5) (Abrahim et al., 2007; Hakanson, 1980).

The modified equation is generalized through elucidating the mC_d as the total of all CF values for all the studied heavy metals segmented by the number of analyzed metals. The modified equation for a generalized procedure to determine the degree of contamination is presented as follows:

$$mC_d = (\sum CF)/n \quad (5)$$

where n represents the number of heavy metals in this study; CF represents the contamination factor. For the categorization and delineation of the mC_d in the sediments, the classifications and gradations from Hakanson (1980) are strictly followed.

3. RESULTS AND DISCUSSION

3.1. Concentrations of Heavy Metals in the Core-Top Sediments

Table 2 indicates the levels of As, Cd, Cr, Cu, Ni and Pb in this study obtained from the core-top sediments of the five sampling stations. It is evident that the concentrations (mg/kg dw) of heavy metals vary considerably from each other (As: 3.66–15.08; Cd: 0.07–0.14; Cr: 11.12–22.79; Cu: 3.31–8.77; Ni: 19.09–44.92 and; Pb: 3.37–12.89).

The distributions of the levels of As, Cd, Cr, Cu, Ni and Pb in the surface marine sediments with error bar at five sampling sites of this study are demonstrated in Figure 2.

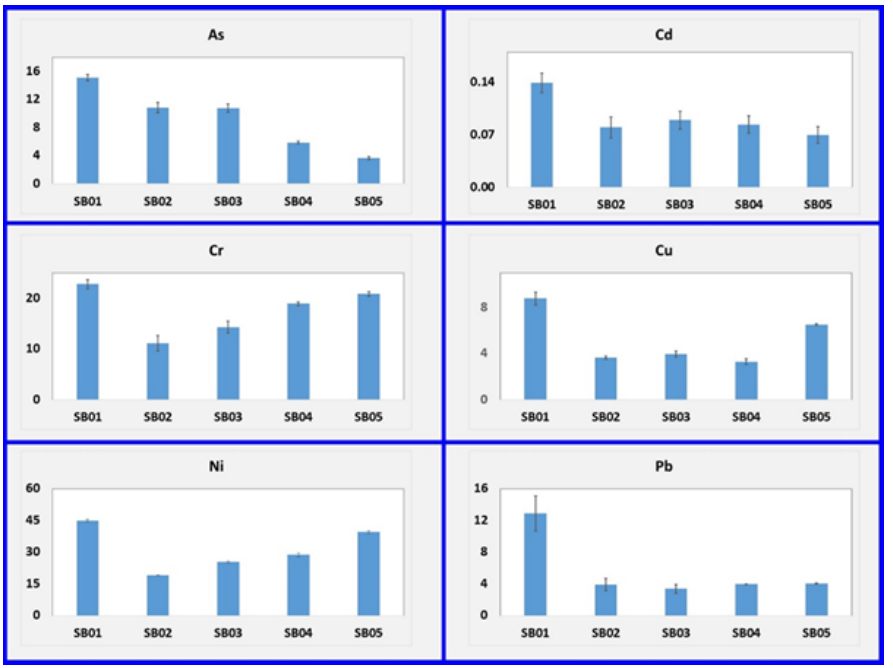

Figure 2. Distributions of heavy metal concentrations (mean ± SD; mg/kg dry weight) in the surface marine sediments of offshore Sabah coastal waters.

Table 2. Heavy metal concentrations (mean ± SE, mg/kg dry weight) measured in the core-top (surface) marine sediments of the offshore Sabah coastal waters

Metal	SB01	SB02	SB03	SB04	SB05
As	15.08 ± 0.43	10.83 ± 0.76	10.75 ± 0.59	5.87 ± 0.17	3.66 ± 0.24
Cd	0.14 ± 0.01	0.08 ± 0.01	0.09 ± 0.012	0.08 ± 0.01	0.07 ± 0.01
Cr	22.79 ± 0.86	11.12 ± 1.52	14.31 ± 1.19	18.92 ± 0.34	20.87 ± 0.47
Cu	8.77 ± 0.56	3.65 ± 0.15	3.97 ± 0.26	3.31 ± 0.25	6.52 ± 0.07
Ni	44.92 ± 0.59	19.09 ± 0.15	25.29 ± 0.41	28.72 ± 0.95	39.45 ± 0.73
Pb	12.89 ± 2.22	3.88 ± 0.78	3.37 ± 0.54	3.95 ± 0.03	4.01 ± 0.06

3.2. Enrichment Factor of Heavy Metals in the Surface Sediments

Table 3 shows the EF values for all metals in the surface (core-top) sediments collected from five sampling sites of the offshore Sabah coastal waters.

Table 3. Enrichment factor (EF) values of heavy metals in the surface marine sediments of the offshore Sabah coastal waters

Sampling sites	As	Cd	Cr	Cu	Ni	Pb
SB01	3.14	1.72	0.69	0.61	1.79	1.52
SB02	4.14	1.80	0.61	0.46	1.40	0.84
SB03	4.26	2.10	0.82	0.52	1.92	0.76
SB04	1.20	1.01	0.56	0.23	1.12	0.46
SB05	0.53	0.59	0.43	0.31	1.08	0.33

The EF values acquired by the normalizer Fe for As and Cd at SB05 stations; Cr and Cu at five stations; and Pb at all stations except for SB01 station are < 1, which revealed the metals had depleted in relation to the crustal abundance in the study area.

However, heavy metals with an EF value of > 1 indicated the levels of these metals in relation to the crustal abundance that may be associated to the sediment pollution. The higher values of EF for As at SB04; Cd at SB01, SB02, and SB04; Ni at all sampling sites; and Pb at SB01 showing minimal enrichment while As at SB01, SB02, and SB03; and Cd at SB03 indicated moderate enrichment.

According to the EF values of heavy metals obtained with Fe normalizer, the Cr, Cu, and Pb (except for SB01) at all sampling sites were non-anthropogenic inputs in the surface sediments. The anthropogenic sources could be due to agricultural and industrial activities. Moreover, the increase of Cd could be contributed by plastic and electric factories while the elevated Pb levels might be due to the sewage and chemical wastes, including gasoline and batteries (Denton et al., 1997).

3.3. Geoaccumulation Index

Table 4 showed the results of the Igeo values for heavy metals in the surface marine sediments collected from the five sampling sites. According to the classifications, the metals (As, Cd, Cr, Cu, Ni, and Pb) fell into the 'Class 0' when compared to the average shale background values (Forstner and Salomons 1984; Turekian and Wedepohl 1961). This demonstrated that all heavy metals at all sampling sites were classified as 'unpolluted'.

Table 4. Geoaccumulation index (Igeo) of the heavy metals in the surface sediments of the coastal Sabah Malaysia in comparison with the average shale baseline values

Surface (Core-Top)	As	Cd	Cr	Cu	Ni	Pb
SB01	-0.37	-1.24	-2.57	-2.74	-1.18	-1.42
SB02	-0.85	-2.05	-3.60	-4.00	-2.42	-3.15
SB03	-0.86	-1.88	-3.24	-3.88	-2.01	-3.36
SB04	-1.73	-1.98	-2.84	-4.14	-1.83	-3.13
SB05	-2.41	-2.23	-2.69	-3.16	-1.37	-3.10

3.4. Modified Degree of Contamination and Contamination Factor

Table 5 showed the mC_d and CF values for of As, Cd, Cr, Cu, Ni and Pb in the marine surface sediments of the offshore Sabah coastal waters. The mC_d values of all heavy metals at five sampling sites ranged from 0.30 to 0.56 (< 1.50), showing very a low degree of contamination in the sediments of the study area. Moreover, the highest mC_d value was found at SB01 and the lowest mC_d value at SB02 and SB04.

Table 5. Modified degree of contamination (mC_d) using average shale baseline values for the heavy metals and contamination factors (CF) of each metal in the surface sediments of the offshore Sabah coastal waters

Sampling sites	mC_d	CF					
		As	Cd	Cr	Cu	Ni	Pb
SB01	0.58	1.16	0.63	0.25	0.22	0.66	0.56
SB02	0.31	0.83	0.36	0.12	0.09	0.28	0.17
SB03	0.34	0.83	0.41	0.16	0.10	0.37	0.15
SB04	0.29	0.45	0.38	0.21	0.08	0.42	0.17
SB05	0.29	0.28	0.32	0.23	0.17	0.58	0.17

Therefore, based on the values of EF, Igeo, mC_d and CF, the present results indicated that the heavy metal pollution level in the offshore Sabah coastal waters is insignificant.

CONCLUSION

The present ecological assessments of As, Cd, Cr, Cu, Ni and Pb in the offshore Sabah coastal waters showed that the area is 'very low contamination'. The present findings were a relief to the public since there was not ecotoxicological risks of the heavy metals to the living resources from the offshore coastal Sabah. However, the governing body should keep on monitoring the toxic chemicals and implement a stricter regulation in order to maintain the current pristine condition of the offshore Sabah coastal waters.

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Chapter 7

ASSOCIATION OF TRACE METALS (CR, CO, MN AND SC) BETWEEN SURFACE SEDIMENTS AND THE MANGROVE SNAIL *CERITHEDEA OBTUSA*: ASSESSMENT OF THE SNAIL AS A BIOMONITOR FOR INTERTIDAL MANGROVE ECOSYSTEM MANAGEMENT

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ABSTRACT

Trace metals Cr, Co, Mn and Sc have not been widely studied in the mangrove snail *Cerithedea obtusa*. The present study aimed to study the associations of the above four metals with their habitat surface sediments. By using a simple regression equation, it was found that the Cr concentrations in the soft tissues (ST) (R = 0.46) and shells (R = 0.39) of snails positively but weakly correlated with surface sediments. Similarly, Co concentrations in the ST (R = 0.51) and shells (R = 0.29) also positively but weakly correlated with surface sediments. However, it was clearly seen that Mn levels in the ST (R= 0.96) and shells (R= 0.91) positively and strongly correlated with the surface sediments. For Sc concentrations, only ST (R = 0.66) showed positive and good correlation with surface sediments but almost no association in the case of shells. Therefore, present findings pointed to the potential use of ST and shells of the snails as a good biomonitor of Mn and ST as a good biomonitor of Sc. The use of *C. obtusa* was important as a biomonitor of Mn and Sc pollution in the mangrove ecosystem and for an effective mangrove management in view of sustainable resources from the intertidal mangrove environment. Further experimental transplantation studies are needed to understand the bioaccumulation patterns in *C. obtusa* and to verify the effectiveness of *C. obtusa* as a good biomonitor based on recommended criteria as biomonitor.

Keywords: biomonitor, trace metals, mangrove snails, correlations

1. INTRODUCTION

Anthropogenic disturbances on marine and estuarine ecosystems and habitats are inevitably affecting the biotic elements in the ecosystem (Mearns et al. 2016). The heavy metal concentrations in aquatic animals are often related to those in the sediments in their natural habitat. This

relationship has been previously reported in numerous studies (Bakary et al. 2015; Dhanakumar et al. 2015; Saleh and Marie 2015). Therefore, it is logical to think that consumption of flora and fauna harvested from contaminated habitat will cause a potential health risk to consumers in the ecological and human sense.

Seafood consumption has been recognised as the major route of heavy metal exposure to human beings (Liu et al. 2014). Contributed from both anthropogenic discharges and natural releases of heavy metal pollutants, mangrove ecosystems can potentially act as a sink for heavy metal pollutants leading to the enrichment with heavy metals (Zhang et al. 2007; Cheng and Yap 2015). These anthropogenic heavy metal pollutants are often readily assimilated, bio-accumulated and potentially bio-magnified by various molluscs and may cause human health risks through the food chain (Cheng and Yap 2015; Wong et al. 2017).

Photo 1. The mangrove snail *Cerithedea obtusa*, collected from the west coast of Peninsular Malaysia.

Cerithedea obtusa is a marine gastropod mollusc species in Potadidae Family. It is a well-received delicacy and traditional therapeutics by Malaysian local populations in coastal areas (Misnan et al. 2016a; Misnan et al. 2016b). Owing to the fact that mollusc inclusive of snails are highly

tolerant and showed high accumulation of heavy metals (Lau et al. 1998; Ragi et al. 2017), the oral consumption of potentially contaminated edible snails may cause a significant chronic health risk to consumers. *C. obtusa* isn't likely to be an exception. Common heavy metals such as Cd, Cu, Fe, Ni, Pb and Zn were reported in the literature for the mangrove snail *C. obtusa* (Photo 1). For examples, Yap and Edward (2009, 2010) and Yap et al. (2017b) studied the different parts of *C. obtusa* while Kumar et al. (2014) reported the Cu levels in *C. obtusa* collected from the mangrove of the west coast of Peninsular Malaysia.

Numerous efforts have been done to study the relationship of the heavy metal concentration in the tissue of an organism with the environment. Positive correlation of Cu, Cr, Pb and Zn with exchangeable and carbonate fraction in the sediment with the respective metal concentrations in six commercial fish species in Cauvery delta region, India (Dhanakumar et al. 2015). The metal levels in sea catfish tissues, *Arius thalassinus* were also found to be responsive to the pollution levels of the sampling sites in Red Sea coast in Hodeida at Yemen Republic (Saleh and Marie 2015). They also identified that fresh catfish *A. thalassinus* still safe for human consumption even though the metal concentration is likely to elevate due to anthropogenic sources. The seasonal variation of Zn and Pb in the sediment in Milliardaires Bay (Cote d'Ivoire) was found to be reflected in the respective metal concentration in edible saltwater clam *Anadara senilis* (Bakary et al. 2015). This study also revealed that *A. senilis* has the ability to maintain the concentration of Cu by removing approximately twelve times of accumulated concentration of Cu during the dry season. There were no significant differences in apparent of concentration gradients of Zn, Cu, Cd and Pb between stations for *A. senilis*, water and sediment. It was also noticed that the concentrations of elements in sediment increased while in *A. senilis* showed a reverse gradient from stations close to Abidjan Harbour towards farther stations. The distribution gradient showed that the contaminated *A. senilis* maybe from their local sources. The correlations of metal concentrations between the contamination and its bioavailability in the sediment in Kruger National Park, South Africa, and the bioaccumulated metals in tigerfish, *Hydrocynus vittatus*, were found (Gerber et al. 2016).

However, the association of heavy metal contents in the soft tissues of a clam to the respective metal levels in their habitat sediments were not necessarily universal. Velez et al. (2015) showed that the element burden in clams (*Ruditapes decussates*, *Venerupis corrugata* and *Ruditapes philippinarum*) was not reflected the sediment contamination and bioaccumulation factor (BAF) values.

Bian et al. (2016) investigated the distribution of heavy metals and benthic macroinvertebrates. They evaluated the relationship between metal pollution based on the river sediments and benthic community structure. They found that the levels of As and Cu in sediments might adversely affect the benthic community. They suggested that the abundance and biomass of oligochaeta of benthic community of study area in the Taihu Basin, China could be used in monitoring for heavy metal pollution.

In this study, BAF of heavy metals of *C. obtusa* against the respective heavy metals was calculated to assess the heavy metal bioaccumulation capability of this edible snail. As mentioned, *C. obtusa* is widely consumed as food. It would be crucial to evaluate the BAF and concentrations of heavy metals that elevated metal levels could be transferred from various exposure pathways to humans causing adverse effects on human health (Singh et al. 2014). The use of BAF in the study of bioaccumulation capability of a species is well established as shown in multiple previous studies (Singh et al. 2014; Li et al. 2015; Das and Choudhury 2016). Analysing the BAF values of lower trophic prey species can be potentially used to predict the concentrations of pollutants in higher trophic predator species (Kwok et al. 2013).

The other aspect of concerns of the bioaccumulation and biomagnification of heavy metal pollutants in marine edible species, is its potential impact on human health by oral consumption of that species. Human health can be affected by the accumulation of high concentrations of metals by edible marine resources (Primost et al. 2017). Primost et al. (2017) analyzed the metals in multiple edible marine gastropods such as *Trophon geversianus*, *Adelomelon ancilla* and *Buccinanops globulosus* and their surrounding sediments. Compared to maximum levels recommended by multiple food safety regulations, only foot of these gastropod species is

recommended to be consumed. However, due to higher Pb levels in sediments and tissues, consumption of these gastropods was not recommended. Their Target Hazard Quotients (THQ) values showed that the THQ of Cd was not high for their local community. However, consumption of the gastropod species studied by Primost et al. (2017) might pose a potential health risk of chronic metal exposure.

The process of estimating the probability of harmful health effect within a specific period of time is known as human health risk assessment (HHRA) (Naz et al. 2016). There are two approaches which can be used to determine the potential health risks associated with heavy metal contamination via consumption of molluscs: 1) comparison of the concentrations of heavy metal levels in edible part of the snails against acceptation limit of internationally dietary guidelines and; 2) determination of HHR indexes, i.e., THQ (Cheng and Yap 2015).

The toxic metals that focused in the present study were Chromium (Cr), Cobalt (Co), Manganese (Mn) and rare-earth element Scandium (Sc). Chromium is mainly used in various industrial processes such as tannery, chrome plating, refractory brick, electroplating, chemical, dyes and pigments, steel alloy, textiles and glass manufacturing (Das and Mishra 2010). Cr(III) and Cr(VI) are two oxidation states of Cr commonly found in the environment. Compared to Cr(III) that is less likely to penetrate into living cells due to less solubility, Cr(VI) is highly reactive and soluble and hence it can pose a higher health risk (ATSDR 1998; USEPA 1998a; USEPA 1998b; Alloway 2012; Deng and Chen 2014). Chronic oral exposure of Cr(VI) may cause an adverse effect on the livers, kidney, gastrointestinal and immune systems, and possibly blood (WHO 1988; ATSDR 1998; USEPA 1998b). High oral dose of Cr(VI) compound has been reported to cause reproductive and developmental toxicity in mice, including decreased foetal weight, increased resorptions, and increased abnormalities. However, a later study in mice and rats determined that hexavalent Cr is not a reproductive toxicant in both sexes (USEPA 1998b). As determined by USEPA (1998b), the reference dose (RfD) of Cr(VI) is 3×10^{-3} mg/kg/day.

However, USEPA (1998b) has also stated that the confidence of the oral reference dose was low due to the small number of animals tested. In contrast, the noncarcinogenic effect of Cr(III) is lagging based on the latest toxicological review by USEPA for Cr(III) (USEPA 1998a).

Mn is an essential element for the human that serving as an activator of several enzymes, and be considered as one of the least toxic of the trace elements. However, it has also been recognized as a causative agent in a syndrome of neurologic and psychiatric disorders in Mn miner. However, ingested Mn has rarely been associated with toxicity (USEPA 1988). Despite the non-alarming background of Mn, the monitoring of Mn levels in the environment and the potential biomagnification in edible organisms must not be ignored under extreme context, This is due to Mn enrichment in an edible organisms might pose considerable risks.

Sc is a member of lanthanides of rare earth elements and it is probably the least studied element in the fourth period in the Periodic Table (Cotton 1991). Naturally, low concentrations of rare earth elements exist in an ecosystem. However, they can be accumulated in the environment following anthropogenic discharges. Tai et al. (2010) studied the biological toxicity of lanthanide elements on algae. The toxicity of lanthanides was found to reduce the growth of algae *Skeletonema costatum*, all single lanthanides (inclusive of Scandium) had a similar toxic effect to the algae. Currently, there is no toxicity study of Sc to the animal model. However, a recent study of chemically identical yttrium compound has shown that no toxicologically significant changes were found in any yttrium-treated mice as compared to the concurrent control group (Wang et al. 2017). Intraperitoneal injected Scandium Chloride was found to have a potential association with renal toxicity in Wistar rat (Tanida et al. 2009).

Since the information on the Cr, Co, Mn and Sc are lacking in *C. obtusa*, the present study aimed to study the associations of the above four metals with their habitat surface sediments by using simple regression analysis and bioaccumulation factor.

2. MATERIALS AND METHODS

2.1. Sampling

This present study was conducted in mangrove area in the west coast of Peninsular Malaysia (latitude: N 05°20′24.7″ to N01°15′58″ and longitude: E100°24′25.2″ to E103°30′39″), covering about 800 km as shown in Figure 1 and Table 1. The 10 locations of the present study were exposed to the different sources of pollution. This included activities of agriculture, aquaculture, industrial, tourism, shipping, port and hydroelectric power plant.

Table 1. Sampling sites and site descriptions (Kumar et al. 2014)

ID	Location Name	Latitudes	Longitudes	Description of nearby activities
L1	Tok Muda, Kapar, Selangor	N 03° 7′ 30.9″	E 101° 20′ 27.7″	Residential area; hydroelectric coal power plant
L2	Sungai SepangBesar, Selangor	N 02° 56′ 16.9″	E 101° 45′ 9.4″	Residential area
L3	Sungai Pasir Gudang, Johor	N 01° 24′ 3.99″	E 103° 57′ 26″	Residential area; shipping area
L4	Kuala Gula, Perak	N 04° 55′ 58″	E 100° 27′ 33.6″	Fishing village; recreational site; aquacultural site
L5	Juru, Penang	N 05° 20′ 24.7″	E 100° 24′ 25.2″	Fishing village; industrial area
L6	Kampung Panchor, Pantai Remis, Perak	N 04° 31′ 33.4″	E 100° 39′ 17.5″	Fishing village; recreational site; aquacultural site
L7	Sungai Kim Kim, Johor	N 01° 26′ 40.2″	E 103° 58′ 14.2″	Residential area; shipping area
L8	Lukut, Port Dickson, Negeri Sembilan	N 02° 34′ 49.4″	E 101° 47′ 53.9″	Residential area; shipping area; recreational site
L9	PulauKukup, Johor	N 01° 19′ 18.7″	E 103° 25′ 30.6″	Residential area; shipping area; aquacultural site
L10	Tanjung Piai, Johor	N 01° 15′ 58″	E 103° 30′ 39″	Residential area; shipping area; recreational site

A collection of the samples was conducted in 2011 from the mangrove areas and the details of the sampling locations and positions are shown in

Table 1 and Figure 1. The sequence of sampling locations, L1 – L10 were based on the sampling periods (Kumar et al. 2014). The identification of the mangrove snail, *C. obtusa* species as shown in the Photo 1, followed the descriptions as mentioned in other studies (Saavedra et al. 2004; Yap et al. 2017b). About 45 individual snails with commercial acceptable sizes were collected to reduce differences in metal contents due to their size factor and reproductive stage.

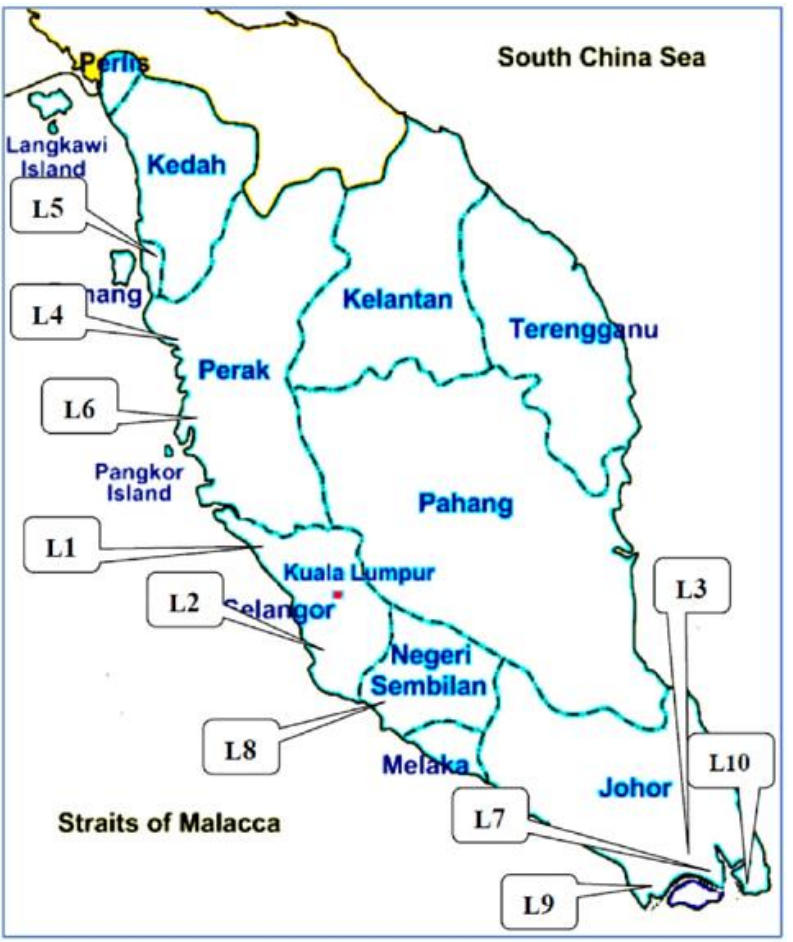

Figure 1. Sampling sites for snails and their habitat surface sediments in the mangrove coastal area of Peninsular Malaysia (Kumar et al. 2014).

