Faculty of Engineering and Science

Ecological Risk Assessment of the Miri Coast, Sarawak, Borneo - A Biogeochemical Approach

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

A. Anandkumar.

A. ANANDKUMAR

04th May 2016

Dedication

To my parents

Mr. Arumugam and Mrs. Vimala

Well-wisher

Mr. Kannan and Mrs. Vanaja

Every challenging works needs self-efforts as well as guidance.

Thanks for your great support and continuous care.

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Frequently used list of abbreviations

AAS	Atomic Absorption Spectrophotometer
ADD	Average Daily Dose
APDC	Ammonium Pyrrolidine Dithiocarbamate
APHA	American Public Health Association
BB	Bungai Beach
BCR	The Community Bureau of Reference
BDL	Below Detection Limit
CASS	Coastal Atlantic Surface Seawater
CF	Contamination Factor
CRM	Certified Reference Material
DO	Dissolved Oxygen
EC	Electrical Conductivity
EC	European Commission
EDLs	Electrodeless Discharge Lamps
ESP	Esplanade Beach
EU	European Union
EUCR	European Union Commission Regulation
FAO	Food and Agricultural Organization
FDA	Food and Drug Administration
FLC	Fish Landing Centre
FSA	Food Standards of Australia
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
HCL	Hallow Cathode Lamp
IBMK	Iso-Butyl Methyl Ketone
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
I_{geo}	Geo-accumulation Index
KBE	Kualabaram Estuary
KPB	Kampong Baraya
LB	Lutong Beach
LULC	Landuse/land cover
MDL	Method Detection Limit
MFR	Malaysian Food Regulations
mg/L	Milligram per Litre

MPHT	Ministry of Public Health, Thailand
MPL	Maximum Permissible Limit
MRE	Miri River Estuary
ND	Not Detected
NE	North-eastern
NTU	Nephelometric Turbidity Unit
OC	Organic Carbon
ORP	Oxidation-Reduction Potential
PBC	Piasau Boat Club Beach
PCA	Pearson Correlation Analysis
PCA	Principal Component Analysis
POM	Post-Monsoon
PVB	Park Everly Beach
RAC	Risk Assessment Code
SEP	Sequential Extraction Procedure
SCS	South China Sea
SFR	Singapore Food Regulation
SPSS	Statistical Package for Social Science
STD	Standard Deviation
SW	South-western
TB	Tanjong Beach
TDS	Total Dissolved Solids
UCC	Upper Continental Crust
USEPA	United State Environmental Protection Authority
USFDA	Food and Drug Administration of the United States
UV-SPEC	Ultra-Violet Spectrometer
WHO	World Health Organization
µg/L	Microgram per Litre
µg/g	Microgram per gram

Abstract

Miri has a dynamic coastal environment mainly influenced by the Baram River. Intensive sedimentation from the Baram River and excessive trace metal loading by the Miri River are the significant environmental concerns in the study area. Thus, in order to make an ecological risk assessment, seawater, coastal sediment and aquatic organisms (fish, crabs, shrimp and bivalves) were collected along a 74 km stretch of the Miri coastal area during the monsoon (December 2013) and post-monsoon (June/July 2014) seasons. Standard protocols (APHA, USEPA and FAO methodologies and modified BCR sequential techniques were employed for the analyses of major ions and trace elements in the seawater, sediment and biological samples. Pearson correlation and factor analysis were employed to explain the reasons for observed variations in the trace metals content of various media.

The water column exhibited seasonal variations in its major ion composition and trace elements content. The physico-chemical parameters of the water column are agitated by the influence of the freshwater inputs from the Baram and Miri rivers apart from several other smaller streams. Pearson's correlation analysis revealed that the levels of all trace elements in the water column are controlled by Mn-oxides. Resuspension, desorption, complexation, sulphide oxidation and ionic interactions exert control over the concentration of trace elements in the seawater. Based on the granulometric analysis, the study area was divided into southwestern (SW) and northeastern (NE) segments. The NE segment is dominated by silt and the SW segment is dominated by fine sand. More than 80% of Cu and Zn concentrations are associated with the exchangeable fraction, which is readily bioavailable. A major source of these elements in the study area is from the natural weathering processes occurring in the river basin.