At each station, habitat surface sediments (0-10 cm) in the mangrove area were also collected. The surface sediment samples of each sampling location were placed in a clean polyethylene bag and placed it into an icebox before transferred to the laboratory. In the laboratory, sediment samples were dried in an oven at 80°C at least for 3 days until constant dry weights.

2.2. Analytical Method

Instrumental neutron activation analysis (INAA) was used to analyze for the concentrations of Cr, Co, Mn and Sc in the snails and sediments because it is the most convenient and accurate method (Kumar et al. 2014). Dried samples were powdered using a pair of glass mortar and pestle. Later, they were sieved by a sieve with a mesh to a particle size < 200μm and were stored in polyethylene pillboxes. Each powdered sample was weighed approximately at 0.15g and 0.20g for short and long irradiations, respectively. All the samples were stored separately in heat-sealed polyethylene vials. Comparative method was used to determine the concentration of the elements in the sediment samples. All samples were irradiated by using pneumatic transport facility with thermal neutron flux of 4.0×10^{12} cm^{-2} s^{-1} at the MINT TRIGA Mark II research reactor which operated at 750kW. The samples were radiated for 60 seconds and counted for 300 and 1200 seconds after a cooling time of 1200 and 8640 seconds, respectively, during short radiation. For long radiation, the samples were irradiated for 21600 and 3600 seconds after a cooling time of 3 – 4 days and 21 – 28 days, respectively. Countings of radiated samples were performed by using calibrated high resolution HPGe detector and c-spectrometry coupled together with a multichannel analyser (MCA). A typical HPGe has an energy resolution of 1.8 keV at 1,332 keV of ^{60}Co.

The element present in the sample weas identified by using the specific energy of delayed gamma rays and the concentration of that particular element was determined based on the intensity of gamma peak. Standard point sources (^{133}Ba, ^{60}Co, ^{57}Co, ^{137}Cs, ^{54}Mn and ^{24l}Am) were used to calibrate the efficiency of gamma spectroscopy system in the energy range

of 60–2 MeV. Throughout the counting, the distance between sample and detector was maintained at 1–2 and 12–14cm for the long and short radiations, respectively. The dead time was maintained at 10% in all the counting processes.

All the samples were analysed in three replicates (Yap et al. 2003). The quality and analytical procedures for the sediments were checked and verified by using IAEA SL-1 (lake sediment), SRM 1566b (Oyster tissues) and SRM 2976 (mussel tissue). The recoveries for each metal are shown in Table 2.

Table 2. Comparison of metal concentrations (mg/kg dry weight) between certified values and measured values by using instrumental neutron activation analysis (INAA)

Metal	Cr	Co	Mn	Sc
Certified values (Lake sediment)	104 (IAEA SL-1)	19.8 (IAEA SL-1)	3460 (IAEA SL-1)	17.3 (IAEA SL-1)
Measured by INAA	86.25	20.19	3370	17.16
Recovery	82.9%	101.9%	97.4%	99.17
Certified values (Oyster/mussel)	0.50 (SRM 2976)	19.8 (SRM 1566b)	33 (SRM 2976)	17.3 (SRM 2976)
Measured by INAA	0.38	30.13	43.6	26.85
Recovery	75.8%	152.2%	131.9%	155.2%

Note: SRM 1566b = oyster tissues; SRM 2976 = mussel tissue.

2.3. Bioaccumulation Factor

The estimation of proportion in which metal occurs in the living organism and in associated sediment, known as bioaccumulation factor (BAF), for selected metals were calculated based on the equation (Szefer et al. 1999) below:

$$BAF = C_{snail}/C_{sediment}$$

where C_{snail} and $C_{sediment}$ are the mean concentrations of metal in the snails (soft tissues and shell) and in associated sediment, respectively. The snail tissues can be classified into macroconcentrator (BAF > 2), microconcentrators (1 < BAF < 2) or deconcentrators (BAF < 1) (Szefer et al. 1999).

3. RESULTS AND DISCUSSION

3.1. Overall Metal Concentrations

Table 3 shows the concentrations of the four metals in all sampling sites. For Co, the ranges (min-max, mg/kg dry weight) for sediments (SED), soft tissues (ST) and shells were 1.84 – 8.58, 0.83 – 6.94, and 0.26 – 0.78, respectively. For Cr, the ranges (min-max, mg/kg dry weight) for SED, ST and shells were 30.91 – 84.73, 1.71 – 23.18, and 1.43 – 120, respectively. For Mn, the ranges (min-max, mg/kg dry weight) for SED, ST and shells were 84.7 – 423, 135 – 2509, and 8.28 – 235, respectively. For Sc, the ranges (min-max, mg/kg dry weight) for SED, ST and shells were 3.98 – 24.4, 0.12 – 2.39, and 0.03 – 0.15, respectively.

Overall, the patterns of metal accumulations were as follow: Cr: SED (61.2) > Shell (36.1) > ST (12.7); Co: SED (5.76) > ST (3.22) > Shell (0.46); Mn: SED (577) > ST (165) > Shell (46.4); Sc: SED (11.5) > ST (0.85) > Shell (0.07). The Cr concentrations in *C. obtusa* were higher than all of the gastropods, including *Nerita lineata* (Cheng and Yap 2015) collected from the west coast mangrove area of Peninsular Malaysia.

The different levels of Mn in the sedimenmts from the present study could be related to bioabsorption differences in the sedimentation rates of the snail habitats. The sedimentation of suspended matter is known to play a role to the elevated pollutant in the sediment (Young and Ishiga 2014; Fan et al. 2015; Wang et al. 2015) and contributed to the comparatively higher metal concentration in some upstream native freshwater clam (Wong et al. 2017).

Table 3. Mean metal concentrations (mg/kg dry weight) in the total soft tissues (ST) and shell of *Cerithedea obtusa* and their habitat surface sediments (SED) of mangrove areas collected from the west coast of Peninsular Malaysia

Site no.	Cr			Co			Mn			Sc		
	SED	ST	Shell	SED	ST	Shell	SED	ST	Shell	SED	ST	Shell
L1	30.9	7.05	1.43	5.46	0.83	0.78	92.1	274	33.1	5.4	0.12	0.150
L2	42.7	13.2	2.94	6.59	4.06	0.31	138	135	12.3	10.2	2.10	0.110
L3	60.1	23.2	120	3.97	2.31	0.53	113	144	31.3	12.8	0.46	0.110
L4	84.7	20.7	48.4	5.84	2.50	0.32	198	738	45.5	11.3	0.17	0.035
L5	82.2	17.3	31.9	8.23	3.23	0.37	423	2510	235	13.1	1.24	0.059
L6	65.0	11.1	32.4	1.84	2.72	0.26	140	466	19.8	3.98	0.48	0.027
L7	70.9	8.18	32.5	6.12	2.26	0.67	140	204	8.28	12.5	0.57	0.051
L8	70.0	9.30	19.3	3.33	2.80	0.31	84.7	286	43.1	10.9	0.85	0.041
L9	55.8	15.4	NA	8.58	4.57	0.72	186	486	20.3	24.4	2.39	0.097
L10	49.8	1.71	NA	7.67	6.94	0.32	137	524	15.21	10.2	0.12	0.065

Note: NA = data are not available.

Sc is a member of lanthanides of rare earth elements and it is probably the least studied elements in the fourth period in the Periodic Ttable (Cotton 1991). Naturally, low concentrations of Sc exist in an ecosystem. However, they can be accumulated in environment following anthropogenic discharges. Tai et al. (2010) studied the biological toxicity of lanthanide elements on algae. The toxicity of lanthanides was found to reduce the growth of algae *Skeletonema costatum*, all lanthanides, including Sc, had a similar toxic effect to the algae. Currently, there is no toxicity study of Sc to the animal model. Intraperitoneal injected Scandium Chloride was found to have a potential association with renal toxicity in Wistar rat (Tanida et al. 2009).

3.2. Relationships between Metals in Snail and Habitat Sediments

The associations of Cr, Co, Mn and Sc between the ST and shells of *C. obtusa* and their habitat surface sediments are given in Figure 2. By using a simple regression equation, there were ignificant positive relationships ($p < 0.05$) for concentrations of Mn in the ST ($R = 0.96$) and shells ($R = 0.91$) of *C. obtusa* in relative to their metal concentrations in the surface sediments. Therefore, the Mn levels in the associated sediments could potentially reflect the availability of the sediment-bound metals to the snails. A linear relationship was also observed for the levels of Sc in the ST ($R = 0.66$) [but not for the shell with $R = 0.09$] of *C. obtusa* in relation to habitat surface sediments. This implied that the accumulations of Mn and Sc proportionally increased with growing concentrations of the two metals in the associated habitat sediments.

On the other hand, levels of Cr in the ST ($R = 0.46$) and shells ($R = 0.39$) of snails showed positive but weak correlations with surface sediments. Similarly, Co concentrations in the ST ($R = 0.51$) and shells ($R = 0.29$) also positively but weakly correlated with surface sediments. It is well known that the metal bioavailability is mainly influenced by abundances of various metal-binding determinants of sediment (Bryan and Langston 1992).

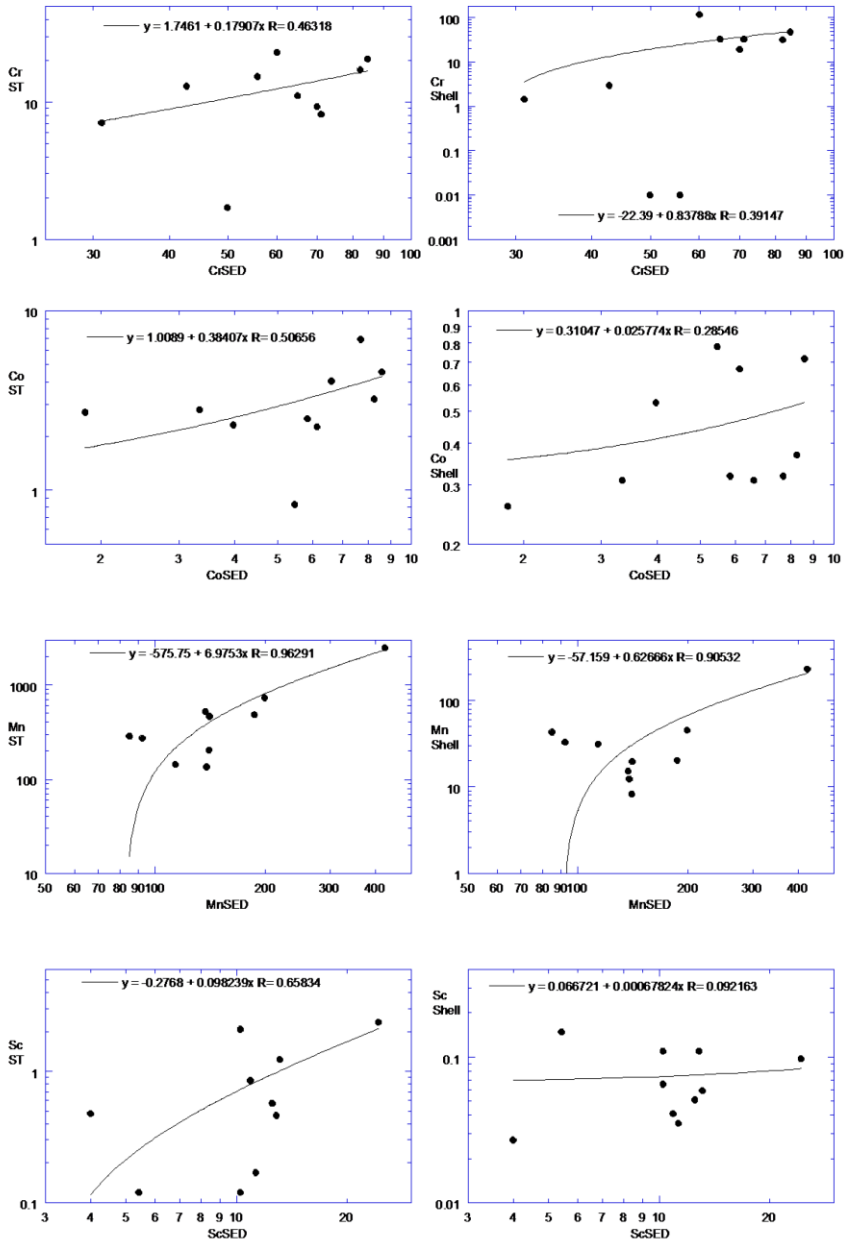

Figure 2. Associations of elements (Cr, Co, M and Sc) between snail *Cerithidea obtusa* (total soft tissues (ST) and shell) and their habitat surface sediments (SED). Both X- and Y-axes are in log10 scale, and in mg/kg dry weight.

The positive relationships of metals between the biota and their environmental matrices such as habitat surface sediments have been utilised as a method to check the potentials of the biota as a good biomonitor of the metal pollution (Yap 2012a). There were numerous studies reporting on the purpose mentioned above, as the studies cited in Table 4.

Table 4. Reported studies of relationships of metal levels between biota and habitat sediments

Biological samples	Part	Metals	Reference
Acantho pleurahaddoni, *Turbo coronatus*, *Ostrea cucullata* and *Pitar* sp. /7 sites /the Gulf of Aden, Yemen	Total ST	Cd, Pb, Zn, Cu, Ni, Co, Cr, Mn and Fe	Szefer et al. (1999)
Mussel *Perna viridis* /10 sites /Peninsular Malaysia	ST	Cd, Cu, Pb and Zn	Yap et al. (2002)
Mussel *Perna viridis* /10 sites /Peninsular Malaysia	Shell	Zn	Yap et al. (2004)
Mussel *Perna viridis* /9 sites /Peninsular Malaysia	Byssus	Zn	Yap et al. (2005)
Mussel *Perna viridis* /6 sites /Peninsular Malaysia	Crystalline style and byssus	Ni	Yap et al. (2006)
Snail *Nerita lineata* /4 sites	ST, shell and operculum	Cd, Cu, Fe, Ni, Pb and Zn	Amin et al. (2009)
Clam *Macoma balthica* /5 sites /southern Baltic Sea	ST	Zn, Cu, Ni, Fe, Mn, Co and Cd	Hendozko et al. (2010)
Snail *Telescopium telescopium* /17 sites/ Peninsular Malaysia	Foot, cephalic tentacle, mantle, muscle, gill, digestive caecum and remaining ST	Zn	Noorhaidah and Yap (2010)
Snail *Telescopium telescopium*/17 sites/ Peninsular Malaysia	Foot, cephalic tentacle, mantle, muscle, gill, digestive caecum and remaining ST	Pb	Yap and Noorhaidah (2010)
Snail *Telescopium telescopium* /18 sites/ Peninsular Malaysia	Foot, cephalic tentacle, mantle, muscle, gill, digestive caecum and remaining ST	Cd	Yap and Noorhaidah (2011)
Mussel *Perna viridis* /15 sites /Peninsular Malaysia	Periostracum	Cd and Pb	Yap and Tan (2011)

Biological samples	Part	Metals	Reference
Snail *Telescopium telescopium* /18 sites /Peninsular Malaysia	Foot, cephalic tentacle, mantle, muscle, gill, digestive caecum and remaining ST	Ni	Yap et al. (2012)
Mussel *Perna viridis* /17 sites with 23 populations /Peninsular Malaysia	Periostracum	Cu and Zn	Yap (2012b)
Snail *Telescopium telescopium* /16 sites /Peninsular Malaysia	Foot, cephalic tentacle, mantle, muscle, gill, digestive caecum and remaining ST	Cu	Yap et al. (2013)
Snail *Telescopium telescopium* /17 sites	Shell	Ni	Yap (2014)
Six commercial fish species	ST	Fe, Mn, Cu, Cr, Pb, Zn and Ni	Dhanakumar et al. (2015)
Sea catfish, *Arius thalassinus*	ST	Fe, Cu, Ni, Pb and Cd	Saleh and Marie (2015)
Plant *Centella asiatica* /9 sites with habitat topsoils	Leaves, stems and roots	Zn	Yap et al. (2017a)
Ruditapes decussates, *Venerupis corrugata* and *Ruditapes philippinarum*	ST	As and Hg	Velez et al. (2015)
Anadara senilis	ST	Cd, Cu, Pb and Zn	Bakary et al. (2015)
benthic macroinvertebrates	ST	Zn, Cr, Cu, Pb, Ni, As, Cd and Hg	Bian et al. (2016)
Tigerfish, *Hydrocynus vittatus*	ST	Metals	Gerber et al. (2016).
Teleost fish species, *Labeo angra*	ST	Mn, Fe, Mg, Ca, Cu, Zn, Cd, Cr, Pb and Ni	Das and Choudhury (2016)
Gastropods *Buccinanops globulosus*, *Adelomelon ancilla* and *Trophon geversianus*	ST	Cd, Al, Fe, Zn, Cu and Pb	Primost et al. (2017)
Three mollusc species	Liver/hepatopancreas or whole organism	Ag, Cd, Co, Cr, Cu, Ni, Pb, Zn and As	Van Ael et al. (2017)
Snail *Cerithedea obtusa*	ST	Cr, Co, Mn and Sc	This study
Snail *Cerithedea obtusa*	Shell	Cr, Co, Mn and Sc	This study

Note: Soft tissues = ST.

Van Ael et al. (2017) collected samples (sediment, aquatic species, eight fish species, polychaeta, oligochaeta, three mollusc species and four crustacean species and suspended matter) from six locations along the Scheldt estuary, Netherlands-Belgium and investigated the relationships between metal concentrations (the metalloid As, Ag, Co, Pb, Cr, Cu, Ni, Zn and Cd). They found that approximately less than half of studied metals were correlated between concentrations of metal in the sediment and liver or hepatopancreas or whole organism.

Hendozko et al. (2010) reported that *Macoma balthica* might be useful as a biomonitor of heavy-metal bioavailability and contamination in the Baltic Sea. Amin et al. (2009) reported significant correlations of Cd concentrations between the shells of snail *Nerita lineata* and surface sediments. Therefore, they suggested the snail shells could be used as a biomonitoring material for Cd. Noorhaidah and Yap (2010) reported that the correlation analysis between snail *Telescopium* and habitat surface sediments generally supported the use of different soft tissues of *T. telescopium* as a more accurate biomonitoring organ for Zn, besides the total ST. Yap et al. (2002)'s findings indicated that Zn was possibly regulated from the soft tissue of *P. viridis* since significant correlations of Zn between the mussel ST and surface sediments were not found.

Bian et al. (2016) reported the abundance and biomass of oligochaeta were most sensitive to heavy metal contamination based on the correlation analysis between the heavy metal risk indices and the benthic community metrics. Das and Choudhury (2015) employed multivariate statistical analysis and showed that there was a strong correlation relationship between geogenic and anthropogenic heavy metals in the sediments and water. High metal pollution index and bioaccumulation factors for these heavy metals in the different tissues revealed that metals were extensively bio-concentrated and bio-accumulated.

3.3. Bioaccumulation Factors

The BAF values are presented in Table 5. For Cr, the BAF values for ST/SED and Shell/SED were 0.034 – 0.386, and 0.046 – 1.999, respectively.

The mean value (0.54) for Shell/SED was higher than that (0.21) of ST/SED. This indicated that shells of the snails had a better capability in accumulating the Cr from the environmental sediments. For Co, the BAF values for ST/SED and Shell/SED were 0.152 – 1.478, and 0.042 – 0.143, respectively. The mean value (0.63) for ST/SED was higher than that (0.09) of Shell/SED. This indicated that ST of the snails had a better capability in accumulating the Co from the environmental sediments.

Table 5. Bioaccumulation factor (BAF) values of Cr, Co, Mn and Sc between the snails (total soft tissues (ST); shell) and their habitat surface sediments (SED)

	Cr		Co		Mn		Sc	
	ST/ SED	Shell/ SED	ST/ SED	Shell/ SED	ST/ SED	Shell/ SED	ST/ SED	Shell/ SED
L1	0.228	0.046	0.152	0.143	2.979	0.359	0.022	0.028
L2	0.308	0.069	0.616	0.047	0.977	0.090	0.206	0.011
L3	0.386	1.999	0.582	0.134	1.269	0.276	0.036	0.009
L4	0.244	0.571	0.428	0.055	3.722	0.229	0.015	0.003
L5	0.211	0.388	0.392	0.045	5.930	0.555	0.095	0.005
L6	0.171	0.499	1.478	0.141	3.325	0.141	0.121	0.007
L7	0.115	0.458	0.369	0.109	1.461	0.059	0.046	0.004
L8	0.133	0.275	0.842	0.093	3.375	0.509	0.078	0.004
L9	0.276	NA	0.533	0.084	2.609	0.109	0.098	0.004
L10	0.034	NA	0.905	0.042	3.834	0.111	0.012	0.006

Note: NA = data are not available.

For Mn, the BAF values for ST/SED and Shell/SED were 0.977–5.93, and 0.059 – 0.555, respectively. The mean value (2.95) for ST/SED was higher than that (0.24) of Shell/SED. This indicated that ST of the snails had a greater capability in accumulating the Mn from the environmental sediments. For Sc, the BAF values for ST/SED and Shell/SED were 0.012 – 0.206, and 0.003 – 0.028, respectively. The mean value (0.07) for ST/SED was higher than that (0.008) of Shell/SED. This indicated that ST of the snails has a better capability in accumulating the Sc from the environmental sediments.

The BAF is a useful tool in the determination of metals accumulation in *M. balthica* in relation to their concentration in habitat sediments (Szefer et al. 1999). The eco-toxicological risk mainly caused by contaminated

sediments and it is depending on metal mobility on sorption characteristics of the soil, amount of organic matter present, and the ability to absorb metals directly from ingested sedimentary particles by living organisms (Szefer et al. 1999). Li et al. (2016) investigated the concentrations of nine heavy metal in the macrobenthos and sediments of the Yellow River Delta. The BAF was used to evaluate the potential bioaccumulation of metals. The BAF results indicated that Cd was bioaccumulated from sediments to macrobenthos.

4. CONCLUSION

The snails *C. obtusa* exhibited a wide range of concentrations of Cr, Co, Mn and Sc in the ST and shells depending on the sampling sites. Relationships of Mn and Sc between the snails and habitat surface sediment might potentially reflect different degrees of their contamination and the possible influence of environmental conditions on metal bioaccumulation. Despites the lack of significant correlations between ST, shells and habitat sediments, there were clear positive relationships between snails and habitat sediment concentrations of Mn and Sc, and to some extents for Cr and Co. This indicated that the metal levels in the associated habitat surface sediments were important sources of metal uptake and bioaccumulation in the ST and shells of *C. obtusa*. Therefore, the present study supported the *C. obtusa* as a good biomonitor for Mn and Sc pollution in the mangrove area of Peninsular Malaysia. Further future studies are still needed to verify its usefulness as a good biomonitor.

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Chapter 8

ECOLOGICAL RISK ASSESSMENTS OF HEAVY METALS IN THE SURFACE SEDIMENT BETWEEN THE ARTIFICIAL GRANITE ROCKY SHORE OF TANJUNG HARAPAN, SELANGOR: IMPACT OF ANTHROPOGENIC ACTIVITIES

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ABSTRACT

Surface sediments were collected from a rocky shore in Tanjung Harapan (TH) and its ecological risk assessments of heavy metals were compared to another nine geographical sampling sites in Peninsular Malaysia. The mean concentration (mg/kg dw) in the rocky shore sediments at TH were 47.1 for As, 1.95 for Cd, 25.8 for Cu, 49.3 for Cr, 23900 for Fe, 45.0 for Pb, and 109 for Zn, while for Hg the concentration was 16.0 µg/kg dw. Based on the sediment quality guidelines, geoaccumulation indexes and enrichment factors, the concentrations of all metals in this study will not cause any possible adverse effects or pollution to the surrounding environment. The potential ecological risk index (PERI) values for all metals in this study fell in the category of 'low ecological risk' at TH. However, PERI value at TH was found to be higher than most (7 out of 9 sampling sites) coastal sediments previously reported from Peninsular Malaysia by Cheng and Yap (2015). This indicated the impact of anthropogenic sources. The data of metal concentrations and ecological risk assessments of metals in TH will serve as an important reference for effective coastal ecosystem management in future.

Keywords: toxic metals, geochemical indices, potential ecological risk index

1. INTRODUCTION

According to the early definition of rocky shore by Connell (1972) and Lewis (1964):

> "A rocky shore is an intertidal area of seacoasts where solid rock predominates. Rocky shores are biologically rich environments, and are a useful "natural laboratory" for studying intertidal ecology and other biological processes. Due to their high accessibility, they have been well studied for a long time and their species are well known."

Photo 1. Sampling sites at Tanjung Harapan in the vicinity of North Port of Port Klang, Selangor (Arrow showing the site where sediment was collected from during the low tide).

Hard engineered structures such as seawalls, groynes and breakwaters are often built to reduce coastal erosion and to maintain a minimal beach width for recreation purposes along coast regions (Luo et al. 2015). According to Airoldi et al. (2005), flooding and coastal erosion represent serious threats along many coastlines, and will become more serious due to human-induced changes and accelerated sea-level rise. To alleviate the problem, hard coastal defense structures have become ubiquitous features of coastal landscapes as a response to these threats. Based on Photo 1, it is inferred that the rocky shore built of TH can reduce the erosion process as well as protecting the shorelines from further negative impacts from human activities.

Hiscock and Goodman (1984) had highlighted the onerous nature of conducting ecotoxicological studies or surveys in rocky shore habitats. Therefore, by focusing on the ecological risk assessments of heavy metals, the monitoring the rocky shore with the use of sediments can provide an understanding on the probable sources of natural and anthropogenic pollution. Rocky shores have been a target site for assessment of

environmental health (Garaffo et al. 2017). According to O'Connor (2013), coastal systems, such as rocky shores, are among the most heavily anthropogenically-impacted marine ecosystems and are also among the most productive in terms of ecosystem functioning. One of the greatest impacts on coastal ecosystems is nutrient enrichment from human activities such as agricultural run-off and discharge of sewage.

Tanjung Harapan (TH) is a recreational tourist attraction site in Selangor (Photo 2). It is known to be one of the rocky beaches of the North Port of Port Klang. TH is described as a small town/city by the sea with a rocky barrier of mix substratum along the shore and, due to its location, it is also regarded as an industrial area by the port (Photo 1; Tengku Ismail et al. 2017). The latter is mainly due to Port Klang being the major port that is running in Malaysia and in addition to that, it is saturated with various anthropogenic activities such as shipping (Photo 3), factories and warehouses.

Photo 2. Tanjung Harapan is a recreational site in Selangor.

Photo 3. Ferry activity near Tanjung Harapan besides the shipping activity at the North Port.

This study attempted to conduct ecological risk assessments of eight metals in the sediments of the rocky shore of TH by utilizing three methods of assessments. First, the current data were compared with established sediment quality guideline (SQG)s developed for marine and estuarine ecosystems (Long et al. 1995; Long and MacDonald 1998; Chapman et al. 1999) based on the effect range low (ERL)/effect range median (ERM)/ interim sediment quality value-low (ISQV-low) and the threshold effect level (TEL)/probable effect level (PEL)/ interim sediment quality value-high (ISQV-high) values. Second, utilizing pollution indexes such as enrichment factor (EF) (Buat-Menerd and Chesselt 1979) and index of geoaccumulation (Igeo) (Muller 1969). Third, ecological risk assessment was applied as proposed by Hakanson (1980). These three methods of approach have been commonly used in the literature for many different aquatic ecosystems around the world (Madiseh et al. 2009; Luo et al. 2010; Guo et al. 2010; Zhao et al. 2012; Kukrer et al. 2014; Ra et al. 2014).

Therefore, the aims of this study were to determine the distributions of the eight metals concentrations and to estimate the ecological risk assessments in the surface sediments from TH, in comparison to another nine geographical sites in Peninsular Malaysia.

2. MATERIALS AND METHODS

2.1. Sampling and Metal Analysis

Surface sediments between 0-10 cm of depth were collected from the rocky shore of TH (100° 09.309'; N 03° 13.591') located in the state of Selangor, Peninsular Malaysia (PM) on 18 May 2011 (Figure 1). Nearby shipping activities and industrial (chemical factories and power plants) were observed in this area.

The sediments were dried (60°C) until constant dry weights (dw) were achieved and sifted with a stainless steel sift (63µm). Three replicates of 0.5 g sediments were obtained from each site. The sediment replicates were then digested in a TFM vessel with acid mixture (9 ml of HCl + 3 ml of HNO_3).

Digestion was carried out in a microwave digester (Milestone ETHOS labstation with easyWAVE or easyCONTROL software HPR1000/10S high pressure segmented rotor) where the digestion was started by increasing the temperature to 200°C for 10 minutes and subsequently kept at 200°C for 15 minutes. The digested samples were then diluted, filtered and kept at 4°C until metal analysis. Analysis of As, Cr and Hg contents in the samples were done by using the Inductively Coupled Plasma-mass Spectrometer with Dynamic Reaction Cell™ (ICP-MS DRC^{plus}) (Perkin Elmer ELAN DRC^{plus}), while analysis of the rest of the metals was carried out with the flame technique Atomic Absorption Spectrophotometer. All collected data were presented in mg/kg dw (except for Hg data in µg/kg). Acid-washing on all tools and equipment was done to avoid possible contaminations while the accuracy and precision methods were tested with certified reference materials for sediments (NIST SRM 1646 Estuarine Sediment), and the

recoveries of the certified reference material were of satisfaction between 89-109%.

In order to avoid negative numbers due to differences between variables and minimize the magnitude of variance, logarithmic transformation [log10 (mean + 1)] was performed to all data, prior to statistical analyses (Zar 1996). Statistical software STATISTICA for Windows (StatSoft, Inc. USA, 1995, Version 8.0) was used to perform correlation analysis, cluster analysis (based on Single Linkage Euclidean distances) and Factor Analysis (based on eigenvalues above 1) on the all data in this study.

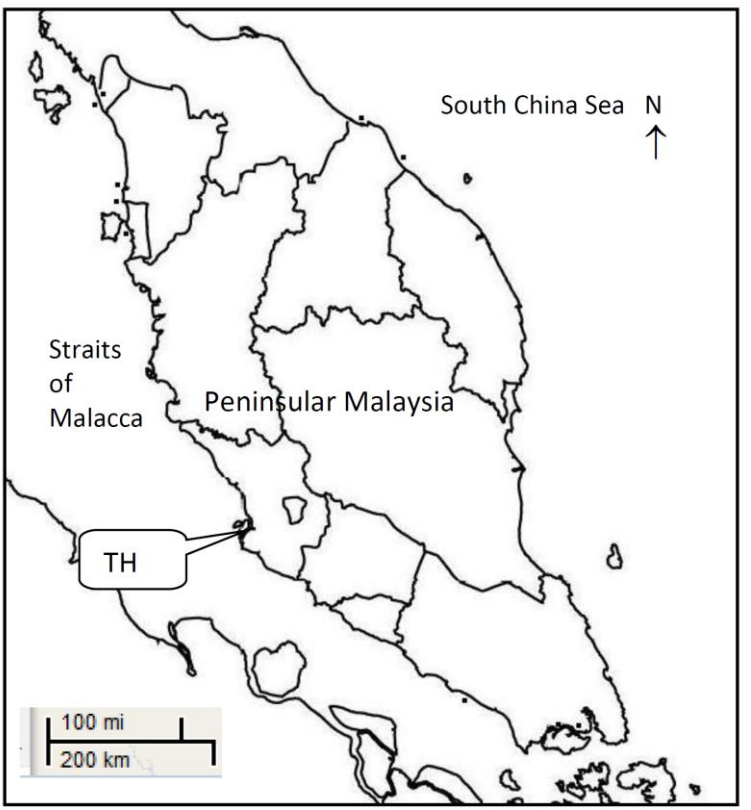

Figure 1. Sampling map at Tanjung Harapan (TH), Peninsular Malaysia.

2.2. Geochemical Indexes

The geochemical indexes applied in this study were index of geoaccumulation (Igeo) and enrichment factor (EF). As proposed by Muller (1969), the formula for Igeo which denotes the degree of metal pollution in aquatic sediments is as below:

$$Igeo = \log_2(Sample/1.5 \times Background)$$

where background level = pre-industrial level (Hakanson 1980), multiplying with 1.5 as correction factor due to lithogenic effluents. Classifications of the values of Igeo are: < 0 = unpolluted; 0-1 = unpolluted to mildly polluted; 1-2 = mildly polluted, 2-3 = mildly to highly polluted, 3-4 = highly polluted, 4-5 = highly to very highly polluted, and >5 = very highly polluted.

As for EF, the formula used in the present study was that proposed by Buat-Menerd and Chesselt (1979):

$$EF = (Me/Fe)_{Sample}/(Me/Fe)_{Background}$$

where $(Me/Fe)_{sample}$ = metal to Fe ratio in the sediments in this study; Background = concentrations of metal and Fe of preindustrial levels depicted from Hakanson (1980). The Fe was chosen as a normalizer to compensate the variation of sediment grain size and mineralogy (Schi and Weisberg 1999). Classifications of the values of EF (Sutherland 2000) are: $EF < 2$ = lack of minimal enrichment; $2 \leq EF < 5$ = mild enrichment; $5 \leq EF < 20$ = significant enrichment; $20 \leq EF < 40$ = very high enrichment; $EF > 40$ = extremely high enrichment.

2.3. Ecological Risk Assessment

The ecological risk evaluation used in the present study were potential risk of individual metal (ER) and potential ecological risk index (PERI) (Hakanson 1980) which have been widely used in determining the degree of risks posed to the environment by heavy metals (Gong et al. 2008; Guo et

al. 2010; Zhu et al. 2012). Hakanson (1980) defined the formula of these indexes as:

$$CF = C_D/C_R$$
$$ER = Tr \times CF$$
$$PERI = \sum ER$$

where CF = contamination factor; C_D = mean metal concentration in this study; C_R = pre-industrial reference values (RV) in sediments (Hakanson 1980); ER = potential risk of individual metal; Tr = toxic-response factor (TF) for a particular metal (Hakanson 1980) (Table 4); PERI = total potential risk of individual metal; m = number of individual metals. Classification of CF are (Hakanson 1980): $CF < 1$ = low contamination; $1 \leq CF \leq 3$ = mild contamination; $3 \leq CF \leq 6$ = considerable contamination; $CF > 6$ = high contamination. Classifications of the values of ER are (Hakanson 1980): $ER < 40$ = minimal potential ecological risk; $40 \leq ER < 80$ = mild potential ecological risk; $80 \leq ER < 160$ = considerable potential ecological risk; $160 \leq ER < 320$ = high potential ecological risk; and $ER \geq 320$ = very high ecological risk. As for PERI the categories of risk are: $PERI < 150$ = minimal ecological risk; $150 \leq PERI < 300$ = mild ecological risk; $300 \leq PERI < 600$ = considerable ecological risk; and $PERI \geq 600$ = very high ecological risk.

3. Results and Discussion

3.1. Heavy Metals Concentrations in the Sediments

The mean concentrations of metals in surface sediments from TH and cited data for Peninsular Malaysia (PM) (Cheng and Yap 2015) from eight sampling sites are presented in Table 1. The present metal concentrations (mg/kg dw) were within those of PM reported by Cheng and Yap (2015), which were 47.1 for As (PM: 21.81 to 59.49), 1.95 for Cd (PM: 1.11 to 2.00), 25.8 for Cu (PM: 5.59 to 28.71), 49.3 for Cr (PM: 18.93 to 62.91), 23900 for Fe (PM: 12973 to 48916), 45.0 for Pb (PM: 25.36 to 172.57), and 109

for Zn (PM: 29.35 to 130.34). The concentration of Hg was 16.0 µg/kg dw (PM: 2.66 to 312 µg/kg dw).

Overall, the concentrations of all eight metals in the sediments of TH were consistent and in a descending order of Fe > Zn > Pb> Cr > As > Cu > Cd > Hg. This agreed with those reported for PM by Cheng and Yap (2015).

The geochemical fractions of heavy metal concentrations collected from TH between 2005 and 2011 are presented in Table 2. Overall, the concentrations of Cd, Cu, Pb, Ni, Zn and Fe were dominated by the resistant fractions except for 2005 Cu, and 2005 Zn. Still, this was difficult to explain because of the specific site of sample collection was slight different based on the different GPS information.

Table 1. Mean metal concentrations (all in mg/kg dw except for those indicated as µg/kg dw and %) in the surface coastal sediments from nine sampling sites in Peninsular Malaysia

Sampling sites	Cr	As	Hg (µg/kg dw)	Pb	Cu	Zn	Cd	Fe (%)
Tg. Harapan	49.3	47.1	16.0	45.0	25.8	109	1.95	2.39
Kg. Pasir Puteh	47.1	25.6	3.00	30.7	28.7	130	1.11	3.36
Sg. Ayam	62.9	21.8	14.0	173	20.5	124	1.97	2.34
Jetty to Pulau Ketam	54.7	41.9	97.0	44.9	23.4	107	1.75	1.75
Sg Janggut	40.5	33.2	91.0	25.4	7.30	29.4	1.15	1.35
Kukup	52.8	38.9	20.0	28.1	11.3	68.9	1.66	3.09
Lukut	27.4	37.3	312	39.1	24.7	64.1	1.99	2.69
Kg. Sg. Melayu	46.2	59.5	61.0	29.2	14.5	73.6	1.13	2.69
Tg. Langsat	18.9	24.3	33.0	31.0	11.3	72.7	1.74	4.89
Sepang	39.1	30.8	30.0	29.8	5.59	35.1	1.60	1.30

Note: Except for Tg. Harapan, all metal data of other sampling sites were cited from Cheng and Yap (2015).

Table 2. Geochemical fractions of heavy metal concentrations (mg/kg dry weight) collected from Tanjung Harapan on 25 April, 2005 (E 101°21.637'; N 03°005.96') and 18 May, 2011 (E 100° 09.309'; N 03° 13.591')

Metal	Year	F1	F2	F3	F4	NR	NR/R	SUM
Cd	2005	0.36	0.45	1.02	4.98	1.83	0.37	6.81
	2011	0.02	0.13	0.20	1.07	0.35	0.33	1.42
Cu	2005	0.14	0.25	4.18	3.83	4.57	1.19	8.40
	2011	0.15	0.03	1.03	17.2	1.21	0.07	18.4
Pb	2005	2.36	2.83	3.67	28.1	8.86	0.32	36.9
	2011	1.47	2.13	3.12	33.1	6.72	0.20	39.8
Ni	2005	1.28	2.49	5.51	11.7	9.28	0.79	20.9
	2011	0.23	0.48	1.59	12.2	2.30	0.19	14.5
Zn	2005	0.26	5.21	28.7	29.7	34.2	1.15	63.8
	2011	1.08	9.30	22.31	103	32.7	0.32	136
Fe	2005	57.8	314	2201	15268	2573	0.17	17841
	2011	2.58	514	1039	18906	1555	0.08	20461

Note: F1 = easily, freely, leachable or exchangeable fraction; F2 = acid-reducible fraction; F3 = oxidisable-organic fraction; F4 = resistant fraction; NR = non-resistant fraction (summation of F1, F2 and F3); SUM = total metal concentrations based on summation of F1, F2, F3 and F4.

Comparing to reference values (Tables 1 and 3), the levels of Cr were higher than the limits reported by Wedepohl (1995) but lower than the pre-industrial reference level by Hakanson (1980), upper continental crust limits reported by Taylor and McLennan (1995) and Rudnick and Gao (2003). The levels of As and Cd in this study exceeded all the reference values. The present Hg level was below those of all established reference values. For Cu, it was below the pre-industrial reference value of Hakanson (1980) and upper continental crust of Rudnick and Gao (2003) but higher than those of Taylor and McLennan (1995) and Wedepohl (1995). For Zn, it was below the pre-industrial reference value of Hakanson (1980) but higher than those of upper continental crust values of Rudnick and Gao (2003), Taylor and

McLennan (1995) and Wedepohl (1995). As for Fe, the sediments from TH were found to be below the Fe limit of the upper continental crust limit by Wedepohl (1995), which was the only comparable reported reference value.

Table 3. Comparisons of metal concentrations (mg/kg dry weight) among present study (samples from 2005 and 2011) with upper continental crusts of different citations

Metals	2005	2011	UCC (Wedepohl, 1995)	Taylor and McLennan (1995)	Rudnick and Gao (2003)
Ag	NA	0.662	0.055	0.050	0.053
As	NA	47.1	2.00	1.50	4.80
Be	NA	2.02	3.10	3.00	2.10
Cd	1.54	1.95	0.102	0.098	0.09
Co	NA	5.97	11.60	17.0	17.3
Cr	NA	49.3	35.00	85	92
Cs	NA	10.2	5.80	4.60	4.90
Cu	6.89	25.8	14.30	25	28
Fe (%)	1.78	2.39	3.09	-	-
Hg (µg/kg)	NA	16	56	-	50
Li	NA	35.9	22.0	20.0	21.0
Mn	NA	469	527	-	-
Ni	15.09		18.60	44.0	47.0
Pb	27.86	45	17.0	17	17
Se	NA	0.35	0.083	0.05	0.09
Sr	NA	79.9	316	350	320
V	NA	69.9	53.0	107	97
Zn	59.89	109	52.0	71	67

Note: NA = data not available. UCC = upper continental crust.

3.2. Ecotoxicological Significance of As and Metal Concentrations in Sediments

Table 4 showed the ecological risks assessment of the sediments from TH by comparing them to SQGs developed by, Chapman et al. (1999)

(ISQV-low/ ISQV-high), Long and MacDonald; 1998 (TELs/PELs), and Long et al. (1995) (ERL/ERM) for all the eight metals. ISQV-low, ERLs or TELs were low range values denoting that the concentrations of metals were not likely to cause detrimental effects on sediment dwelling fauna. On the contrary, the ISQV-high, ERMs and PELs were high range values denoting the concentrations of metals that were likely to cause detrimental effects (Long and MacDonald, 1998). In addition to that, the U.S. National Oceanic and Atmospheric Administration (NOAA) guidelines also proposed the classification of sediments in three range namely, rarely (<ERL), occasionally (≥ERL and <ERM) or frequently (≥ERM) causing detrimental effects on the ecosystem (Birch and Taylor, 2006).

Table 4. Sediment quality guidelines and values of toxic-response factors employed in this study (Cheng and Yap, 2015)

	As	Cd	Cr	Cu	Hg	Pb	Zn	References
Sediment Quality Guidelines								
Effects range low (ERL)	8.2	1.20	81	34.0	150	46.7	150	Long et al. (1995)
Effects range median (ERM)	70	9.60	370	270	710	218	410	Long et al. (1995)
ISQV-low	8.20	1.50	80.0	65.0	280	75	200	Chapman et al. (1999)
ISQV-high	70.0	9.60	370	270	1000	218	410	Chapman et al. (1999)
Treshold effect level (TEL)	7.24	0.68	52.3	18.7	130	30.2	124	MacDonald et al. (1996)
Probable effect level (PEL)	41.6	4.21	160.4	108.2	700	112.2	271	MacDonald et al. (1996)
Toxic-response factor (Tr)	10.0	30.0	2.00	5.00	40.00	5.00	1.00	Hakanson (1980)
Rocky shore of Tanjung Harapan	47.1	1.95	49.3	25.8	16.	45.0	109	This study

Note: All concentrations are presented in mg/kg dry weight except for Hg data in µg/kg dry weight, and Tr values are unitless.

As shown in Table 4, the As value was higher than ERL but lower than ERM, higher than ISQV-low but lower than ISQV-high, and higher than those of both TEL and PEL. For Cd, the present value was higher than ERL but lower than ERM, higher than ISQV-low but lower than ISQV-high, and higher than TEL but lower than PEL. For Cr, Hg and Zn, these three metal levels were lower than those of all sediment quality guidelines. The present values of Cu and Pb were lower than those all sediment quality guidelines except for TEL.

The classification of sediments based on the ERL-ERM and ISQV suggested that Cr, Hg and Zn in sediments from TH were not likely (<ERL and <ISQV-low) to cause detrimental effects on the surrounding organisms. The levels of As, Cd, Cu and Pb exceeded the TEL value, denoting the likelihood of detrimental effects from long-term exposure of these metals.

3.3. Geochemical Indexes

The EF and Igeo values for seven metals (As, Cd, Cu, Cr, Hg, Pb and Zn) are shown in (Figure 2). The EF values were 4.06 for As (PM: 1.02 to 5.06), 2.52 for Cd (PM: 1.02 to 3.82), 0.668 for Cu (PM: 0.14 to 0.83), 0.71 for Cr (PM: 0.13 to 1.07), 0.083 for Hg (PM: 0.01 to 1.44), 0.831 for Pb (PM: 0.28 to 3.26), and 0.806 for Zn (PM: 0.26 to 1.08). Based on the classification by Sutherland (2000), all EF values for Cu, Cr, Hg, Pb and Zn were categorized as lack of minimal enrichment ($EF < 2$). For As and Cd, the present values fell between $2 \leq EF < 5$ denoting mild enrichment.

The Igeo values were 1.07 for As (PM: 0.05 to 1.40), 0.38 for Cd (PM: -0.43 to 0.41 for), -1.54 for Cu (PM: -3.75 to -1.39), -1.45 for Cr (PM: -2.83 to -1.10), -4.55 for Hg (PM: -6.97 to -0.27), -1.22 for Pb (PM: -2.05 to 0.72) and -1.27 for Zn (PM: -3.16 to -1.01). According to Muller (1969), all values for Cu, Cr, Hg, Pb and Zn fell in the category of unpolluted ($Igeo \leq 0$). The Cd was categorized as unpolluted to mildly polluted ($0 < Igeo \leq 1$) while As fell in the category of mildly polluted ($1 < Igeo \leq 2$). Based on the data reported by Costa-Böddeker et al. (2017)

on the surface sediment samples collected from Thi Vai Estuary and in the Can Gio Mangrove Forest (Vietnam), the Igeo values were categorized as 'low contamination' for Co, Cu and Zn, and 'moderate contamination' for Cr and Ni. Overall, metal levels in this study were lower than expected for this highly industrialized region, probably due to dilution, suggesting that erosion rates and hydrodynamics might also play a role in metal content distribution.