The total concentration of elements at the test sites was compared with the soil quality guideline values. Except for Cu and Zn, all remaining elements are below the acceptable limits. Based on the pollution indices viz., the geo-accumulation index and contamination factor, the coastal sediment samples are contaminated with Cu and Zn, and there may be a threat to local aquatic organisms, which was further confirmed by the RAC values. The LULC changes will have an impact on the trace elements accumulating in the

beach sediments. Since 1963, around 90% of the primary and secondary forest was reduced to 5% in 2014. Shoreline has shown a decadal cyclic reversal of erosion and accretion process.

Studies on aquatic organisms revealed that essential elements like Cu and Zn concentrations in their tissue organs are higher compared to other toxic metals such as Pb and Cd. Among the organs, the liver has accumulated a higher concentration of trace elements/metals followed by the gills, gonad, and muscles. The level of trace metals' concentrated in the muscles of aquatic organisms is low compared to the maximum permissible limits of the WHO (1989) and the Malaysian Food Standards (1985) on a wet weight basis. Thus, the aquatic organisms from the Miri coast are less toxic for human consumption, which is well supported by human health risk assessment indexes.

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Chapter 1 **Introduction**

1.1 Borneo: An Overview

Borneo is the world's third largest island situated between latitude 04°S to 07°N and between longitude 109°E to 114°E in Southeast Asia, and it is a tectonically complex region (Wilson and Moss 1999). This island is divided into three countries: Indonesia in the south consisting of 73% of the island; East Malaysia (Sarawak in the Northwest and Sabah in the Northeast) consisting of 26% and Brunei (1%) in the north. It has a tropical climate and provides a home to one of the oldest rainforests in the world; around 140 million years old (MacKinnon et al. 1996). The Borneo forest is an ecologically sensitive and fragile ecosystem due to deforestation activities. This island is surrounded by the South China Sea, the Sulu Sea, the Java Sea and the Celebes Sea. There are a number of large riverine systems throughout this island namely, the Kapuas (1143 Km), the Mahakam (980 Km), and the Barito (880 Km) situated in Indonesia; as well as the Rajang (560 Km) and the Baram Rivers (466 Km) situated in Sarawak state of East Malaysia (State-Planning-Unit 2015). Annual rainfall in this region varies between 3300 mm to 4600 mm/year with the highest rainfall observed between the December and March monsoon period (State-Planning-Unit 2015). The tributary system to the delta of the Rajang River is about 50,000 Km^2 and the monthly drainage-basin discharge is calculated to average about 3600 m^3/S but it fluctuates in the range of 1000 to 6000 m^3/S annually. Peat deposits occur in this river delta plain and is found to be 15 to 25 m thick (Staub et al. 2000).

The drainage-basin area, water and sediment discharges for the Baram River are 1.92×10^4 Km^2, 1445 m^3/S and 2.4×10^{10} kg/year respectively (Sandal 1996). The rainfall in the Baram basin is quite high, averaging 3225 mm annually and occurs throughout the year (Source: Jabatan Meterologi, Kuching, Malaysia). These two rivers play an important role in the discharge of freshwater and sediments from the upper elevations of Borneo, which can be clearly observed from satellite images. The Baram River (466 Km) is the second largest river in Sarawak, originating from the Kelabit Highlands and flowing westward and then northward through the tropical rainforest and drains into the South China Sea at the city of Miri through a single confluence point without any tributaries.

The Baram River's outlet is in the Kualabaram village near Miri city, which has a direct impact on the coastal area of Miri because it does not have a typical estuarine system due to the absence of any tributaries, whereas the coastal area of Miri itself exhibits the characteristics of an estuary. Due to the tropical rainforest conditions, land use changes and logging activities in the Upper Baram, the soil erosion rate is increasing. The delta of the Baram River basin is primarily covered with peat soils, which were formed thousands of years ago by geological processes. This contributes today to an increase in suspended solids and as has also been observed, a greater deposition of organic debris along the Miri coast. The maximum amount of deposition is noticed during the monsoon seasons between December and March. The Baram River also discharges a significant amount of nutrients loads from the numerous oil-palm plantation sites, into the South China Sea.