3.4. Ecological Risk Assessments

Figure 2 shows the CF, ER and PERI values of the surface sediments from TH. The CF values were 3.14 for As (PM: 1.45 to 3.97), 1.950 for Cd (PM: 1.11 to 2.00), 0.517 for Cu (PM: 0.11 to 0.57), 0.55 for Cr (PM: 0.21 to 0.70), 0.064 for Hg (PM: 0.01 to 1.25), 0.643 for Pb (PM: 0.36 to 2.47) and 0.624 for Zn (PM: 0.17 to 0.74). The values for Cu, Cr, Hg, Pb and Zn fell in the category of low contamination ($CF \leq 1$) (Hakanson 1980). The Cd fell in the category of mild contamination ($1 < CF \leq 3$) while As was within the category for considerable contamination ($3 < CF \leq 6$). Costa-Böddeker et al. (2017) also reported that the CF values of his study fell in the category of mild to considerable pollution for Cr and Ni, while EF suggested anthropogenic sources of Cr, Cu and Ni.

The ER values were 31.42 for As (PM: 14.54 to 39.66), 58.50 for Cd (PM: 33.35 to 59.9), 2.58 for Cu (PM: 0.56 to 2.87), 1.10 for Cr (PM: 0.42 to 1.40), 2.56 for Hg (PM: 0.48 to 49.92), 3.21 for Pb (PM: 1.81 to 12.33) and 0.62 for Zn (PM: 0.17 to 0.74). According to Hakanson (1980)'s classification, the ER values of As, Cu, Cr, Hg, Pb and Zn were below 40, falling into the category of minimal potential ecological risk (<40) for these metals, while the Er values of Cd fell in the category of mild potential ecological risk ($40 \leq ER < 80$). Lastly, the PERI value in the rocky shore of TH was 100, denoting minimal ecological risk ($RI < 150$) from the combination of all the seven metals (Hakanson 1980).

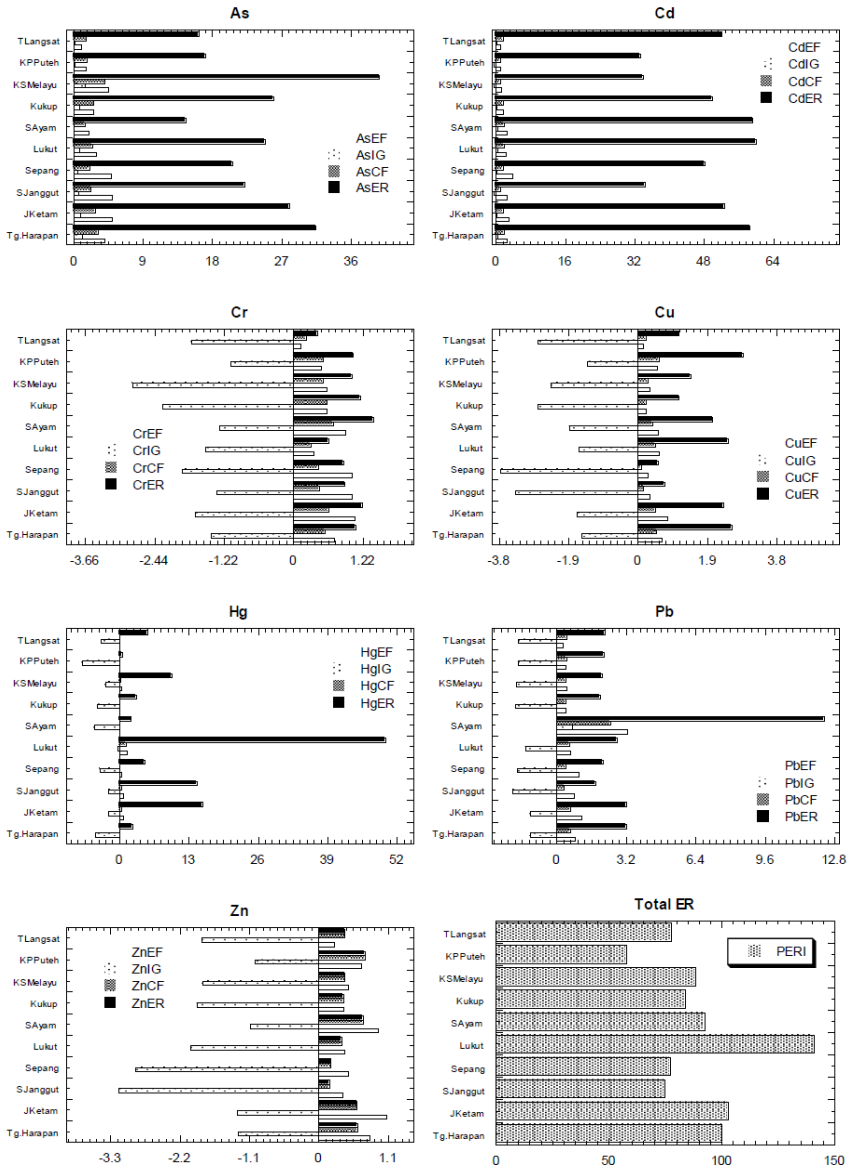

Figure 2. Values of enrichment factor (EF) and index of geoaccumulation (IG) of heavy metals, values of the contamination factor (CF), potential risk of individual metal (EF), and) and the potential ecological risk index (PERI) of Tg. Harapan in comparison to the sampling sites as reported by Cheng and Yap (2015).
Note: The data except for Tg. Harapan were cited from Cheng and Yap (2015).

Feng et al. (2017) reported that the PERI values of seven metals in the sediments along the polluted Dongbao River, during the wet and dry season were 327 and 1681, respectively. This denoted considerable ecological risk ($300 \leq PERI < 600$) on wet season and very high ecological risk ($PERI \geq 600$) on wet season in the area of Dongbao River. ElNemrn et al. (2016) reported that PERI values were < 150 in most of the sediment samples collected from the Egyptian Red Sea coast. This indicated that the Red Sea region would not pose any ecological risk for all the investigated metals. Lin et al. (2016) reported that an average PERI value of 431 based on eight heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in 42 surface sediments of Erhai Lake. This PERI value denoted that the heavy metals might pose high ecological risks to the surrounding environment, particularly from As, Cd and Hg.

The impacts of anthropogenic input on the rocky shores has been reported in the literature. According to Garaffo et al. (2017), efficient ecological indices can reflect the differences between impacted (sewage-affected rocky shores) and non-impacted sites, leading to significant variations at the contaminated sites. They reported that the impacted sites showed an increase in the ecological index values over time, indicating a deterioration of environmental conditions. This showed the anthropogenic impact due to sewage discharges. O'Connor (2013) investigated the potential effects of sewage discharges on the biotic diversity of rocky shores as well as to test current tools for assessing the ecological status of rocky shores. They reported the spatial variability of assemblages was greater at sites adjacent to sewage outfalls compared to shores without presence of sewage outfalls. Therefore, the finding pointed to the importance of anthropogenic impacts on the rocky shores.

Based on sediment cores collected in six freshwater discharge outlets of the Pearl River Estuary, Song et al. (2016) found that the temporal distributions of Cr, Pb, and Cd in the collected sediments were of a slight increase from 1970s to 2000s. They concluded that the findings were useful in proposing measures for strategic environmental control in estuaries. Based on surface sediments collected from the port of Cagliari

(Sardinia, Italy), which included the oil terminal of one of the largest oil refineries in the Mediterranean, Schintu et al. (2016) found significant trace metal concentrations in the whole port area. The living assemblages were characterized by low diversity in samples collected close to the port areas. This signified the impact of the anthropogenic impacts to the surrounding area.

4. CONCLUSION

This study provided a comprehensive baseline data of eight metals in the rocky shore sediments of TH. Based on the three approaches to evaluate the ecological risks, the surface sediments in TH were not likely to pose detrimental effects on the surrounding biota but regular monitoring of hazardous pollutants in such recreational rocky shorelines should be carried out.

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Conflict of Interest

The authors declare that there are no conflicts of interest.

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Chapter 9

COPPER POLLUTION IN SEDIMENTS: A REVIEW FROM THE LITERATURE AND THE ECOLOGICAL AND CHILDREN'S HEALTH RISK ASSESSMENTS

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ABSTRACT

Geographical spatial distribution and the ecological and children's Health Risk Assessments (HRA) of Copper (Cu) in aquatic ecosystem ranging from rivers, mangrove, estuaries and offshore areas were investigated using Cited Cu Data In The Sediments (CCDITS) from 100 randomly selected published papers in the literature. All CCDITS were estimated for the ecological and children's HRA. In general, three major patterns could be concluded based on the present review. Local point Cu sources and natural occurrence were the main controlling factors of Cu distribution. Sediment Quality Guidelines (SQG), geo-accumulation index and enrichment factor were used to assess the toxicity of Cu in the CCDITS. Results showed that overall sediments contained a moderate to highly Cu enrichment levels. This enrichment posed a high risk despite measured Cu levels were found below SQG at most areas. This also posed a serious Cu accumulation or Cu poisoning overtime in both adults and children. While adults might be resistant to the extent of hazard, the situation might be highly critical if analysis was conducted specially for children. For children's HRA, the present cited data were also calculated for Hazard Quotient (HQ), which were the average daily dose via the oral ingestion pathway/ oral reference dose, as reported in many studies recently. The slow accumulation of Cu in a child might prove to be more hazardous over time. All CCDITS were found below 1.0 for HQ while only 1% of the HQ values exceeded 1.0, indicating a low chance of Cu non–carcinogenic effects in most areas. The only site reported by Ionnides et al. (2015) at Lake Pamvotis of Greece (24985 mg/kg) was found to have higher than 1, indicating very potential chance of Cu non–carcinogenic effects at this site. The wide spatial variation in CCDITS was closely associated with both natural and anthropogenic activities. It is recommended that regular monitoring of Cu pollution in the sediments of an aquatic ecosystem needs to be conducted with a view of abating the risk of Cu exposure to children's health and to avoid injurious impacts on the aquatic ecosystem.

Keywords: Copper; Sediments; Geochemical indexes; Health risk assessment

1. INTRODUCTION

As one of the earliest metal that was utilized by the human beings, Copper (Cu) has an enormous impact on the development of human civilization (Rédei 2008). Nowadays, Cu has been extensively applied in various industries. It is useful in the manufacturing of textiles, antifouling paints, electrical conductors, plumbing fixtures and pipes, and cooking utensils etc. Its compounds are commonly found as active ingredients in various applications, such as wood preservatives, pesticides, fungicides as well as fertilizers (CCME 1999; Fu et al. 2009). In natural context, a high quantity of Cu occurs in the form of sulfide minerals (CCME 1999). Rapid urbanization and reclamation have eventually caused a significant pollution to the aquatic ecosystem. Therefore, it is necessary to address the role of anthropogenic activities on the occurrence of heavy metal pollution (Zhang et al. 2017).

Sediment refers to a layer of solid particles on the bed of a water body, which consists of any insoluble particulate matters (i.e., rock and soil particles) that could be transported from terrestrial areas to oceans by various means, such as wind, glaciers and flowing rivers. Throughout the fate of a sediment particle, there might be a temporary settlement in between its origin and its final resting place (sea floor). These sediments may also get settled in a delta at the river mouth or becoming beach deposits by the action of tides, currents, and waves. The exact composition of these clay minerals differs depending on their locations, but kaolinite, illite, chlorite, and smectite are the major constituents of the deep-sea sediments (Allen 1982). Coastal sediments are a major sink for metals of both anthropogenic and natural origin. Under certain conditions, these accumulated metals in sediment may be remobilized, changing the surrounding aquatic ecosystem (Zhu et al. 2016).

Both direct and indirect pathways are likely to play a role in the entering of sediment-bound metals into the human body (Perrodin et al. 2014). Therefore, heavy metal pollution in coastal ecosystem draws a serious concern. Despite these concern, there is rarely a study focusing or investigating the impact of sediment-bound metals on human health risk

directly. The heavy metals bound to beach sand particles could enter the human body by inhalation of the sand or dust particles and direct ingestion via hand-to-mouth action (Duggan and Inskip 1985). Therefore, it would be implicative that humans, especially children playing on the beaches may be exposed to these metal contaminants settled in the sand.

Hazard Index (HI), or Hazard Quotient (HQ) or Target Hazard Quotient (THQ) is often used to assess the potential health risk posed by heavy metals on human health. Compared to the adults, the HI value was reported to be higher in children in Beijing parks (Du et al. 2013). Compared with the inhalation and dermal absorptions of dust particles, the Average Daily Dose (ADD) of metals in re-suspended dust particles through ingestion was found to be much higher. Therefore, the risk posed by the route of ingestion of dust particles by both children and adults were the highest followed by dermal contact. The exposure of surface dust to children could also cause more health impact than on adults (Ma and Singhirunnusorn 2012). Therefore, the health risk assessments for children should be put on higher priority besides adults.

The objectives of this paper were to review Cu concentrations in the sediments from 100 publications from 1980 until 2017 based on Scopus database and to evaluate the ecological and children's health risk assessments based on the cited Cu levels in the sediments.

2. METHODOLOGY

2.1. Data Collection

Cu data reported in the literature were cited based on Scopus database ranging from 1980 to 2017, searched on August 2017. A total of 100 publications were randomly selected, with special focus on different regions and countries. The keywords for the search were 'sediment pollution risk metal' which was found in the title of the articles. However, only those papers reporting the ranges of minimum and maximum concentrations of Cu were selected for easy and direct comparative purpose and the

standardization of the calculation of HQ index in the present study. Therefore, the Cu data in the sediments cited in the present study might not be comprehensive but at least can provide a baseline review information of Cu levels in the sediments.

2.2. Data Treatment

2.2.1. Ecological Risk Assessment

The values of geo-accumulation index (Igeo) were calculated according to Muller (1969)'s formula below:

$$Igeo = Log_2 (C/1.5 \times B)$$

where C is the sediment Cu concentrations and B is the preindustrial reference value of Cu (50 mg/kg dw), which is referred as geochemical background value of Cu (Hakanson 1980). In order to minimize the possible variation in the background value due to non-anthropogenic metals in the sediment, a factor of 1.5 was introduced (Al–Haidarey et al. 2010). It permits the fluctuations of a pollutant in the environment due to minute anthropogenic influences (Loska et al. 1995). Classification of pollution status based on Igeo is based on seven categories as proposed by Muller (1969).

Contamination factor (CF) was used to describe the contamination of toxic substances in an aquatic environment (Hakanson 1980). The CF was calculated using a formula below:

$$CF = C/B$$

where C is the mean Cu concentration in the sediment; B is the Cu preindustrial reference values as mentioned above. Classification of pollution status on CF was based on four categories as proposed by Hakanson (1980).

According to Hakanson (1980), the potential ecological risk (ER) for individual metal can be calculated by using a formula as follows:

$$ER = T_r \times CF$$

where T_r is the toxic-response factor for Cu (5.0; Hakanson 1980). The degree of Cu pollution level based on ER for Cu can be described by using Hakanson (1980)'s classification which is based on five categories.

2.2.2. Average Daily Dose and Hazard Quotient

Copper in the sediment particles could be exposed to children via three pathways: ingestion (D_{ing}), inhalation (D_{inh}) and dermal contact (D_{dermal}) (Zhu et al. 2016). However, in this paper, only D_{ing} was calculated because the reference concentrations for inhalation and dermal contact to yield an HQ, are not available based on the Integrated Risk Information System (IRIS) provided by US Environmental Protection Agency (IRIS 2014). Since only Oral Reference Dose (RfD) for Cu is available, the present study focussed on ingestion (oral) pathway. The dose acquired through the ingestion pathways was determined and adopted from the US Environment Protection Agency (USEPA 1989; USEPA 1996) and used by previous studies such as Zhu et al. (2016).

Ingestion pathway can be also interpreted as the daily dosage of Cu via direct ingestion of sand particles through hand-to-mouth action (Ma and Singhirunnusorn 2012.). The Average Daily Dose (ADD) via the ingestion pathway can be calculated using the following equation:

$$ADD = (C \times I_{ng}R \times EF \times ED)/(BW \times AT) \times 10^6$$

where C is the Cu concentration (mg/kg) in the sediments. $I_{ng}R$ refers to oral ingestion rate for Cu (200 mg/day; USEPA 2001). EF is the exposure frequency (180 days/year; Ferreira–Baptista and De Miguel 2005). ED is the exposure duration (6 years); BW is the average body weight for children (15kg; USEPA 1989); AT is the averaging time (ED × 365 days).

For Non-carcinogenic Risk (NCR) assessment, the dose for ingestion exposure pathway was subsequently divided by the corresponding oral reference doses (RfD; 0.04 mg/kg per day for Cu) to yield an HQ. The HQ based on NCR can then be calculated using the following equation:

$$HQ = ADD/RfD$$

A HQ under 1 is expected to be safe. There is an implicative risk of NCR if HQ or HI is > 1. The probability of the occurrence of these adverse effects is directly proportionate to the value of HQ (USEPA 2001).

3. Results and Discussion

Figure 1 shows the world map of all countries or areas for the Cu levels in the sediments cited from 100 publications. All the Cu levels in the sediments from 100 papers are presented in Table 1. A total of 32 countries (Table 2) had been coincidentally documented with their respective Cu levels in the sediments, mostly reporting Cu levels in combination with other heavy or trace metals in the sediments from the coastal area, mangrove, rivers, lakes, or estuaries. Clearly, many studies of Cu levels were reported from Asian countries and scattered studies from Europe and African countries. Among the Asian countries, China topped the list with 27 papers, followed by Malaysia (18), India and Tunisia (5), Japan (4), Hong Kong (3), Singapore (3), Indonesia (3), 8 countries with 2 papers, and 16 other countries with 1 paper.

Table 1 also shows the Cu concentrations (mg/kg dw) in the sediments cited from the literature published between 1980 and 2017. The values of Igeo, CF, ER, ADD and HQ of Cu through children's hand–to–mouth ingestion of sedimentary particles based on cited Cu data, are also presented in Table 1.

Table 1. Cu concentrations (mg/kg dw) in the sediments cited from the literature published between 1980 and 2017, and their calculated values of geoaccumulation index (Igeo), contamination factor (CF), ecological risk (ER), average daily dose (ADD) and hazard quotient (HQ) of Cu through children's hand-to-mouth ingestion of sedimentary particles based on cited Cu data

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
1	Tolo Harbour, Hong Kong	6.80	231	-3.46	1.62	0.14	4.63	0.68	23.1	4.50E-05	1.50E-03	1.10E-03	3.80E-02	Wong et al. (1980)
2	Belfast Lough, Ireland	6.50	420	-3.53	2.49	0.13	8.40	0.65	42.0	4.27E-05	2.76E-03	1.07E-03	6.90E-02	Manga et al. (1982)
3	Chao Phraya Estuary, Thailand	3.34	37.5	-4.49	-1.00	0.07	0.75	0.33	3.75	2.20E-05	2.50E-04	5.50E-04	6.20E-03	Polprasert (1982)
4	Ganges Estuary, India	4.00	53.0	-4.23	-0.50	0.08	1.06	0.40	5.30	2.60E-05	3.50E-04	6.60E-04	8.70E-03	Subramanian et al. (1988)
5	Java Sea, Indonesia	6.00	54.0	-3.64	-0.47	0.12	1.08	0.60	5.40	3.90E-05	3.60E-04	9.90E-04	8.90E-03	Everaats (1989)
6	Fly River Delta, Papua New Guinea	20.0	71.0	-1.91	-0.08	0.40	1.42	2.00	7.10	1.30E-04	4.70E-04	3.30E-03	1.20E-02	Baker and Harris (1991)
7	Singapore River	10.0	80.0	-2.91	0.09	0.20	1.60	1.00	8.00	6.60E-05	5.30E-04	1.60E-03	1.30E-02	Sin et al. (1991)
8	Tokyo Bay, Japan	16.6	79.8	-2.18	0.09	0.33	1.60	1.66	7.98	1.10E-04	5.20E-04	2.70E-03	1.30E-02	Fukushima et al. (1992)
9	Bintulu coastal waters, Malaysia	7.00	13.0	-3.42	-2.53	0.14	0.26	0.70	1.30	4.60E-05	8.50E-05	1.20E-03	2.10E-03	Ismail (1993)
10	Juru River, Malaysia	14.0	72.0	-2.42	-0.06	0.28	1.44	1.40	7.20	9.20E-05	4.70E-04	2.30E-03	1.20E-02	Lim and Kiu (1995)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
11	Victoria Harbour, Hong Kong	45.2	3790	-0.73	5.66	0.90	75.8	4.52	379	3.00E-04	2.50E-02	7.40E-03	6.20E-01	Wong et al. (1995)
12	Scheldt Estuarine, Netherlands	1.00	2600	-6.23	5.12	0.02	52.0	0.10	260	6.60E-06	1.70E-02	1.60E-04	4.30E-01	Zwolsman et al. (1996)
13	Johore Straits, Malaysia	10.8	92.9	-2.80	0.31	0.22	1.86	1.08	9.29	7.10E-05	6.10E-04	1.80E-03	1.50E-02	Wood et al. (1997)
14	Osaka Bay, Japan	18.0	35.0	-2.06	-1.10	0.36	0.70	1.80	3.50	1.20E-04	2.30E-04	3.00E-03	5.80E-03	Fukue et al. (1999)
15	Izmir Bay, Turkey	4.00	79.0	-4.23	0.07	0.08	1.58	0.40	7.90	2.60E-05	5.20E-04	6.60E-04	1.30E-02	Kucuksezgin (2001)
16	Offshore and intertidal west coast of Peninsular Malaysia	0.25	315	-8.23	2.07	0.01	6.30	0.03	31.50	1.60E-06	2.10E-03	4.10E-05	5.20E-02	Yap et al. (2002)
17	Pearl River Delta, China	8.70	140	-3.11	0.90	0.17	2.80	0.87	14.0	5.70E-05	9.20E-04	1.40E-03	2.30E-02	Cheung et al. (2003)
18	Coastal Alang-Sosiya, India	85.2	313	0.18	2.06	1.70	6.26	8.52	31.3	5.60E-04	2.10E-03	1.40E-02	5.10E-02	Reddy et al. (2004)
19	Semarang, Indonesia	33.0	72.0	-1.18	-0.06	0.66	1.44	3.30	7.20	2.20E-04	4.70E-04	5.40E-03	1.20E-02	Takarina et al. (2004)
20	Kelana Jaya Lakes, Malaysia	7.37	73.6	-3.35	-0.03	0.15	1.47	0.74	7.36	4.80E-05	4.80E-04	1.20E-03	1.20E-02	Ismail et al. (2004)
21	South west coast, Spain	41.0	336	-0.87	2.16	0.82	6.72	4.10	33.6	2.70E-04	2.20E-03	6.70E-03	5.50E-02	Morillo et al. (2004)
22	Mangrove area, Singapore	7.06	32.0	-3.41	-1.23	0.14	0.64	0.71	3.20	4.60E-05	2.10E-04	1.20E-03	5.30E-03	Cuong et al. (2005)

Table 1. (Continued)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
23	Ebrie Lagoon, Ivory Coast	3.00	86.0	-4.64	1.72	0.20	0.30	0.06	8.60	1.97E-05	1.97E-05	4.93E-04	4.93E-04	Kouadio and Trefry (1987)
24	Western Moreton Bay, Australia	1.00	31.0	-6.23	-1.27	0.02	0.62	0.10	3.10	6.60E-06	2.00E-04	1.60E-04	5.10E-03	Cox and Preda (2005)
25	Balaton Lake, Hungary	0.70	36.0	-6.74	-1.06	0.01	0.72	0.07	3.60	4.60E-06	2.40E-04	1.20E-04	5.90E-03	Nguyen et al. (2005)
26	Mandovy Estuary, India	11.5	77.5	-2.71	0.05	0.23	1.55	1.15	7.75	7.60E-05	5.10E-04	1.90E-03	1.30E-02	Alagarsamy (2006)
27	Kranji and Tekong Island, Singapore	7.70	17.9	-3.28	-2.07	0.15	0.36	0.77	1.79	5.10E-05	1.20E-04	1.30E-03	2.90E-03	Cuong and Obbard (2006)
28	Izmit Bay, Turkey	60.6	139	-0.31	0.89	1.21	2.78	6.06	13.9	4.00E-04	9.10E-04	1.00E-02	2.30E-02	Pekey (2006)
29	Agbabu Bitumen Deposit Area, Nigeria	2.91	23.3	-4.69	0.47	-1.69	0.29	0.06	2.33	1.91E-05	1.53E-04	4.78E-04	3.83E-03	Olubunmi and Olorunsola (2010)
30	Tg. Piai, Peninsular Malaysia	3.43	3.81	-4.45	-4.30	0.07	0.08	0.34	0.38	2.30E-05	2.50E-05	5.60E-04	6.30E-04	Yap et al. (2006)
31	Mvudi River, South Africa	13.2	1027	-2.50	20.54	3.78	1.32	0.26	103	8.69E-05	6.75E-03	2.17E-03	1.69E-01	Edokpayi et al. (2016)
32	Lakes of southwest Japan	13.0	44.0	-2.53	-0.77	0.26	0.88	1.30	4.40	8.55E-05	2.89E-04	2.14E-03	7.23E-03	Bibi et al. (2007)
33	Kaoshiung Harbor, Taiwan	5.00	946	-3.91	3.66	0.10	18.9	0.50	94.6	3.30E-05	6.20E-03	8.20E-04	1.60E-01	Chen et al. (2007)
34	Pearl River Estuary, China	8.90	351	-3.08	2.23	0.18	7.02	0.89	35.1	5.90E-05	2.30E-03	1.50E-03	5.80E-02	Li et al. (2007)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
35	Western Xiamen Bay, China	19.0	97.0	-1.98	0.37	0.38	1.94	1.90	9.70	1.20E-04	6.40E-04	3.10E-03	1.60E-02	Zhang et al. (2007)
36	Sepang River, Malaysia	2.88	161	-4.70	1.10	0.06	3.22	0.29	16.1	1.90E-05	1.10E-03	4.70E-04	2.60E-02	Yap et al. (2007a)
37	Polluted drainage sediments from Peninsular Malaysia	8.77	1019	-3.10	3.76	0.18	20.4	0.88	102	5.80E-05	6.70E-03	1.40E-03	1.70E-01	Yap et al. (2007b)
38	Victoria Harbour, Hong Kong	16.0	280	-2.23	1.90	0.32	5.60	1.60	28.0	1.10E-04	1.80E-03	2.60E-03	4.60E-02	Chloe et al. (2008)
39	Manchar Lake, Pakistan	15.6	29.7	-2.27	-1.34	0.31	0.59	1.56	2.97	1.00E-04	2.00E-04	2.60E-03	4.90E-03	Arain et al. (2008)
40	East, South and West coasts of Peninsular Malaysia	12.9	38.8	-2.53	-0.95	0.26	0.78	1.30	3.88	8.50E-05	2.60E-04	2.10E-03	6.40E-03	Yap et al. (2008a)
41	Old Nakagawa River, Japan	340	1565	2.18	4.38	6.80	31.3	34.0	157	2.24E-03	1.03E-02	5.59E-02	2.57E-01	Zakir et al. (2008)
42	Southern part of Peninsular Malaysia	9.48	116	-2.98	0.63	0.19	2.32	0.95	11.6	6.23E-05	7.63E-04	1.56E-03	1.91E-02	Yap and Wong (2011)
43	Six intertidal area and four urban drainage sites, Selangor, Malaysia	6.64	123	-3.50	0.71	0.13	2.45	0.66	12.3	4.40E-05	8.10E-04	1.10E-03	2.00E-02	Yap et al. (2008b)
44	Yangtze River Estuary, China	11.7	46.6	-2.66	-0.65	0.24	0.96	1.19	4.79	7.80E-05	3.10E-04	1.90E-03	7.90E-03	An et al. (2009)

Table 1. (Continued)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
45	Yangtze River, China	6.87	49.7	-3.45	-0.59	0.14	0.99	0.69	4.97	4.50E-05	3.30E-04	1.10E-03	8.20E-03	Zhang et al. (2009)
46	Dumai coast, Indonesia	1.61	13.8	-5.54	-2.44	0.03	0.28	0.16	1.38	1.10E-05	9.10E-05	2.60E-04	2.30E-03	Amin et al. (2009)
47	Sri Serdang Industrial Area, Malaysia	21.7	348	2.21	2.21	6.95	6.95	34.8	34.8	2.30E-03	2.30E-03	5.70E-02	5.70E-02	Yap et al. (2009)
48	Laguna Lake, Philippines	9.70	18.7	-2.95	-2.00	0.19	0.37	0.97	1.87	6.40E-05	1.20E-04	1.60E-03	3.10E-03	Pradit et al. (2010)
49	Northwestern part of Peninsular Malaysia	4.79	119	-3.97	0.67	0.10	2.39	0.48	11.9	3.10E-05	7.90E-04	7.90E-04	2.00E-02	Yap and Pang (2011)
50	Urban river Suzhou City, China	41.0	173	-0.87	1.21	0.82	3.46	4.10	17.3	2.70E-04	1.10E-03	6.70E-03	2.80E-02	Meri et al. (2011)
51	Kebir Rhumel Basin, Algeria	9.00	446	-3.06	2.57	0.18	8.92	0.90	44.6	5.90E-05	2.90E-03	1.50E-03	7.30E-02	Sahli et al. (2011)
52	Beysehir Lake, Turkey	24.0	90.3	-1.64	0.27	0.48	1.81	2.40	9.03	1.60E-04	5.90E-04	3.90E-03	1.50E-02	Aktumsek et al. (2011)
53	West Port, Malaysia	7.40	27.6	-3.34	-1.44	0.15	0.55	0.74	2.76	4.90E-05	1.80E-04	1.20E-03	4.50E-03	Sany et al. (2011)
54	Perlis River, Malaysia	7.31	35.9	-3.36	-1.06	0.15	0.72	0.73	3.59	4.80E-05	2.40E-04	1.20E-03	5.90E-03	Jamil et al. (2014)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
55	West coast of Peninsular Malaysia	5.59	28.7	-3.75	-1.39	0.11	0.57	0.56	2.87	3.70E-05	1.90E-04	9.20E-04	4.70E-03	Cheng and Yap (2015)
56	Hugli River Estuary and Sundarban Mangrove Wetland, India	11.6	102	-2.69	0.45	0.23	2.05	1.16	10.3	7.60E-05	6.70E-04	1.90E-03	1.70E-02	Antizar-Ladislao et al. (2015)
57	Lake Pamvotis, Greece	15.0	24985	-2.32	8.38	0.30	499	1.50	2499	9.90E-05	1.60E-01	2.50E-03	4.10E+00	Ioannides et al. (2015)
58	Sundarban, India and Bangladesh	36.0	82.0	-1.06	0.13	0.72	1.64	3.60	8.20	2.40E-04	5.40E-04	5.90E-03	1.30E-02	Kumar et al. (2015)
59	Shuangtaizi Estuary, China	1.80	17.7	-5.38	-2.08	0.04	0.35	0.18	1.77	1.20E-05	1.20E-04	3.00E-04	2.90E-03	Li et al. (2015)
60	Old Yellow River Estuary, China	18.3	38.5	-2.04	-0.96	0.37	0.77	1.83	3.85	1.20E-04	2.50E-04	3.00E-03	6.30E-03	Liu et al. (2015a)
61	Libyan Mediterranean coast	9.10	22.7	-3.04	-1.72	0.18	0.45	0.91	2.27	6.00E-05	1.50E-04	1.50E-03	3.70E-03	Nasr et al. (2015)
62	Qinghai section of the Yellow River, China.	11.8	57.0	-2.66	-0.40	0.24	1.14	1.19	5.70	7.80E-05	3.70E-04	1.90E-03	9.40E-03	Ren et al. (2015)
63	Serbia	11.5	870	-2.71	3.54	0.23	17.4	1.15	87.0	7.60E-05	5.70E-03	1.90E-03	1.40E-01	Sakan et al. (2015)
64	Laizhou Bay, China	7.57	21.3	-3.31	-1.82	0.15	0.43	0.76	2.13	5.00E-05	1.40E-04	1.20E-03	3.50E-03	Zhang and Gao (2015)

Table 1. (Continued)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
65	Xiangjiang River and Dongting Lake, China	29.0	217	-1.37	1.53	0.58	4.34	2.90	21.7	1.90E-04	1.40E-03	4.80E-03	3.60E-02	Zhang et al. (2015)
66	Mangrove sediment of west coast of Peninsular Malaysia	5.59	28.7	-3.75	-1.39	0.11	0.57	0.56	2.87	3.70E-05	1.90E-04	9.20E-04	4.70E-03	Cheng and Yap (2015)
67	Gulf of Thailand	6.00	36.0	-3.64	-1.06	0.12	0.72	0.60	3.60	3.90E-05	2.40E-04	9.90E-04	5.90E-03	Qiao et al. (2015)
68	Leizhou Peninsula, China	3.37	33.4	-4.48	-1.17	0.07	0.67	0.34	3.34	2.20E-05	2.20E-04	5.50E-04	5.50E-03	Liu et al. (2015b)
69	Gulf of Guinea	0.20	29.3	-8.55	-1.36	0.00	0.59	0.02	2.93	1.30E-06	1.90E-04	3.30E-05	4.80E-03	Mahu et al. (2015)
70	Nador lagoon, Morocco	10.2	398	-2.88	2.41	0.20	7.97	1.02	39.8	6.70E-05	2.60E-03	1.70E-03	6.50E-02	Maanan et al. (2015)
71	Changshou Lake, China.	21.2	74.9	-1.82	0.00	0.42	1.50	2.12	7.49	1.40E-04	4.90E-04	3.50E-03	1.20E-02	Liang et al. (2015)
72	Gansu section of Yellow River, China	15.5	57.5	-2.27	-0.38	0.31	1.15	1.55	5.75	1.00E-04	3.80E-04	2.60E-03	9.50E-03	Shang et al. (2015a)
73	Yinchuan section of Yellow River, China	18.8	28.9	-1.99	-1.38	0.38	0.58	1.88	2.89	1.20E-04	1.90E-04	3.10E-03	4.70E-03	Shang et al. (2015b)
74	Kaohsiung Harbor, Taiwan.	16.0	760	-2.23	3.34	0.32	15.20	1.60	76.0	1.10E-04	5.00E-03	2.60E-03	1.20E-01	Chen et al. (2016)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
75	Minjiang River, China	2.45	95.8	-4.94	0.35	0.05	1.92	0.25	9.58	1.60E-05	6.30E-04	4.00E-04	1.60E-02	Fang et al. (2016)
76	Shima River, China.	10.8	630	-2.80	3.07	0.22	12.6	1.08	63.0	7.10E-05	4.10E-03	1.80E-03	1.00E-01	Gao et al. (2016)
77	Coast of Ain Temouchent, Algeria	12.5	31.2	-2.59	-1.26	0.25	0.63	1.25	3.13	8.20E-05	2.10E-04	2.10E-03	5.10E-03	Kourdri et al. (2016)
78	Mangrove area of Shenzhen, China	50.0	75.0	-0.58	0.00	1.00	1.50	5.00	7.50	3.29E-04	4.93E-04	8.22E-03	1.23E-02	Li et al. (2016)
79	Trabzon Harbor, Turkey	54.3	247	-0.47	1.72	1.09	4.94	5.43	24.7	3.60E-04	1.60E-03	8.90E-03	4.10E-02	Ozsaker et al. (2016)
80	Northern South China Sea, China	7.10	38.1	-3.40	-0.98	0.14	0.76	0.71	3.81	4.70E-05	2.50E-04	1.20E-03	6.30E-03	Xu et al. (2016)
81	Huaihe River Basin, China	19.6	35.9	-1.94	-1.06	0.39	0.72	1.96	3.59	1.30E-04	2.40E-04	3.20E-03	5.90E-03	Yuan et al. (2016)
82	West Guangdong coast, China	11.5	78.8	-2.71	0.07	0.23	1.58	1.15	7.88	7.60E-05	5.20E-04	1.90E-03	1.30E-02	Zhao et al. (2016)
83	Southern coast of Sfax, Tunisia	8.23	28.6	-3.19	-1.39	0.16	0.57	0.82	2.86	5.40E-05	1.90E-04	1.40E-03	4.70E-03	Zohra and Habib (2016)
84	Haihe River Basin, China	6.47	179	-3.50	1.25	0.13	3.57	0.66	17.9	4.40E-05	1.20E-03	1.10E-03	2.90E-02	Liu et al. (2016)
85	Brisbane River, Australia	20.0	110	-1.91	0.55	0.40	2.20	2.00	11.0	1.30E-04	7.20E-04	3.30E-03	1.80E-02	Duodu et al. (2016)
86	Chabahar Bay, Oman	5.00	26.0	-3.91	-1.53	0.10	0.52	0.50	2.60	3.30E-05	1.70E-04	8.20E-04	4.30E-03	Agah et al. (2016)
87	Gabes Gulf, Tunisia	0.59	5.80	-6.99	-3.69	0.01	0.12	0.06	0.58	3.90E-06	3.80E-05	9.70E-05	9.50E-04	El Zrelli et al. (2016)

Table 1. (Continued)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
88	Chenab River, Pakistan	6.00	8.70	-3.64	-3.11	0.12	0.17	0.60	0.87	3.90E-05	5.70E-05	9.90E-04	1.40E-03	Hanif et al. (2016)
89	Zhangjiangkou Mangrove National Nature Reserve, China	10.8	26.7	-2.80	-1.49	0.22	0.53	1.08	2.67	7.10E-05	1.80E-04	1.80E-03	4.40E-03	Wang et al. (2016)
90	Three Gorges Reservoir area, China	46.5	85.7	-0.65	1.72	0.96	0.30	4.79	8.60	3.10E-04	1.97E-05	7.90E-03	4.93E-04	Zhuo et al. (2016)
91	Gorgan Bay, Iran	8.10	12.4	-3.21	-2.60	0.16	0.25	0.81	1.24	5.30E-05	8.20E-05	1.30E-03	2.00E-03	Ghorbanzadeh et al. (2017)
92	Tongi Canal, Bangladesh	18.3	101	-2.03	0.43	0.37	2.03	1.83	10.1	1.20E-04	6.70E-04	3.00E-03	1.70E-02	Hossen et al. (2017)
93	Liaohe Estuary, China	1.70	47.9	-5.46	-0.65	0.03	0.96	0.17	4.79	1.10E-05	3.10E-04	2.80E-04	7.90E-03	Li et al. (2017)
94	Xiangjiang River, China	9.56	81.8	-2.97	0.13	0.19	1.64	0.96	8.18	6.30E-05	5.40E-04	1.60E-03	1.30E-02	Liu et al. (2017)
95	Jiaozhou Bay, China	4.50	179	-4.06	1.25	0.09	3.57	0.45	17.9	3.00E-05	1.20E-03	7.40E-04	2.90E-02	Xu et al. (2017)
96	Rivers near Kinshasa, DR Congo	18.2	325	-2.04	2.12	0.36	6.50	1.82	32.5	1.20E-04	2.10E-03	3.00E-03	5.30E-02	Kilunga et al. (2017)
97	Bayan Lepas, Malaysia	1.92	387	-5.29	2.37	0.04	7.74	0.19	38.7	1.30E-05	2.50E-03	3.20E-04	6.40E-02	Khodami et al. (2017)

No.	Area	Cu		Igeo		CF		ER		ADD		HQ		References
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
98	Dakar coast and Saint Louis Estuary, Senegal	12.9	121	-2.54	0.69	0.26	2.42	1.29	12.1	8.50E-05	8.00E-04	2.10E-03	2.00E-02	Diop et al. (2017)
99	Ennore to Poomphar, India	1.35	15.8	-5.80	-2.25	0.03	0.32	0.14	1.58	8.90E-06	1.00E-04	2.20E-04	2.60E-03	Kumar et al. (2017)
100	Mand River Delta, Iran	25.0	87.0	-1.58	0.21	0.50	1.74	2.50	8.70	1.60E-04	5.70E-04	4.10E-03	1.40E-02	Pourkerman et al. (2017)

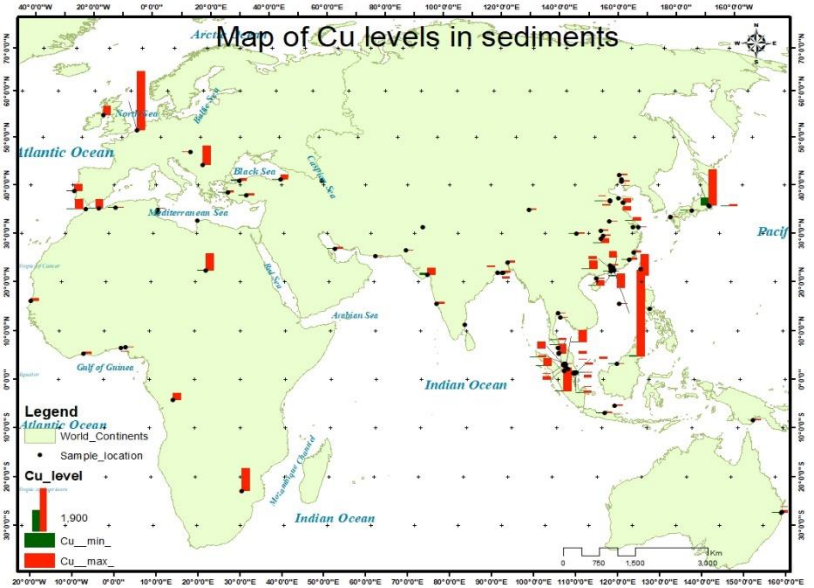

Figure 1. World map of all counties covering continents of Africa, Europe and Asia-Pacific areas for the Cu levels in the sediments cited from 100 publications.

Based on 100 reviewed papers, there are 10 papers (10%) documenting Cu levels more than 500 mg/kg dw (Table 1; Figure 2). These papers included Lake Pamvotis of Greece (24985 mg/kg; Ionnides et al. 2015)> Victoria Harbour of Hong Kong (3790 mg/kg; Wong et al. 1995)> Scheldt Estuarine of the Netherlands (2600 mg/kg; Zwolsman et al. 1996), Old Nakagawa River of Tokyo, Japan (1565 mg/kg; Zakir et al. 2008)> Mvudi River of South Africa (1027 mg/kg; Edokpayi et al. 2016)> polluted drainage sediments from Peninsular Malaysia (1019 mg/kg; Yap et al. 2007b)> Kaohsiung Habour of Taiwan (946 mg/kg; Chen et al. 2007)> Serbia (870 mg/kg; Sakan et al. 2015)> Kaohsiung Habour of Taiwan (760 mg/kg; Chen et al. 2016)> Shima River of China (630 mg/kg; Gao et al. 2016). From this top ten citations with elevated Cu levels in the sediments, Kaohsiung Habour of Taiwan had been reported two times as high as between 760-946 mg/kg by Chen et al. (2007) and Chen et al. (2016), respectively. However, based on HQ, only Lake Pamvotis of Greece (24985 mg/kg; Ionnides et al. 2015) was found to have higher than 1, indicating very potential chance of Cu NCR at this site.

Table 2. Overall number of paper (NP) reported from different countries out of 100 papers cited in the present study

No.	Country	NP	No.	Country	NP
1	China	27	17	Netherland	1
2	Malaysia	18	18	Ghana	1
3	India	5	19	Greece	1
4	Tunisia	5	20	Hungary	1
5	Japan	4	21	Ivory Coast	1
6	Hong Kong	3	22	Libya	1
7	Indonesia	3	23	Morocco	1
8	Singapore	3	24	Netherland	1
9	Algeria	2	25	Nigeria	1
10	Australia	2	26	Oman	1
11	Bangladesh	2	27	Papua New Guinea	1
12	Iran	2	28	Philippines	1
13	Pakistan	2	29	Senegal	1
14	Taiwan	2	30	Serbia	1
15	Thailand	2	31	South Africa	1
16	Tunisia	2	32	Spain	1

Table 3 shows the comparisons of average concentrations (mg/kg dw) of Cu sediment quality guidelines of available literature, with the overall statistics of 100 reviewed Cu data in the present study. To compare with the above guidelines, three patterns can be observed. First, the mean Cu value (16.6 mg/kg) for minimum ranges of 100 Cu data reviewed were below all the guideline values in Table 3. This indicated that the minimum ranges generally created no ecological risks to the biota or ecosystem. However, the mean Cu value (475 mg/kg) for maximum ranges exceeded all the guidelines values of effect range median (ERM), interim sediment quality value (ISQV)-high, probable effect level (PEL), upper continental crusts (UCC) by Taylor and McLennan (1985), Wedepohl (1995) and Rudnick and Gao (2003). Therefore, ecological risks for the maximum ranges for Cu could be present.

Secondly, the Igeo mean value (-3.06) for minimum ranges is considered as 'practically unpolluted' (Igeo < 0; Muller 1969), CF (0.42) as 'low contamination factor' (CF< 1.0; Sutherland 2000) and ER (2.00) as 'low potential ecological risk' (ER< 40; Hakanson 1980). However, the mean

values for the Igeo mean value (0.46) for maximum ranges is considered as 'unpolluted to moderately polluted' (0< Igeo< 1; Muller 1969), CF (9.28) as 'very high contamination factor' (CF≥ 6.0; Sutherland 2000) and ER (47.5) as 'moderate potential ecological risk' (40 ≤ ER< 80; Hakanson 1980).

Thirdly, the mean HQ values for both minimum and maximum ranges are below 1. Therefore, there is no potential chance of Cu non-carcinogenic effects in all countries, except for Lake Pamvotis of Greece which has been previously discussed.

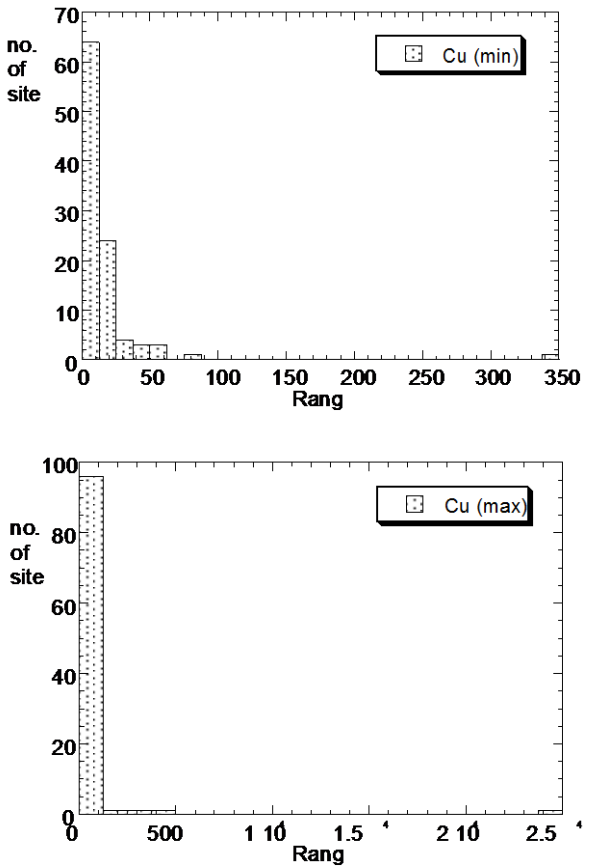

Figure 2. Overall percentages of ranges of minimum (a) and maximum (b) concentrations (mg/kg dw) based on the Cu data reviewed from 100 papers.