1.2 Miri City - Geographical Location

Miri City is one of the eleven administrative divisions in Sarawak and is the second largest city in Sarawak (Sarawak-Tourism-Board 2014). It is located in East Malaysia on the island of Borneo. It has a total area of 26,777.1 square kilometers and is the second largest division after the Kapit Division. Miri city is the gateway to northern Sarawak and is also close to the neighboring country of Brunei. It has a population of 300,543 (source: Department of Statistics Malaysia, census report, 2010) and has an area covering 978 sq.km. including a long coastline from the Baram River outlet in the north to Esplanade Beach in the south.

Miri city was the first city in Malaysia to develop a petroleum industry. The 'Grand Old Lady' was the first oil well constructed by Shell in 1910 and the discovery of petroleum played a significant role in Miri's initial economic development. Apart from the petroleum industry the other major industries in the area include timber processing, Ship building and oil palm plantation estates. There is also a growing tourism sector. Miri city is the hub of major industrial activities on the banks of the two major rivers (Baram and Miri) which runs through the city. The city contains major public sector industries such as the Sarawak Timber Processing Plant, and Miri port as well as private sector industries such as the Shin Yang shipyard, logging company, timber processing. During last three decades, industrial development has increased four-fold and has contaminated the land and marine environment in this region either directly or indirectly (Lau et al. 1996).

1.3 Climatic Conditions

Miri city has a tropical climate characterized by southwest and northeast monsoons, with semidiurnal tides and a temperature range of 23 to 32˚C. The annual mean rainfall in the study area varied from 2247 to 3499 mm between 1981–1990 (Avg. 2715 mm), 2228– 3265 mm for the period of 1991–2000 (Avg. 2682 mm), 2516–3267mm in 2001–2010 (Avg. 2916) and 3246-3125 mm through 2011-2013 (Avg. 3022) respectively (Source: Jabatan Meterologi, Malaysia, Miri). Due to the heavy rainfall in the upper Baram region, sediments and organic debris are washed from the deforested agricultural lands, mixed with the Baram River and finally drains into the Miri coast. An enormous amount of sedimentation has led to the creation of a Barrier Island in front of the Baram River and during the monsoon seasons, a heavy input of finer sediments and suspended particles builds up this Barrier Island and sand spit extending it southward (Nagarajan et al. 2015a).

Due to the formation of this sand spit, the ecological pressure was created in the intertidal region of the Miri coast. Freshwater influence, suspended solids and organic debris from the Baram River are diverted towards the southern Miri coast and with the help of littoral currents, are deposited on this shoreline which affects seawater quality of the Miri coastal region. In addition to natural influences, the presence of offshore oil and gas platforms near the Miri coast also adds additional stress and affects the seawater quality and aquatic organisms present on this coast.

1.4 Regional Geology

The geology of Sarawak has been divided into three distinct provinces: namely West Sarawak, Central Sarawak and North Sarawak. The North Sarawak region is located north and east of the Rajang-Baram watershed. The adjacent offshore area is named the Luconia Block (Hutchison 1989). This North Sarawak region is underlain by Neogene sediments of the NW Borneo Basin and the sediments are younging towards North and NNE with Oligocene base rocks. The North Sarawak region is underlain by thick sequences of shallow and deep marine sediments, such as sand and shale formations respectively (Liechti et al. 1960). The formations are Nyalau, Setap, Tangap, Sibuti, Belait, Lambir, Miri and Tukau and range in age from Oligocene to Pliocene. Among these, Nyalau, Belait, Lambir, Tukau and Miri Formations have formed under shallow marine to deltaic environments whereas the other formations are considered to have been deposited in open marine environments. This is based, among other things on the relative absence of planktic foraminifera's in shallow marine to deltaic sediments and their presence in the open marine environments. In the Baram Delta region of NE Sarawak, there was a very dramatic change in sedimentation from Setap shale to the very sandy Lambir Formation at the SE margin of the Lambir hills. The sediments of NW Borneo are mainly derived from Rajang-Croker accretionary prism, as a recycled source with some input from mafic-ultramafic rocks (Van Hattum et al. 2013; Nagarajan et al. 2014b; 2015).

Sibuti, Lambir, Tukau and Miri Formations covering the study area with numerous sea cliffs belongs to these Formations (Figure 1.1). Sibuti Formation mainly consists of shale with sandstones and minor limestones/marl limestones. Geochemically the lithology is classified as wacke, arkose, litharenites and quartz arenites with some marl limestone beds (Nagarajan et al. 2015). This Formation is underlined by the Suai Formation (fault contact) and overlain by the Lambir Formation along a conformable, abrupt boundary (Banda 1998; Hutchison 2005). Recently work in a muddy, carbonate ramp settings with a total thickness (80 m) was reported from an abandoned quarry near Kampong Opak (Nagarajan et al. 2015). The Sibuti Formation is folded gently to moderate and formed shallow anticlinal and synclinal folds (Wannier et al. 2011). Common fossils reported and observed from this formation are shell fragments, bivalves, gastropods, fossil crabs, corals, foraminifera and trace fossil burrows and minor fossils such as fish and shark's teeth, sand dollars, bryozoans, sea urchin spikes are also reported (Wannier et al. 2011; Nagarajan et al. 2015). The age of Sibuti Formation is Early Miocene to Late Middle Miocene (Hutchison 2005; Simon et al. 2014), and assigned as early Miocene based on the presence of planktonic foraminifera *globigerionoides obliquus* (Simmons et al. 1999), *florschuetzia levipoli* and *florschuetzia meridionalis*. The Sibuti Formation is time-stratigraphically equivalent to Setap shale Formation and termed Sibuti member of Setap shale formation (Hutchison 2005). However, lithogically Sibuti Formation is different from Setap Shale Formation (Hutchison 2005; Nagarajan et al. 2015) and also can be distinguished from the Setap shale formation based on high fossil content, predominant marl lenses and thin limestone beds. Concretions are common in Sibuti Formation and these concretions can be grouped into Mn-rich and Phosphate rich concretions (Peng et al. 2004; Nagarajan et al. 2015).

The Lambir Formation was deposited during the early Mid Miocene, based on the occurrence of the planktic foraminifers such as *Orbulina suturalis-Globorotalia (Turborotalia peripheronda)*. The Lambir Formation was deposited in deltaic and fluvial environments based on the interpretation of the different sedimentary structures (Yasin 1990). It consists of sandstones, shales and some limestones and are classified as shale, wacke, arkoses, litharenites, Fe-sands and quartz arenites based on their geochemical characteristics. Mineralogically sandstones of Lambir Formation mainly consist of quartz, illite/muscovite, and a minor amount of plagioclase whereas mudstones are dominated by quartz, illite/muscovite, amorphous phase, chlorite, plagioclase, and calcite. The limestone consists of calcite, ankerite, quartz, chlorire, illite/muscovite and a trace amount of aragonite (Nagarajan et al. 2016). The Lambir Formation is underlain by Sibuti or Setap Shale Formations and is overlain by the Tukau Formation. The Lambir Formation is dominated by sandstones with a number of cycles with hummocky cross-bedding at the basal part, whilst at the top the sandstone consists of low angle planar cross bedding indicates a beach depositional environment (Hutchison 2005). The sequence shows a distinctive shallowing upwards transition from marine to coastal conditions, associated with the change in orientation of the coastline and uplift of interior Borneo (Change from Cycle III to IV) (Hutchison 2005).The change in coastline orientation and uplift may have had an impact on the provenance of sediments deposited in the basin. Foraminifera, Ophiomorpha and coal laminations are observed within these sediments (Nagarajan et al. 2016).

Tukau sediments are exposed in the western part of Miri city and along the beaches, which extends inland. The basal part of Tukau Formation conformably overlies the Lambir Formation near Sungai Liku in the eastern Lambir Hill area, whereas it is conformably overlain by the Liang Formation near Miri. Wilford (1961) has studied the brackish water fauna from Tukau such as *Ammobaculites sp., Glomospira sp., Haplophragmoides sp.* and *Trachamiina sp*. and has suggested that these fossils cannot be used for age determination. The age of Tukau Formation is assumed to be Upper Miocene, to Lower Pliocene. The absence of foraminifers (except some brackish water forms), the presence of lignite layers and amber balls have lead Hutchison (2005) to infer that the Tukau Formation was deposited on a coastal plain. The Tukau Formation mainly consists of sandstones, shales and alternated interbedded shales and sandstones with minor conglomerates. Geochemically these sediments are classified into wacke; arkoses, litharenites and quartz arenites (the lower part of Tukau Formation; (Nagarajan et al. 2014b) and shales are reported in addition to the above sandstone types from the upper part of Tukau Formation (Nagarajan et al. 2016 In Prep). Mineralogically, the sediments of the Tukau Formation are dominated by quartz, clay minerals (illite is more dominant than kaolinite), feldspars and some heavy minerals such as tourmaline, zircon, rutile/anatase, chromian spinels, ilmenite, and pyrite (Nagarajan et al. 2014b). Pyrite concretions are common which are enriched by Fe, S, Ni, Mo, As and Nb compared to parent rocks and mineralogically these concretions are made up of pyrite, quartz, arsenopyrite, cattierite, goethite and berlinite (Nagarajan et al. 2014a).