Table 3. Comparisons of average concentrations (mg/kg dw) of Cu sediment quality guidelines of available citations, with the overall statistics of 100 reviewed Cu data in the present study

No.	Guidelines	Cu	Igeo	CF	ER	ADD	HQ	References
1	Effects range low (ERL)	34.0	-1.14	0.68	3.40	2.20E-04	5.60E-03	Long et al. (1995)
2	Effects range median (ERM)	270	1.85	5.40	27.0	1.80E-03	4.40E-02	Long et al. (1995)
3	Interim sediment quality value (ISQV)-low	65.0	-0.21	1.30	6.50	4.30E-04	1.10E-02	Chapman et al. (1999)
4	Interim sediment quality value (ISQV)-high	270	1.85	5.40	27.0	1.80E-03	4.40E-02	Chapman et al. (1999)
5	Threshold effect level (TEL)	18.7	-2.00	0.37	1.87	1.20E-04	3.10E-03	MacDonald et al. (1996)
6	Probable effect level (PEL)	108.2	0.53	2.16	10.8	7.10E-04	1.80E-02	MacDonald et al. (1996)
7	Pre-industrial reference level	50.0	-0.58	1.00	5.00	3.30E-04	8.20E-03	Hakanson (1980)
8	Upper continental crust	25.0	-1.58	0.50	2.50	1.60E-04	4.10E-03	Taylor and McLennan (1995)
9	Upper continental crust	14.3	-2.39	0.29	1.43	9.40E-05	2.40E-03	Wedepohl (1995)
10	Upper continental crust	28.0	-1.42	0.56	2.80	1.80E-04	4.60E-03	Rudnick and Gao (2003)
11	Minimum	0.20	-8.55	-1.69	0.02	1.30E-06	3.30E-05	This study (minimum ranges)
	Maximum	340	2.21	6.95	34.7	2.30E-03	5.70E-02	
	Mean	16.9	-3.06	0.42	2.00	1.33E-04	3.32E-03	
	Median	9.52	-2.98	0.19	0.93	6.27E-05	1.58E-03	
	Standard error	3.56	0.17	0.10	0.49	3.21E-05	7.98E-04	
	Skewness	7.72	-0.23	4.99	6.02	6.03E+00	6.03E+00	
12	Minimum	3.81	-4.30	0.08	0.38	1.97E-05	4.93E-04	This study (maximum ranges)
	Maximum	24985	20.5	499	2499	1.60E-01	4.10E+00	
	Mean	475	0.46	9.28	47.5	3.07E-03	7.77E-02	
	Median	78.1	0.07	1.49	7.82	4.92E-04	1.22E-02	
	Standard error	253	0.29	5.05	25.3	1.62E-03	4.15E-02	
	Skewness	9.29	3.73	9.31	9.29	9.27E+00	9.29E+00	

Note: Igeo= Geo-accumulation index; CF= Contamination factor; ER= Ecological risk; ADD= Average daily dose; HQ= Hazard quotient

4. COMMENTS ON THE HAZARD QUOTIENTS OF CHILDREN

From the present estimation of the children's HRA based on Cu levels in the sediments, it is rather far from reality. The ingestion pathway was included in this study with two assumptions that 1) Children spend more time on the beach (or muddy sediment area in the coastal area), and 2) the sediment-bound metal pollutants could be introduced into children's body via direct ingestion of the small particles by hand-to-mouth action. The first assumption is arguable that the definition for children should be well defined. Most of the papers reviewed in this study did not specify clearly the age groups for their children's HRA. Ages 1-2 are different from those 10-12 years old. The resistance and sensitivity of the children's bodies are very different between the two groups of ages. Therefore, if ages 2 to 12 are all considered children, erroneous assumptions could be reached and conclusions would be invalid. Perhaps, specifying a body weight of the child can reduce the error. However, similar body resistance and maturity of children between a 5 and a 12-year-old, with a similar body weight of 40 kg, can be assumed. Since obesity among children has become an issue nowadays, the estimation HQ through the ingestion pathway in a child is somehow questionable.

5. CONCLUSION

This review of Cu levels in the sediments were based on 100 publications revealed three interesting points. First, the present review found that China was the country with the highest number (27%) of papers published between 1980 until 2017, out of 32 countries. Second, the mean value for maximum ranges exceeded all the guidelines values of ERM, ISQV-high, PEL, and UCC. This indicated that ecological risks for the maximum ranges for Cu could be present. Also, the mean values for maximum ranges of Igeo was considered as 'unpolluted to moderately polluted', CF as 'very high contamination factor' and ER as 'moderate potential ecological risk'. Third, the calculated HQ values based on 100

papers were found to be below 1, indicating no potential chance of Cu non–carcinogenic effects except for Lake Pamvotis of Greece.

Lastly, it is still recommended that regular monitoring of Cu levels by using Sediment Watch should be carried out in view of the expansion of domestic wastes related to urbanization, and mismanagement of effluents related to industrialization. All these issues are complicated since they are blended integration of socio-economic and environmental factors that are difficult to decide which one is responsible in the first place and which one takes the priority from governing body's point of view, whether of problem solver or trouble maker.

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Chapter 10

GEOCHEMICAL SPECIATION AND RISK ASSESSMENT OF HEAVY METALS IN SOUTHWESTERN TAIWAN COASTAL SEDIMENTS

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ABSTRACT

Numerous investigations on aquatic heavy metal distributions in Asia reveal that the riverine and coastal sediments are the major heavy metal carriers responsible for anthropogenic activities. The mobility and accumulation of heavy metals in those sediments are therefore the fundamental knowledge for risk assessment on biotic species. To better constrain the essential parameters influencing the heavy metal distributions, a large-scale systematic investigation is demanded. Hence more than 11 studies were included to re-analyze the heavy metal distribution for their risk assessments in southwestern Taiwan marine sediments. Literature data on the six heavy metals, i.e., Hg, Cd, Cr, Cu, Pb,

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and Zn, as well as basic characteristics of sediments, in the estuaries, harbors, coast, offshore, and dumping sites were cited. On the other hand, sequential extraction procedure (SEP), isolating metal species among different geochemical forms, was applied on sediments to provide information regarding metal geochemical behavior in details. Although the related literature data is limited, there are already a few papers that have reported geochemical forms of separated heavy metal distribution in the sediment cores. By using statistical analyses on the collected dataset coupled with the SEP data, this study sheds lights on: (1) spatial distribution of heavy metals in the marine sediments of southwestern Taiwan; (2) the essential driving factors influencing the heavy metal distribution; and (3) ecological risk assessment of heavy metal in the Taiwan coastal environments.

Keywords: heavy metals, sequential extraction, sediment, enrichment factor, risk assessment

INTRODUCTION

Estuarial and coastal sediments are considered as the major sink of heavy metals, sourced from either lithological weathering or anthropogenic production (Chen and Kandasamy 2008; Fang and Yang 2010; Gao et al. 2016). Heavy metals in sediments usually act as the most important metal sources for the overlying water column and benthic organisms (Chapman et al. 1998). However, a systematic investigation of heavy metals in Asian estuaries revealed that the estuarine sediments are severely contaminated with heavy metals and hence the most serious ecological risk to aquatic biota and even to human health (Fang and Yang 2010). Therefore, a comprehensive assessment of heavy metal distribution, enrichment, and the associated ecological risks in the estuarial sediments are needed for future environmental remediation.

Because of the rapid economic and industrial development, metal contamination in the estuarine sediments in southwestern Taiwan has increased significantly over the past few decades (Hung 1995). Substantial studies have been conducted on the sediments of the estuaries, along with the coastline, and inside the harbor basins, respectively, in southwestern Taiwan to assess the distribution and accumulation of heavy metals. Some

of the investigation on the surficial sediments in this region reported that the fine sediments are the dominant carriers for the heavy metals (Huang and Lin 1994; Lee et al. 1998), while some suggested the organic matters (OM) are the dominant factor influencing heavy metals (Lee et al. 2000; Dong et al. 2016; Chen et al. 2007), or either both of them (Hung and Hsu 2004; Chen et al. 2018). In fact, there is a general agreement among the scientific communities that metal binding with geochemical fractions fluctuates among various heavy metals, sedimentation environments, and seasons (O'Day et al. 2000;Bostick et al. 2001; Souch et al. 2001). Heavy metal mobility and availability depend on the binding behaviors of the elements, and their reactivity with the components of the geochemical matrices. However, lacks in financial support results in those conducted studies solely focused on relatively small areas. Indeed, a large-scale investigation for a better constraining of critical factors controlling the heavy metal accumulated in the sediments is urgently needed.

In this work, we quantify the heavy metals in the sediments with their basic characteristic data to evaluate the driving factors that controlling the heavy metal mobility in southwestern Taiwan marine sediments. Our strategy is to analyze the spatial characteristics of heavy metal distribution, enrichment, and the associated potential ecological risk by compiling the sparse available literature data. The main objectives focus on (1) spatial distribution of heavy metals in the sediments, (2) the critical factors influencing the heavy metal distribution, and (3) associated ecological risk by the heavy metals.

MATERIALS

This study includes several works reported in the literature on southwestern Taiwan surficial sediments, i.e., estuaries, coast, harbors, and dumping sites. Although more than 40 relevant studies have been made in this area over the past two decades, only 11 have been selected due to their available integrated information of sediment basic characteristics and heavy metal concentrations (Table 1).

Table 1. Published data of surficial sediment basic characteristics, and heavy metal concentration used in this study

Reference	Sampling period	Region	Basic sediment characteristics	Determined heavy metals	n
Lee et al. 1998, 467	1994-1995	Mid-western Taiwan river mouths	GS	Cd, Cr, Cu, Pb, Zn, Ni	12
Huang and Lin 1994, 96	-	Mid-western Taiwan coast	OM, GS, CC	Mn, Cu, Pb, Zn	25
Dong et al. 2016, 29278, 29280	2011	Tainan harbor, harbor entrances, and river mouths	OM, TG, GS	Hg, Cd, Cr, Cu, Pb, Zn	10
Chen and Liu 2013, 5	2001-2006	Tainan coast	OM, GS	Hg, Cr, Cu, Pb, Zn, Ni	20
Chen et al. 2013a, 549, 551-552	2008	Kaohsiung harbor, harbor entrances, and river mouths	OM, GS	Mn, Hg, Cd, Cr, Cu, Pb, Zn, Ni	11
Chen et al. 2016, 71	-	Kaohsiung harbor, harbor entrances, and river mouths	OM, TG, GS	Hg, Cd, Cr, Cu, Pb, Zn	6
Chen et al. 2007, 1433, 1437	2002-2005	Kaohsiung harbor, harbor entrances, and river mouths	OM, TG, GS, TN, TP	Hg, Cd, Cr, Cu, Pb, Zn	6
Chen et al. 2013b, 305	2009	Kaohsiung harbor, harbor entrances, and river mouths	OM, GS, TN, TP	Hg, Cd, Cr, Cu, Pb, Zn	20
Lee et al. 2000, 895	1996	Kaohsiung coast	GS	Mn, Cd, Cr, Cu, Pb, Zn, Ni	40
Chen et al. 2018, 558	2012 (estimated)	Kaohsiung offshore and dumping sites	OM, GS	Mn, Cd, Cr, Cu, Pb, Zn, Ni	8
Chen and Kandasamy 2008, 1337, 1341	1995	Kaohsiung coast, offshore, and dumping sites	OM, GS, CC	Mn, Cd, Cr, Cu, Pb, Zn, Ni, V	20

OM = organic matter, TG = total grease, GS = grain size (mean grain size or proportion of clay, slit, and sand), TN = total nitrogen, TP = total phosphorous, CC = carbonate content.

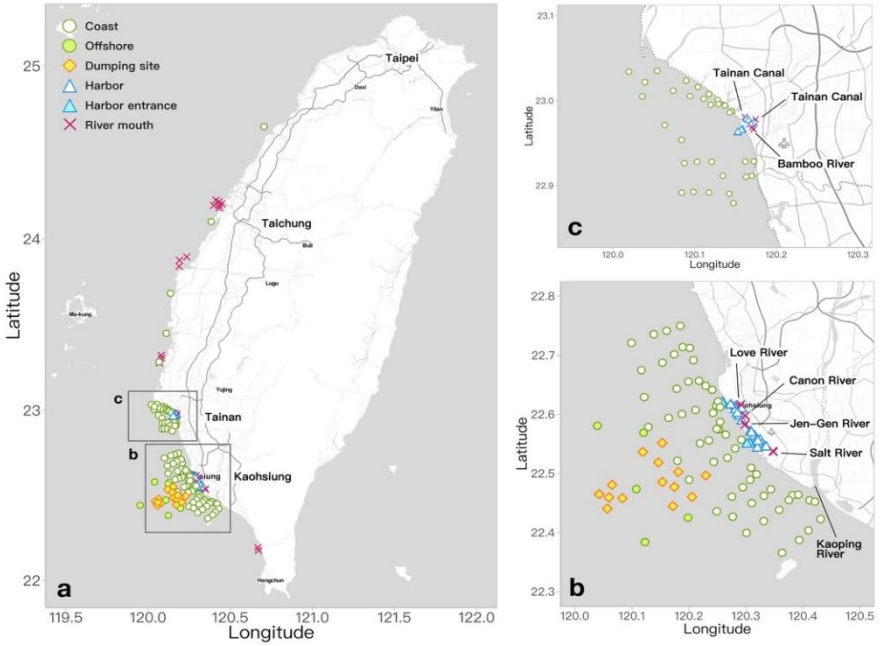

Figure 1. Locations of surficial sediments from river mouths, coast, offshore, harbor systems, and dumping sites included in this study (See Table 1 for details).

The collected dataset has approximately 178 observations, located along the coastline in southwestern Taiwan (Figure 1a). According to their geographic distribution, those observations can be divided into various groups, including two harbor systems, and sediments collected from estuaries as well as along the coastline.

Kaohsiung Harbor and Adjacent Coastal Sediments

The Port of Kaohsiung is the largest modern harbor in Taiwan and closely adjacent to the Kaohsiung City, which has the most massive industrial development and has the second largest population in Taiwan. Four major rivers, namely Love River, Canon River, Jen-Gen River, and Salt River, flow through the city and eventually discharge into the harbor. Many factories, such as petrochemical, machinery, metal plating, and leather

manufactories, situated along the river banks and subsequently to mix with domestic sewage for contaminating these rivers. Moreover, the polluted effluent may cause amounts of sedimentary particles and pollutants accumulated in the harbor basin, especially in the river-port junction area (Chen et al. 2012). Hence, to maintain the waterway of the harbor, local Environmental Protection Agency set up an offshore disposal place for handling the harbor dumping material. In this area, literature data of surficial sediments in the Kaohsiung Harbor, i.e., the four river mouths, harbor interior, harbor entrance (Chen et al. 2007; Chen et al. 2013a,b; Dong et al. 2013; Chen et al. 2016), coastal (Lee et al. 2000; Chen and Kandasamy 2008; Chen et al. 2018), and the dumping sites (Chen and Kandasamy 2008; Chen et al. 2018) were included (Figure 1b).

Tainan Harbor and Adjacent Coastal Sediments

Anping Harbor (Tainan Harbor) is the essential auxiliary port of Kaohsiung in southwestern Taiwan. Tainan Canal and Bamboo River are the two main water flow through the Tainan downtown to the harbor. Due to their poor sewer systems, domestic and industrial, e.g., metal processing, electronic and foundry, wastewaters are directly discharged into the canal and Bamboo River. All pollutants are eventually transported and accumulated within the Anping Harbor. Sediment data in the river mouths and interior of the harbor were collected from Chen and Liu (2013) and Dong et al. (2016) in this study (Figure 1c).

On the other hand, there are three other rivers, i.e., Erren River, Jhengwen River, and Yanshuei River, draining the Jianan Plain, where the Tainan City situated. In which, the Erren River is a severely contaminated flow with heavy metals and organic pollutants, mainly derived from the recycled electronic and aquaculture wastes. Thus, sediments along the Tainan coastline and the three riverine estuaries were acquired as well (Chen and Liu 2013).

Estuarial and Coastal Sediments

In addition to the sediments accumulated interior and exterior of the harbors, estuarial and coastal sediments were also included in this study. Five coastal and another five estuarial sampling sites along the coastline of western Taiwan were collected as the reference for comparison with sediments in the harbor systems (Figure 1a).

DATA ANALYSIS

Data analysis and figures, using statistical methods, were performed by R (version 3.4.1) in this study. To test the correlation between sediment characteristics (i.e., particle size, OM, and total grease) and heavy metal concentrations, Pearson correlation analysis was used. The enrichment factor (EF) and potential ecological risk index (RI) were applied to evaluate the degree of heavy metal contamination and their potential ecological risk, respectively. It should be noted that all the EF and RI data presented in this study were re-calculated by the heavy metal concentrations because of inconsistent reference values were applied in the selected literature.

The EF is carried out by normalizing the metal concentrations based on the geological characteristics of the sediments. It is defined as follows,

$$EF = \frac{(C_m/C_{Al})_{Sediment}}{(C_m/C_{Al})_{Crust}} \quad (1)$$

where C_m and C_{Al} are the metal and Al content in sediments or in the continental crust, respectively. However, some studies did not measure Al content of sediments, Fe content, replaced Al, will be used to calculate the EF ratios (e.g., Huang and Lin 1994; Lee et al. 1998; Lee et al. 2000; Chen et al. 2018). This is based on the fact that Al and Fe are abundant contents in the crust or sediments, and rather difficult to be influenced by human factors. The mean content of Hg, Cd, Cr, Cu, Pb, Zn, Al, and Fe in the continental crust applied in this study are 0.04 mg/kg, 0.1 mg/kg, 126 mg/kg,

25 mg/kg, 14.8 mg/kg, 65 mg/kg, 7.96%, and 4.32% (Wedepohl 1995, 1220), respectively.

The RI is defined as the summation of the potential ecological risk factors for metals (Hakanson 1980),

$$RI = \sum Er_m \tag{2}$$

$$Er_m = CF \times T_m \tag{3}$$

where Er_m is the metal potential ecological risk factor, CF is the contamination factor defined as the ratio of metal concentration measured in the sediments and background, T_m is the biological toxicity factor, i.e., 40, 30, 2, 5, 5, and 1 for Hg, Cd, Cr, Cu, Pb, and Zn (Hakanson 1980), respectively. In this study, the metal concentration of the continental crust was taken as the background concentration in the CF calculation.

RESULTS AND DISCUSSION

General Sediment Characteristics

The particle grain size and OM content are two critical factors affecting the heavy metal distribution in sediments (Hung and Hsu 2004; Chen et al. 2018).

Sediment characteristics of the collected observations by each group are summarized in Table 2. The results of particle size analyses reveal that the percentage compositions of clay (<2 μm), silt (2-63 μm), and sand (>63 μm) varied significantly within each sediment group, except for the sediments at the dumping sites (Figure 2). In fact, particle transportation and deposition are strongly driven by hydrological dynamics in the sedimentary environments. Taking Kaoping River, nearby the Kaohsiung Harbor (Figure 1b), as an example, the offshore sedimentation is mainly affected by the combined effects of longshore current, flood tide, and ebb tide (Liu 1999). As a result, the fine grain particles (clay) derived from the Kaoping River

are likely to be accumulated in the canyon, and the coarser particles (mud, <63 μm) spread in the lateral sides of the canyon and offshore of the coastline (Hung and Hsu 2004). Although our dataset covers a much broader study area, the data gets a similar pattern of particle size distribution in the surficial sediments as the above-mentioned Kaoping system. According to the boxplot of particle size distribution (Figure 2a-c), surficial sediments in the estuaries, harbor, offshore and dumping sites are dominated by silt, while the coastal sediments are mainly composed of sand. The fine grain particles, namely clay, range from 4.5 to 54% in the coastal sediments but exist <20% in the other sediments (Figure 2a).

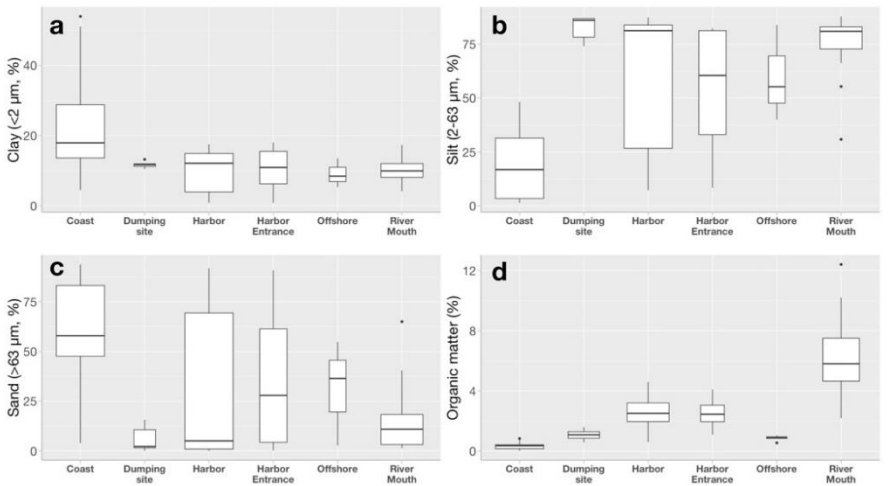

Figure 2. Distribution of particle grain size and organic matter in the sediments.

Table 2. Basic characteristics of collected sediments

Item	Offshore	Coast	Dumping site	Horbor entrance	Harbor	River mouth
Clay (<2 μm, %)	5.3-13.5	4.5-54.0	10.4-13.2	0.8-18.0	0.8-17.5	4.1-17.3
Silt (2-63 μm, %)	40.0-83.8	1.4-48.2	74.0-86.8	8.4-82.3	7.3-87.3	30.8-87.8
Sand (>63 μm, %)	2.7-54.8	3.9-93.8	0.0-15.6	0.2-90.8	0.0-91.9	1.4-65.0
OM (%)	0.55-1.05	0.02-0.84	0.67-1.60	1.10-4.10	0.6-4.6	2.2-12.4
TG (mg/kg)	N.D.	N.D.	N.D.	140-939	590-2314	899-4600

N. D. = No Data, OM = organic matter, TG = total grease.

The OM contents ranged from 0.02 to 12.4% in the surficial sediments (Table 2 and Figure 2d). However, the contents show significant heterogeneity among the sediment groups. The highest OM contents are found in the estuarial sediments, followed by the sediments accumulated in the harbor basins. While the OM contents in the coastal, and offshore sediments are minor (<1%). It is supported by the geochemical evidence of $\delta^{13}C_{org}$ and organic C/N ratios that continental input is the major source of OM to marine (Lai 2003, 104). The OM content usually enriches in fine grain sediments, hence has positive correlations with either clay (<2 μm) or mud (<63 μm, = clay + silt contents) (Hung and Hsu 2004) contents. Figure 3 shows the correlation between different particle grain size and OM contents, indicating that the OM distribution is correlated with mud content ($r = 0.46$, $p < 0.01$) in most of the sediments collected in this study.

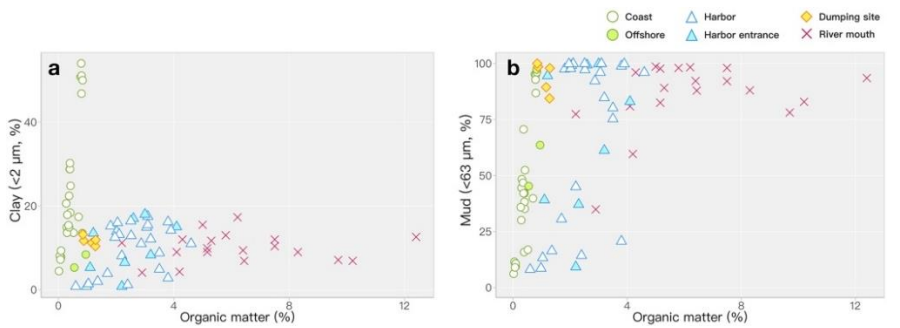

Figure 3. Correlation of organic matter and particle grain sizes in the surficial sediments.

Distribution of Heavy Metals in Sediments

Heavy metal concentrations in the bulk sediments range from 0.031 to 6.4 mg/kg for Hg, 0.006 to 2.4 mg/kg for Cd, 7.5 to 820 mg/kg for Cr, 0.14 to 766 mg/kg for Cu, 2.5 to 140 mg/kg for Pb, and 0.02 to 1900 mg/kg for Zn, respectively. Those metal contents vary from two to five orders of magnitudes, and the variabilities follow the order of Zn > Cu > Cd > Hg > Cr > Pb. Sediments metal contents by each group are shown in Figure 4. As

shown in the figure, the highest contents for the six metals are found in the estuarial sediments, followed by the sediments that accumulated in the harbors. Furthermore, the highest Cr content is in the estuarial sediments at the Anping Harbor, while the other five metals are found the highest levels in the estuarial sediments inside the Kaohsiung Harbor. In comparison with sediments in the estuaries and harbor basins, heavy metal contents are much lower in the coastal and offshore sediments.

Table 3. Pearson correlation coefficients among sediment characteristics and heavy metal concentration

Item	Mud	Sand	OM	TG	Hg	Cd	Cr	Cu	Pb
Sand	-1.00[a]								
OM	0.46[a]	-0.46[a]							
TG	0.25	-0.26	0.74[a]						
Hg	0.33[a]	-0.15	0.66[a]	0.54[a]					
Cd	0.34[a]	-0.23	0.66[a]	0.66[a]	0.77[a]				
Cr	0.35[a]	-0.18	0.36[a]	0.51[a]	0.26[a]	0.48[a]			
Cu	0.41[a]	-0.36[a]	0.76[a]	0.73[a]	0.53[a]	0.63[a]	0.47[a]		
Pb	0.51[a]	-0.50[a]	0.75[a]	0.81[a]	0.68[a]	0.74[a]	0.62[a]	0.75[a]	
Zn	0.25[a]	-0.21	0.61[a]	0.57[a]	0.84[a]	0.84[a]	0.31[a]	0.64[a]	0.58[a]

[a]Correlation is significant at the 0.01 level (2-tailed). OM = organic matter, TG = total grease.

Pearson correlation was performed to test the correlation between heavy metal concentrations and sediment characteristics (Table 3). Both mud and OM contents are positively correlated with the heavy metals. Apparently, it indicates mud and OM are essential carriers for river-borne metals. However, the correlation coefficients suggest that the six metals have moderate to high correlations with OM ($0.4 < r < 0.8$), but modest correlations with mud ($0.3 < r < 0.5$). Thus, OM, instead of particle grain sizes, is likely to be the first order control on the heavy metal distributions. Taking Cu and Pb as examples, Figure 5 presents the two metals have markedly different relationships with OM and clay contents. Only the coastal sediments have better correlations with sediment particle sizes, probably owing to fewer OM contents in the sediments (Table 4). In fact, this phenomenon is as a result of the metal speciation in sediments. Sediment

geochemical forms separated studies reported that OM is the important carrier for Cu and Pb (Chen et al. 2013b). Hence, sediment characteristics and the biogeochemical properties of the elements will influence the heavy metal distribution in sediments.

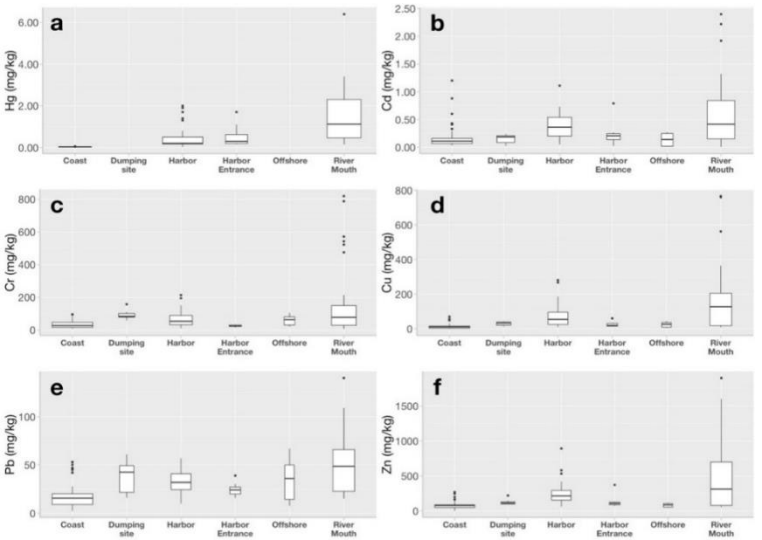

Figure 4. Distribution of the heavy metal concentration of the surficial sediments.

Table 4. Pearson correlation coefficients among the coastal sediment characteristics and heavy metal concentration

Item	Mud	Sand	OM	TG	Hg	Cd	Cr	Cu	Pb
Sand	-1.00[a]								
OM	0.86[a]	-0.86[a]							
TG	-	-	-						
Hg	-	-	-	-					
Cd	0.46[b]	-	-0.02	-	-				
Cr	0.84[a]	-	0.79[b]	-	-0.08	0.48[a]			
Cu	0.39[a]	0.15	-0.13	-	-0.30	0.47[a]	0.60[a]		
Pb	0.27[b]	-0.83[a]	-0.10	-	-0.59[b]	0.64[a]	0.42[a]	0.69[a]	
Zn	0.01	-0.15	-0.28	-	-0.28	0.53[a]	0.65[a]	0.79[a]	0.69[a]

[a]Correlation is significant at the 0.01 level (2-tailed). [b]Correlation is significant at the 0.05 level (2-tailed). OM = organic matter, TG = total grease.

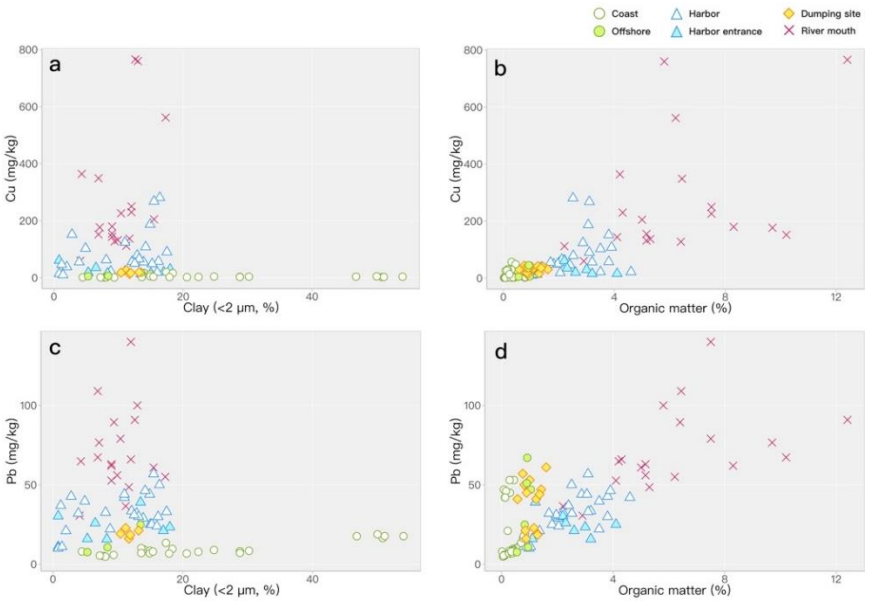

Figure 5. Correlation of heavy metals (Cu and Pb), fine grain particle content (clay, <2 μm), and organic matters.

Heavy Metal Speciation and Enrichments in Sediments

Numerous indices have been proposed quantifying for the degree of heavy metal contamination in sediments, i.e., EF, geo-accumulation index (I_{geo}, Müller 1981), and pollution load index (PLI, Tomlinson et al. 1980). The rationales for I_{geo} and PLI are the ratio of heavy metal concentration in sediments to the background metal concentration. Recall that EF is defined as the ratio of heavy metal concentration to the average metal concentration in the continental crust. Therefore, in comparison with EF, I_{geo} and PLI are more sensitive to the localized metal contamination, because of heterogeneous metal contents of uncontaminated sediments in different areas. In fact, published data for background metal concentrations (or metal concentration in uncontaminated sediments) is rather limited. We, therefore, present the EF values of the six heavy metals in this study to describe the level of metal contamination in the sediments (Figure 6). The EF values can

be classified into seven categories (Birth 2003): (1) no enrichment for EF < 1; (2) minor for 1 ≤ EF <3; (3) moderate for 3 ≤ EF < 5; (4) moderately severe for 5 ≤ EF < 10; (5) severe for 10 ≤ EF < 25; (6) very severe for 25 ≤ EF < 50; and (7) extremely severe for EF ≥ 50. As shown in the figure, the enrichment of Hg in the estuarial sediments are classified as the extremely severe level. Metal enrichment in the other sediments is classified between the levels of minor to very severe.

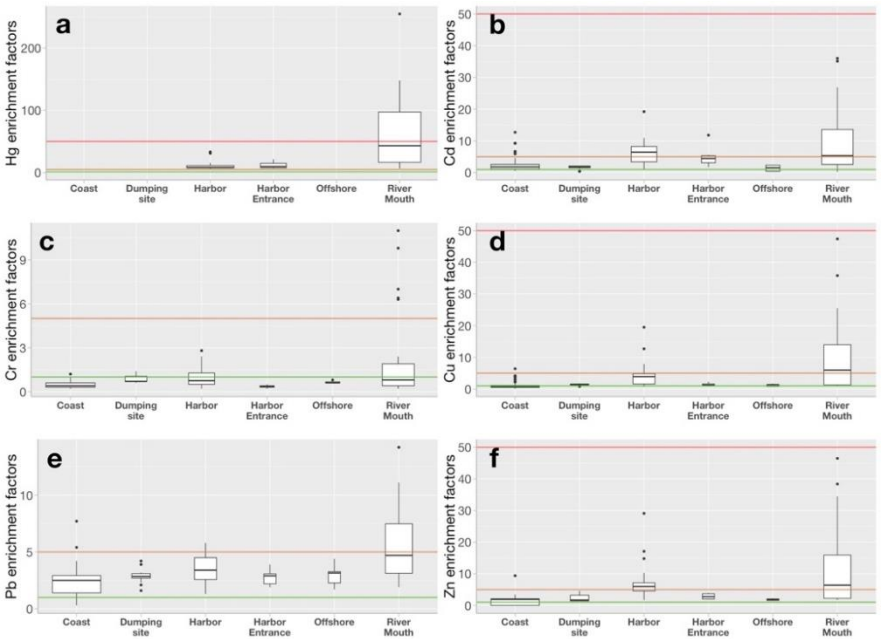

Figure 6. Distribution of the heavy metal enrichment factors of the surficial sediments. The horizon lines represent the EF values of 1 (green), 5 (orange), and 50 (red) for the classification of no, minor to moderate, moderate to very severe, and extremely severe metal enrichments, respectively.

Sequential extraction procedures (SEP), isolating different metal species among sorbent phases, can provide information regarding metal biogeochemical behavior (Yuan et al. 2004; Caplat et al. 2005; Li et al. 2007; Wang et al. 2010). Hence, application of SEP on sediments aims for

fundamental knowledge of metal speciations and mobility. Furthermore, metal EF values coupled with SEP information will shed some light on better constraining the heavy metal contamination in sediments. For instance, Hg is found the highest EF values in the estuarial sediments interior the Kaohsiung Harbor. SEP studies reported that Hg exists the highest relative level in the residual fraction (mainly silicate, 77.6~95.3%), followed by the OM fraction (3.8~14%), the Fe-Mn oxides fraction (0.7~8.0%), the carbonate fraction (<7.1%), and the exchangeable fraction (~0%) (Chen et al. 2013b). Probably due to the strong methylation of Hg with carbon, the OM dominates the non-residual fraction of Hg (Stumm and Morgan 1996). The preferential uptake of Hg by organic carbon is consistent with the high correlations between Hg concentration and OM content in sediments (Table 3). Accordingly, the OM may faithfully reflect the localized Hg pollution. It is reasonable that the flourish developments of petrochemical industry nearby the Canon River are considered as the primary Hg source delivered into the Kaohsiung Harbor.

In comparison with Hg, the other five heavy metals (Cr, Cd, Cu, Pb, and Zn) are relatively mobile, with higher percentages in the non-residual fractions of sediments in heavy metal polluted regions (i.e., carbonate, Fe-Mn oxides, and OM (Souch et al. 2001;Caplat et al. 2005; Li et al. 2007; Wang et al. 2010; Chen et al. 2013b)). The partition of metals in various particulate phases of the sediment is strongly affected by both of chemical and surface properties of the geochemical forms. Metals, e.g., Mn, Cu, Cd, Pb, and Zn, are easily adsorbed onto the surface of carbonates, followed by their incorporation into the carbonate lattices to form solid solutions of $Me_xCa_{1-x}CO_3$ (Billon et al. 2002). Fe-Mn oxides are known to be effective scavengers for many trace metals in estuarine waters (Danielsson et al. 1983; Hunter et al. 1988). Transition metals, e.g., Fe, Cr, Cu, Zn, and Mo, favorably adsorbs onto the surfaces of Fe-Mn oxides due to their large surface area (Trivedi and Axe 2000; Balistrieri et al. 2008; Pokrovsky et al. 2008). Organic matter is another critical factor affecting heavy metal mobility. Metal like Cu has the high affinity for organic components and easily forms stable complex formation with OM (Caplat et al. 2005).

Sediment SEP studies conducted in the Kaohsiung Harbor reported that metals of Cr, Zn, Cd, and Pb in the sediments mainly enriches in the Fe-Mn oxide fraction, followed by either the OM fraction or the carbonate fractions (Chen et al. 2013b). Indeed, there is no such systematic trend of heavy metal enrichment found in the sediment cores offshore mid-western Taiwan. Liu et al. (2013) reported comparable levels of some heavy metals in the Fe-Mn oxide and the carbonate fractions. Besides, this study further emphasized the consistent trend of increasing heavy metal contents in the two geochemical fractions in the severely polluted environments. Moreover, correlation analysis of the heavy metal distribution in estuarial sediments offshore southern Taiwan suggested no conclusive proof that Cr, Co, Ni, Cu, Zn, and Pb were bound to either carbonate or Mn-oxides. Instead of that, OM or other oxides are suggested to be more probable carriers for those metals (Yu et al. 2001). Although there is no SEP data in our dataset, the moderate to high correlations between heavy metal and OM contents implies that the OM is the essential factor influencing the metal distribution from the southwestern Taiwan estuary to the offshore area (Chen et al. 2007). Consequently, the relative proportions of geochemical components in sediments may strongly affect metal enrichment.

Potential Ecological Risk of Heavy Metals in Sediments

The potential ecological risk associated with the six metals in the surficial sediments is assessed using Er_m and RI index. Er_m and RI are used for evaluating the potential risk of one metal and combination of multiple metals, respectively (Hakanson 1980).

The Er_m is the product of metal contamination factor multiply the biological toxicity factor. Thus, Hg and Cr are the most significant elements having severe impacts on ecological systems. For better readability, we simplified the dataset to present the average Er_m and RI values of sediments in the two harbor systems. Figure 7 shows the RI values for the six metals in harbor sediments, and each stack in the bar chart represents the Er_m value of each metal. The Er_m values can be categorized into five classes of

potential ecological risk: (1) low risk for $Er_m < 40$; (2) moderate risk for $40 \leq Er_m < 80$; higher risk for $80 \leq Er_m < 160$; (4) high risk for $160 \leq Er_m < 320$; and (5) serious risk for $Er_m \geq 320$. Consequently, the Hg and Cd are classified as serious- and high-risk interior the harbors, respectively. On the other hand, the RI values can be categorized into four classes of potential ecological risk: (1) low risk for $RI < 150$; (2) moderate risk for $150 \leq RI < 300$; considerable risk for $300 \leq RI < 600$; and (4) very high risk for $RI \geq 600$. Except for the river mouth sediments inside the Kaohsiung Harbor, all the harbor relevant sediments have the potential ecological risks at moderate to considerable levels. It is not surprising that river mouth sediments interior the Kaohsiung Harbor has the most serious ecological risk, which is majorly contributed by Hg contamination. Figure 8 further presents the spatial distribution of RI values in the two harbors. Apparently, the highest risks are in the river mouths of Canon River and Love River, flowing through the largest petrochemical industrial zone in Taiwan.

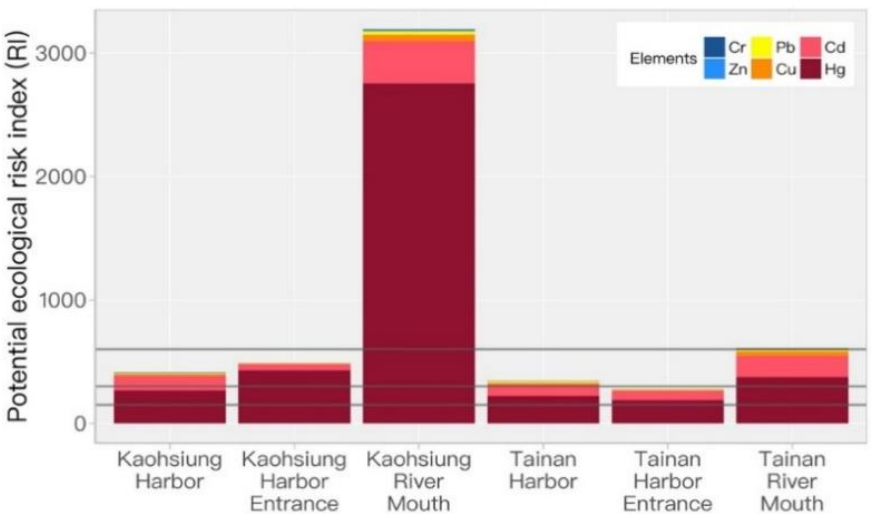

Figure 7. Distribution of mean potential ecological risk indices for the six metals in the surficial sediments of Tainan Aping Harbor and Kaohsiung Harbor systems. The horizon lines represent the RI boundary values of 150, 300, and 600 for low, moderate, considerable, and very high risk.

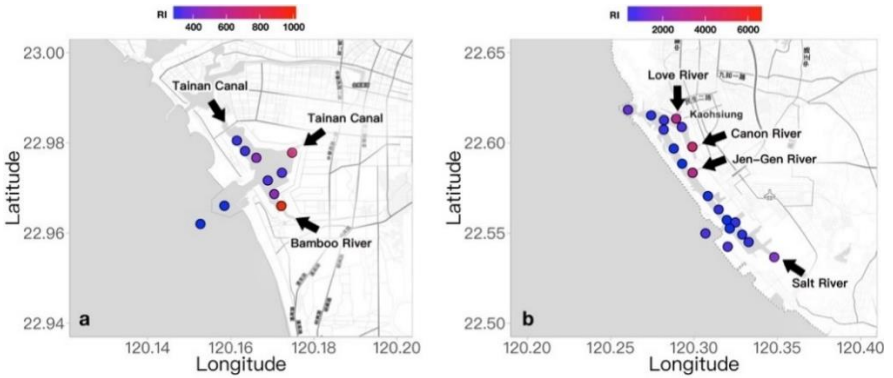

Figure 8. Spatial distribution of heavy metal associated potential ecological risk indices in the surficial sediments of (a) Tainan Anping Harbor, and (b) Kaohsiung Harbor.

CONCLUSION

In the present study, literature data on the sediment basic characteristics and heavy metal contents in southwestern Taiwan were summarized and re-analyzed using statistical methods. Surficial sediments in the estuaries, harbor basins, harbor entrances, coastal, and dumping sites were included in our dataset. Our data show that Hg and Cd are the most toxic metals in the sediments, especially in the estuarial environments. It is not surprising that heavy metal enrichment and potential ecological risk are found the highest level in the estuarial sediments, mainly attributed to the contaminated effluents, followed by the sediments accumulated in the interior of harbors. While, the metal enrichment and the associated risk are minor in the coastal, offshore, and dumping site sediments. Numerous SEP studies reported that the metal speciation in the sediment non-residual fraction, namely the OM, carbonate, and Fe-Mn oxide fractions, is strongly controlled by the chemical and surface properties of the geochemical forms. Indeed, two major features of heavy metal distribution were found in our dataset by the results of Pearson correlation analysis. For one hand, the concentrations of the analyzed heavy metals have higher correlations with sediment OM content, instead of particle size. On the other hand, the correlation between metal content and particle size is only validated in the coastal sediments, probably

due to very few OM contents in the sediments. Hence the OM content in the sediment may be the first order control on the six heavy metal distributions in southwestern Taiwan marine sediments. The re-analyzed dataset emphasizes the fact that the relative proportions of the geochemical fractions in the sediments are the indispensable factor influencing the heavy metal mobility and distribution in aquatic systems.

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Chapter 11

ND ISOTOPE EVOLUTION IN SEDIMENTARY MN/FE OXIDES: TRACING THE VARIATIONS OF WEST PACIFIC OCEANOGRAPHIC EXCHANGE DURING THE LAST 27KA

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ABSTRACT

The Nd isotopic ratios of ancient seawater deduced from sedimentary Fe-Mn hydroxides can be used to trace variations of terrestrial input or ocean circulation with a centennial time-scale resolution in high sedimentation rate regions. The Pacific Ocean plays an essential role in global ocean circulation and climate due to its volume and role as a potential carbon reservoir but received little attention compared with the

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Atlantic. Here we present the Nd isotope compositions in the Fe-Mn hydroxides from two marine cores in west Pacific during the past 27 Ka. These cores, MD972143 and MD012403 were collected from the Benham Rise in the western Philippine Sea and southern Okinawa Trough, respectively. For core MD012403, εNd values range between -10.2 to -7.8 and the range of εNd values of MD972143 are -3.0 to -1.8. They show similar down core variations in εNd, both display about 5 ε units of variation during the past 27 Ka. The similarity of the Nd isotopic variation in MD012403 and MD972143 reveals basin-wide ocean circulation change during the Last Glacial Maximum and the last deglaciation. The negative Nd isotope excursions shown in both cores suggested intensify of Antarctic Intermediate Water or increasing terrestrial input from continental shelf in the period of last glacial-interglacial transition. The lowest εNd values were detected at approximately 12 to 14 Ka after the LGM, which could be resulted from a high terrestrial input with less radiogenic Nd.

Keywords: Nd isotope, sedimentary Fe-Mn hydroxides, Pacific Ocean

INTRODUCTION

Neodymium (Nd) isotopic composition is generally expressed as $\varepsilon Nd = (((^{143}Nd/^{144}Nd)_{measured}/(^{143}Nd/^{144}Nd)_{CHUR})-1)\times 10^4$, where CHUR stands for Chondritic Uniform Reservoir with a present-day value of 0.512638 (Jacobsen & Wasserburg 1980). εNd in various rocks varies largely depended on Sm/Nd ratio and age, because ^{147}Sm decays to ^{143}Nd with a half-life of 1.06×10^{11} yr. Continental crust (with low Sm/Nd) has less radiogenic εNd values of -36 to -10; in contrast, mantle-derived igneous rock (with high Sm/Nd) has more radiogenic values, ranged from 0 to +10 (Goldstein and Hemming 2013 and references therein). The dissolved Nd isotope ratio of seawater is widely used as water mass tracer in the different ocean basins (Andersson et al. 2008; Amakawa et al. 2009; Basak et al. 2015; Stichel et al. 2012; Kazuyo et al. 2017). The Nd isotope signatures of seawater do not change with evaporation or particulate scavenging processes, but only by mixing of water masses or an external input of Nd with different isotopic ratios. Through river (i.e., suspended and

dissolved loads) and wind-driven (i.e., eolian dust) processes, Nd produced by weathering process is transported to the ocean (Frank 2002). Boundary exchange can also has an impact on the Nd isotopic composition of seawater at the continental margin (Lacan and Jeandel 2005). These unique features, together with mixing of water masses, determine regional seawater εNd in the ocean because the residence time (~600–1200 yrs) of Nd in the ocean is shorter than the ocean mixing time (~1500 yrs, Jeandel 1993; Tachikawa et al. 1999; Goldstein and Hemming 2013). For example, North Atlantic Deep Water has a narrow range of εNd values (-13 to -14, Piepgras and Wasserburg 1987; Lacan and Jeandel 2005), reflecting weathering of old shield material, while Pacific Deep Water (PDW) has an average value of -4 to -6 (Donald and Jacobsen 1988; Amakawa et al. 2004), as a consequence of water mass mixing and input of young volcanic material. As a result, seawater Nd isotopes are considered as quasi-conservative tracers for studying water-mass mixing. According to the previous study done by Amakawa et al. (2009), North Pacific Intermediate Water (NPIW) has εNd values of -5.3 to -2.7. The εNd values of Antarctic Intermediate Water (AAIW) range from -8 to -6, reflecting a mixture of Atlantic and Pacific waters at the source region. Below the intermediate waters, there are PDW and Antarctic Bottom Water (AABW). At the source region in the North Pacific, εNd values of PDW range from -5 to -3 (Amakawa et al. 2004, 2009), representing a mixture of AABW (with a εNd value of -8.1, Donald and Jacobsen 1988) and regional Pacific waters.

The Pacific Ocean plays an essential role in global ocean circulation due to its volume and role as a potential carbon reservoir, which, in turn, also has a significant climatic implication. Despite its importance, changes in intermediate/deep-water in the West Pacific during the last deglaciation have only received comparatively little attention compared with the Atlantic, partly due to poor preservation of marine carbonate in the Pacific sediments. The deficiency of well-preserved carbonate hinders paleoceanographic investigation on ocean circulation and ventilation in the past, because proxy reconstructions mainly rely on carbonate fraction

(e.g., foraminiferal ^{14}C age, $\delta^{13}C$ and Cd/Ca) in sediments. On the other hand, Nd isotopes in dispersed Fe–Mn oxide coatings in marine sediments can provide not only high-resolution sediment records. In this study we use Nd isotopic data retrieved from sedimentary Fe-Mn hydroxides to track the West Pacific hydrological variation in the past 27 Ka.

MATERIALS AND METHODS

Core Location and Age Model

Giant piston cores, MD012403(123.28°E, 25.07°N, 1420 m water depth; 36 m long) and MD972143 (124.65°E, 15.87°N, 2989 m water depth; 36 m long), was taken by RV Marion Dufresne in 2001 and 1997, respectively (Figure 1) during the IMAGES cruise. Core MD012403 is located on southern Okinawa Trough, penetrating down to the Last Glacial Maximum layer. The sediment are composed of gray clay and dark green silt and the depositional age of these sediments was determined by analysis of the radiocarbon content of planktonic foraminfera; so the $\Delta^{14}C_{org}$ at time of deposition can be estimated (Kao et al. 2005). Core MD972143 was collected from the Benham Rise in the western Philippine Sea. The coring site is above the carbonate compensation depth and near the Philippine archipelago; therefore the sediments consist mainly of olive-brown hemi-pelagic calcareous ooze with intercalated tephra layers of 1 – 15 cm thickness. The core top (0 – 0.12 m) is void and cracks occur between sub-bottom depths of 0.78 and 0.87 m. MD972143 has detailed age models derived from an astronomically-tuned oxygen isotopic stratigraphy(Horng et al. 2002; C. S. Horng et al. 2003).

Sample Preparation

Nd was extracted from dispersed Fe–Mn oxide coating on bulk sediments by a sequential leaching protocol, modified from Chester and

Hughes (1967), Piotrowski et al. (2004) and (Lugmair and Carlson 1978). Approximately 0.2 g dried bulk sediments were firstly leached with deionized water and pH-buffered (at pH 5) sodium acetate to completely remove residual salt and carbonate, respectively. The decarbonated samples were then treated with 0.02 M hydroxylamine hydrochloride (HH)-25% acetic acid for 2 h at room temperature to extract the Fe–Mn oxides fractions. The 1/5 of the HH-leached solution was set for Nd and Sm concentration measurements. The other 4/5 was dried down at 85°C and further processed with column separation for Nd isotopic analyses.

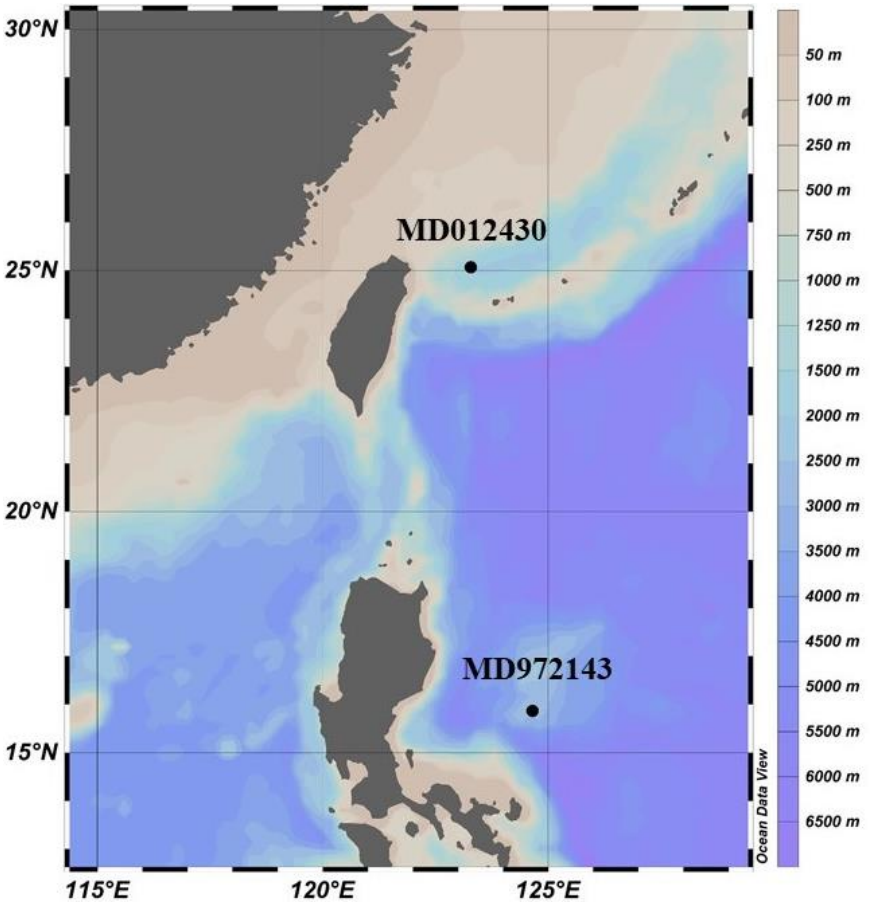

Figure 1. Locations of core MD012403 and MD972143.

Nd Purification

HH-extractions from the cored sediments were passed through conventional two-step column chemistry in preparation for the Nd isotopic analyses. Before column chemstry, Nd and Sm concentrations of the splits of the HH-extractions were analyzed on the Element 2 HR-ICP-MS (Thermo-Fisher) coupled to a desolvation system (Aridus, Cetac). The samples were diluted approximately 500 times with 0.3 N HNO_3 and analyzed at low resolution mode ($m/\Delta M = 400$). CeO^+/Ce^+ ratios were monitored in order to check the level of oxide formation during the course of measurements. Typically, CeO^+/Ce^+ were lower than 0.05%, which can significantly eliminate the potential spectral interferences. Quantification of the rare earth element (REE) concentration was achieved by external calibration using a set of gravimetric standards (High-Purity, Inc.). The uncertainty on our Nd and Sm analyses was assessed by running two international standard solutions of BHVO-1 and BCR2 The average analytical precision on Nd and Sm concentrations are better than ± 5% (2SD). Once the Nd concentrations were determined, an aliquot of HH-leached solution containing ~ 50ng of Nd was loaded to a first column with RE resin (50 - 100 mesh, Eichrom) and 3N HNO_3 as an eluent was used to separate REE from other HH-extraction matrix. After drying down at 85°C and re-dissolved in 0.2 N HCl, the REE fraction was then passed through a second column (Ln-spec resin, 100-200 mesh, Eichrom) to further isolate Nd from Sm and the other REE using 0.2 N HCl. Total procedure blank for Nd was < 15 pg and is negligible compared to the Nd (~50 ng) loaded into columns. The Nd recovery is better than 90%.

Nd Isotope Analyses

Nd isotopic analyses of the HH-leached solution were carried out in static mode on a Thermo-Fisher Scientific Triton TIMS installed in National Cheng Kung University, Tainan, Taiwan. Nd fractions after the column separation were dried down and re-dissolved in 1μl 0.2 N HNO_3, and then

loaded onto a 99.999% zone-refined rhenium filament (0.7 mm×0.04 mm, H Cross Co.) in the smallest possible increments. All filaments were outgassed in a vaccum chamber at approximately 1800°C for 45 min prior to use. A current of 0.5 A was continuously applied during loading. Once the sample had dried, the filament current was increased until the filament glowed dark red. This current was maintained for 5 s and then quickly reduced to zero. Generally, around 80 ng of Nd were loaded on the filament. Instrumental settings were carefully tuned to optimize stability and maximize signal intensity for each sample. Gain calibrations were run every day before starting the analytical session to correct for amplifier efficiency. For the Nd isotopic analyses, data were collected in 15 blocks, with 10 ratios per block and 4.196 s acquisitions per measurement. The measured $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$ for mass fractionation correction. International standards, La Jolla and JNdi-1, were run during each analytical session. The measured $^{143}Nd/^{144}Nd$ ratios for La Jolla and JNdi-1 were 0.511838 ± 0.000008 (2SD, n = 15)and 0.512104 ± 0.000007 (2SD, n = 15), respectively. These values are in agreement with the reported values of 0.511858 ± 0.000007 for La Jolla (Tanaka et al. 2000) and 0.512115 ± 0.000006 for JNdi-1 (Amakawa et al. 2009).

RESULTS AND DISCUSSION

Nd Isotopic Composition of Authigenic Fe-Mn Oxyhydroxide

Nd isotopic compositions obtained on the sedimentary Fe-Mn oxide are listed in Table 1. Figure 2 shows the seawater εNd record in Benham Rise and Okinawa Trough. In general, the Nd isotope of authigenic Fe-Mn oxide in Benham Rise sediment are more radiogenic than those of Okinawa Trough. For core MD012403, εNd values range from -10.2 to -7.8 and the range of εNd values of MD972143 are between -3.0 to -1.8. The principal first-order feature of the Nd data of Benham Rise is the shift from less radiogenic values (εNd ~ -2) at 25 Ka to more radiogenic values (εNd ~ 2) at 8 ka. They show similar down core variations in εNd, both display about

5 ε units of variation during the past 27 Ka. At the beginning of the last deglaciation, a significant negative shift of εNd, from -8.1 (~18 Ka) to a minimum value of -10.2 (~12 Ka), is observed in MD012403. This negative excursion of εNd values was followed by a subsequent increase from 10.2 to -7.8 between 11 Ka and 8.8 Ka. Such variations could be induced by three potential processes: (1) major changes in the εNd values of end-member water masses and/or changes in the relative contributions of water masses during the last 27 kyr; (2) a modification of the paleohydrography in deep-basins that are characterised by contrasting εNd signatures; (3) potential changes in seawater εNd values in the Phillipine Sea and East China Sea due to temporal variations in lithogenic Nd input from Asian rivers associated with variations in land-sea configuration and/or East Asian summer monsoon rainfall.

Table 1. Nd isotopic composition from Fe-Mn hydroxides of core MD012403 and MD792143

Sample ID	Core Depth (cm)	Calendar age (kyr BP)	$^{143}Nd/^{144}Nd$	εNd
MD012403 (Okinawa Trough)				
MD012403_01-07	15	0.29	0.512185 ± 09	-8.8
MD012403_01-43	97	1.34	0.512199 ± 04	-8.6
MD012403_02-22	199	2.56	0.512207 ± 05	-8.4
MD012403_02-66	299	3.76	0.512213 ±05	-8.3
MD012403_04-23	501	6.77	0.512219 ± 07	-8.2
MD012403_05-02	603	8.77	0.512239 ± 07	-7.8
MD012403_05-45	701	9.23	0.512213 ± 07	-8.3
MD012403_06-22	799	9.68	0.512171 ± 11	-9.1
MD012403_07-02	903	10.17	0.512151 ± 05	-9.5
MD012403_07-45	1001	10.63	0.512140 ± 09	-9.7
MD012403_08-22	1099	11.1	0.512117 ± 05	-10.2
MD012403_08-66	1199	11.8	0.512117 ± 06	-10.2
MD012403_09-45	1301	12.7	0.512183 ± 09	-8.9
MD012403_10-66	1499	14.4	0.512156 ± 05	-9.4
MD012403_12_22	1700	16.1	0.512196 ± 08	-8.6
MD012403_13-10	1822	16.9	0.512201 ± 08	-8.5
MD012403_13-66	1949	17.9	0.512216 ± 06	-8.2
MD012403_14-22	2000	18.1	0.512223 ± 11	-8.1
MD012403_15-01	2101	18.6	0.512220 ± 07	-8.2
MD012403_16-66	2399	20.3	0.512188 ± 06	-8.8
MD012403_19-01	2701	22.0	0.512198 ± 08	-8.6

Sample ID	Core Depth (cm)	Calendar age (kyr BP)	$^{143}Nd/^{144}Nd$	εNd
MD012403_21-10	3022	23.8	0.512193 ± 06	-8.7
MD012403_22-62	3291	25.3	0.512178 ± 06	-9.0
MD012403_24-66	3599	27.0	0.512192 ± 06	-8.7
MD972143(Benham Rise)				
MD972143_1-10	34	7.9	0.512729 ± 20	1.8
MD972143_1-12	38	10.0	0.512654 ± 08	0.3
MD972143_1-14	43	12.1	0.512595 ± 16	-0.8
MD972143_1-16	48	13.6	0.512486 ± 10	-3.0
MD972143_1-18	52	14.6	0.512624 ± 17	-0.3
MD972143_1-20	57	15.5	0.512620 ± 11	-0.4
MD972143_1-22	61	16.5	0.512609 ± 14	-0.6
MD972143_1-24	66	17.5	0.512626 ± 12	-0.2
MD972143_1-26	71	18.5	0.512628 ± 09	-0.2
MD972143_1-28	75	19.5	0.512640 ± 16	0.0
MD972143_1-30	80	20.5	0.512583 ± 14	-1.1
MD972143_1-32	84	21.5	0.512589 ± 10	-1.0
MD972143_1-34	89	22.4	0.512608 ± 09	-0.6
MD972143_1-36	94	23.4	0.512593 ± 12	-0.9
MD972143_1-38	98	24.4	0.512571 ± 12	-1.3
MD972143_1-40	103	25.4	0.512544 ± 11	-1.8
MD972143_1-42	107	26.4	0.512593 ± 09	-0.9

Variability in the εNd Signature of the Deep Water Flowing into the Western Pacific since the Last Glacial Period

It is crucial to establish the εNd values of the water masses circulating in the western Pacific before we can address these different scenarios. Recent studies have shown that that the εNd values of these water masses varied significantly in their areas of formation during the last glacial period compared to the Holocene (Horikawa et al. 2010; Noble et al. 2013; Hu et al. 2016). Besides that, the potential glacial-interglacial modification of their Nd isotopic compositions during their circulation along the wesern margin of the Pacific Ocean, also needs to be taken into consideration. Several previous studies suggested that the North Pacific Deep Water was likely produced in different areas and thus modified the seawater εNd values. Horikawa et al. (2010) have shown that NPIW εNd values, obtained from the authigenic fraction of sediments from a core located in the Bering Sea,

are more radiogenic (~ -0.8) during glacial times than they are during the Holocene (~ -2). But this can neither explain the Nd isotope date obtain from core MD972143 which featured higher εNd values during Holocene, nor the similar εNd values in MD012403 during Holocene and Last Glacial Maxmium (LGM). During the period of 27 to 18 Ka (LGM), seawater-derived εNd values obtained from HH-leached fraction of sediment in Core MD972143 range from -1.8 to -0.0 (Figure 2b) and show slightly increasing trend. This range is consistent with the ambient deep water Nd signature reported for the Upper Circumpolar Deep Water (UCDW) (between -0.7 and -4) (Grenier et al. 2013; Hu et al. 2016). At greater water depth (below 3000 m), present-day εNd values for Lower Circumpolar Deep Water (LCDW) are significantly lower (between -7.2 and -5.4) in the western equatorial Pacific (Grenier et al. 2013). Taking into consideration the fact that vertical mixing takes place in the Philippine Sea, changes in the relative contribution of UCDW and LCDW in the Philippine Sea are still not well established. In particular, potential reinforcement of the northward penetration of the UCDW during glacial times may have modified the latitudinal distribution of the εNd values in the South Pacific Ocean(Wu et al. 2017).

Glacial seawater εNd values extracted from Core MD012403 range from -9.0 to -8.1, similar to those of the late Holocene (-8.8 to -7.8) suggesting that εNd values of the UCDW that entered the Okinawa Trough during glacial times were quite similar to those of Holocene. During the early stage of the LGM, the negative Nd isotopic excursion indicates that AAIW intensified. This implies that glacial εNd values for AAIW in the western Pacific did not change significantly through time, at least not over the last 27 cal kyr BP. Other possible factor which may have caused the negative εNd excursion is the variation of sedimentary source. This will be further discussed in next section. The similarity of the Nd isotopic variation in MD012403 and MD972143 reveals basin-wide ocean circulation change during the LGM and the last deglaciation. However, more high-resolution seawater εNd record at the intermediate deep water depth is still necessary for in depth discussion of excursions during the deglaciation and its linkage with potential drastic climate changes in the region.

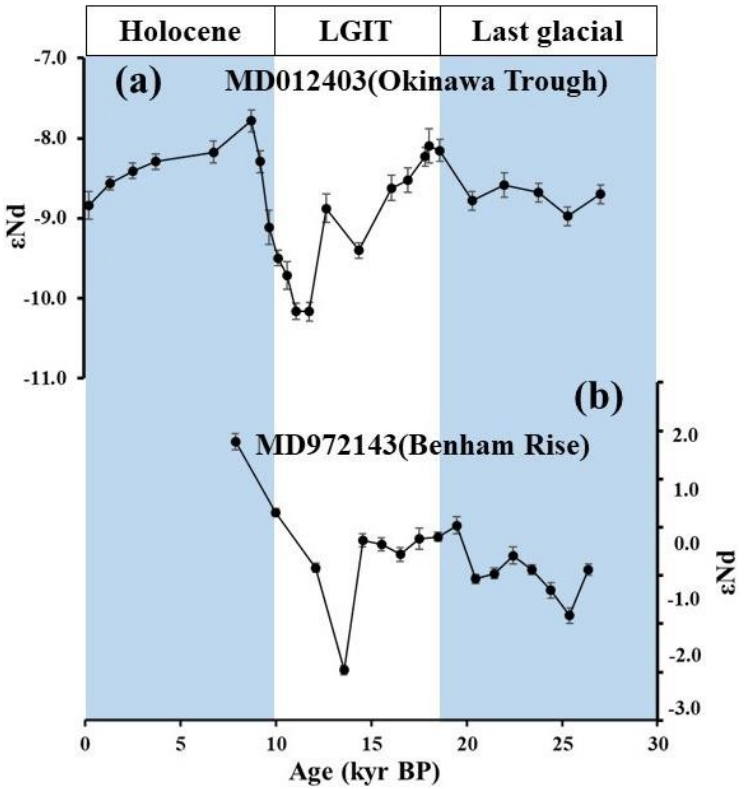

Figure 2. Nd isotopic record from (a) MD012403 and (b) MD972143.

Influences of Terrigenous Nd Input from Asian Rivers

At the present time, εNd values for the deep-water masses of the deep Philippine Sea similar and greater water depths (-4.4 to -3.6) (Wu et al. 2015) are similar to those of PDW. This suggests that the PDW is not modified via exchange processes with the unradiogenic sediments of the Luzon Arc. However, during glacial low sea-level stand, the land-sea configuration was drastically different in the northern South China Sea and freshwater and sediment discharge from Asian rivers could have modified the Nd budget in this region (Geyh, Streif, and Kudrass 1979; Hanebuth et al. 2000; Bird et al. 2007). The early Holocene record (10 - 8 Ka) of Nd isotope data obtained from MD972143 are more radiogenic (εNd = 0.3 -1.8) than those of

surrounding water masses (εNd ~ -4). The εNd values of MD972143 increased gradually from -1.8 to -0.3 since 25 to 14.5 Ka, indicating a possibly enhanced terrestrial input from Luzon volcanic arc. Grenier et al. (2013) showed that the εNd signature of modern UCDW is strongly modified during its northward penetration by "Boundary Exchange" with volcanic sediments on the western South Pacific margin at the present time. Since the sediment of Benham Rise is mainly derived from the volcanic arc of Luzon (Jiang et al. 2013) which has a εNd value of ~6. The boundary exchange processes at continental margin are believed to play significant roles at early Holocene.

Both down-core Nd isotope records in Fe-Mn oxide featured clear negative excursions in the period of last glacial-interglacial transition (LGIT). An increased input of terrestrial materials could shift the εNd value to a less radiogenic value. However, by examining the REE patterns of Fe–Mn oxyhydroxides obtained from this warm period, they did not show any characteristics of detrital fractions contribution. This result indicates that the HH-leaching protocol applied here would not significantly attack the detrital fraction of the marine sediments. In addition, following the mass balance calculations established by Gutjahr et al. (2007), the calculated deviation of εNd in Fe–Mn oxyhydroxides is always smaller than our analytical uncertainty, even the difference in εNd between seawater and detritus is greater than 15 ε unit. Thus, a potential artifact for authigenic Nd isotopes due to extensive leaching of detrital fraction can be ruled out. Another potential source of the Fe–Mn oxyhydroxide fraction is the "pre-formed" Fe–Mn oxyhydydroxides (i.e., terrigenous origin), which can be introduced by continental inputs and eventually deposited in the deep-sea sediments (Bayon et al. 2004). Any contamination from detrital and dust deposits could substantially influence the radiogenic eNd of marine Fe–Mn deposits (Bayon et al. 2004 and references therein). As had been shown by Bayon et al. (2004), a strong positive correlation between the pre-formed Fe–Mn oxyhydroxides and terrestrial inputs (fluvial and dust deposits) was observed in the marine sediment cores near continents. Therefore, it can be expected that the down-core eNd values in the HH-exactions would have been affected by the variations of the terrestrial input.

CONCLUSION

In the present study, we present the εNd values analysed on HH-extractions of sediment from the core MD012403 and MD972143. This high-resolution Nd isotope record enables us to investigate intermediate and deep-water circulation changes in the west Pacific Ocean since the last glaciation.

For core MD012403, εNd values range from -10.2 to -7.8 and the range of εNd values of MD972143 are between -3.0 to -1.8. They show similar down core variations in εNd, both display about 5 ε units of variation during the past 27 Ka. The similarity of the Nd isotopic variation in MD012403 and MD972143 reveals basin-wide ocean circulation change during the LGM and the last deglaciation.

The negative Nd isotope excursions shown in both cores suggested intensify of AAIW or increasing terrestrial input from continental shelf in the period of LGIT. The lowest εNd values were detected at approximately 12 to 14 Ka after the LGM, which could be resulted from a high terrestrial input with less radiogenic Nd. However, a significant time difference of excursion observed between the two cores needs further evaluation.

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Dr. Chee Kong YAP is an academician for more than 15 years in UPM and 20 years as a researcher, He has supervised more than 73 undergraduates and 30 postgraduate students (as a Chairman and Member of Supervisory Committee) in the fields of ecotoxicology, environmental biology, environmental sciences, water quality and ecotoxicological genetics. His research area is mainly focused on biomonitoring and monitoring of inorganic pollutants (heavy metals) in the aquatic environment using mollusks and sediments. He has published more than 254 papers in refereed academic journals, 2 books, 10 book chapters. Until January 2018, 179 of them have now been indexed in *Elsevier's Scopus* with an H-index of 22 (>1886 citations). He has also been invited in honorary as Editorial Board members for more than 20 international academic journals (Scopus) since 2010. In recognition of his scientific achievement and research outputs, his biography has been selected for inclusion in the *Marquis Who's Who in the World.*

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