The Miri Formation is geologically a very complex NE-SW elongated anticline, bound to the east by a steep NW dipping fault, known as the Shell Hill Fault. The downthrown block of the Shell Hill Fault is divided into a series of steep NW dipping additional faults and a series of flat SE dipping antithetic faults. Further to the east, and underneath the Shell Hill Fault, three NW dipping thrusts faults are present: the Canada Hill Thrust and the Inner and Outer Kawang Thrusts. The rocks exposed in and around Miri city, belong to the Miri Formation (Middle Miocene), and are the uplifted part of the subsurface, oil-bearing sedimentary strata of the Miri oilfield (Jia and Rahman 2009). Miri Formation is divided into Upper and Lower Formations, which consists of marine sandstone and shale alternations. The Upper Miri Formation is more arenaceous than the Lower Formation and consists of repeated and irregular sandstone-shale alternations, with the sandstone beds passing gradually into clayey sandstone and sandy or silty shale. The Lower Miri Formation consists of well-defined beds of sandstones and shales, with the shales slightly dominant. The sandstones vary from very fine grained, laminated, one-centimeter-thick tidal deposits, to medium-grained, massive cross-bedded or bioturbated shoreface and bar deposits; their lateral continuity is generally at the scale of the field. Seepage of crude oil from the faults zones is common during the rainy season.

The alluvial coastal plain can be observed along the shoreline of Miri coast and the alluvium Formation can be seen on the banks of the rivers in the study area. The shoreline areas near the Baram and Miri River are characterized by peat soils, mangrove, nipah, swamp forest and tidal inundation. As a result, of its composition and the tropical monsoon climate in central Borneo, erosion rates in this range have been amongst the highest in the World since the Eocene (Sandal 1996; Straub et al. 2012). The coast of Miri consists of well-developed sandy beaches, resulting from a strong SW longshore drift and relatively high offshore wave action.

The beaches in this region are dominated by sandy texture with open stands of *Casuarina equisetifolia*, coarse grasses and shallow swamps running parallel to the coast in most places. The Miri-Kualabaram highway, part of the Lutong beaches area, the Miri River estuary area, Marina bay and the Marriot Resort and Spa are protected by seawalls and breakwater structures to prevent wave erosion (DID 2009). Parts of the shoreline, such as the crude oil station in Lutong and the Tanjong Beach area are protected with groins. The purpose of these groins is to interrupt the water current flows and limits the movement of sediments. In some places (the Kualabaram River mouth and Tusan beach) wave erosion is commonly noticed during the monsoon (NE monsoon) season due to strong waves from the South China Sea, while sediment input from the Baram River is likely to be deposited all along the coast due to longshore currents as indicated by a low salinity regime prevailing across the coastal region (though there are seasonal variations).

Soils of the Miri Series are characterized by the presence of an albic horizon and a thick spodic horizon. The spodic horizon, which has an upper boundary between 50 to 100 cm from the soil surface is strongly cemented and has a chroma of less than 3 in more than 50% of its thickness. Soils of the Miri Series are commonly associated with soils of the Karamatoi Series (weakly cemented spodic) and the Buso Series (spodic < 50 cm and weakly cemented). All these soils have a humus-rich spodic horizon. Where iron content increases they may be associated with soils of the Silimpopon series (iron-rich, cemented spodic) (Soil-Profiles 2012). This region receives heavy rainfall and has a highly humid climate (Aggarwal et al. 2004).

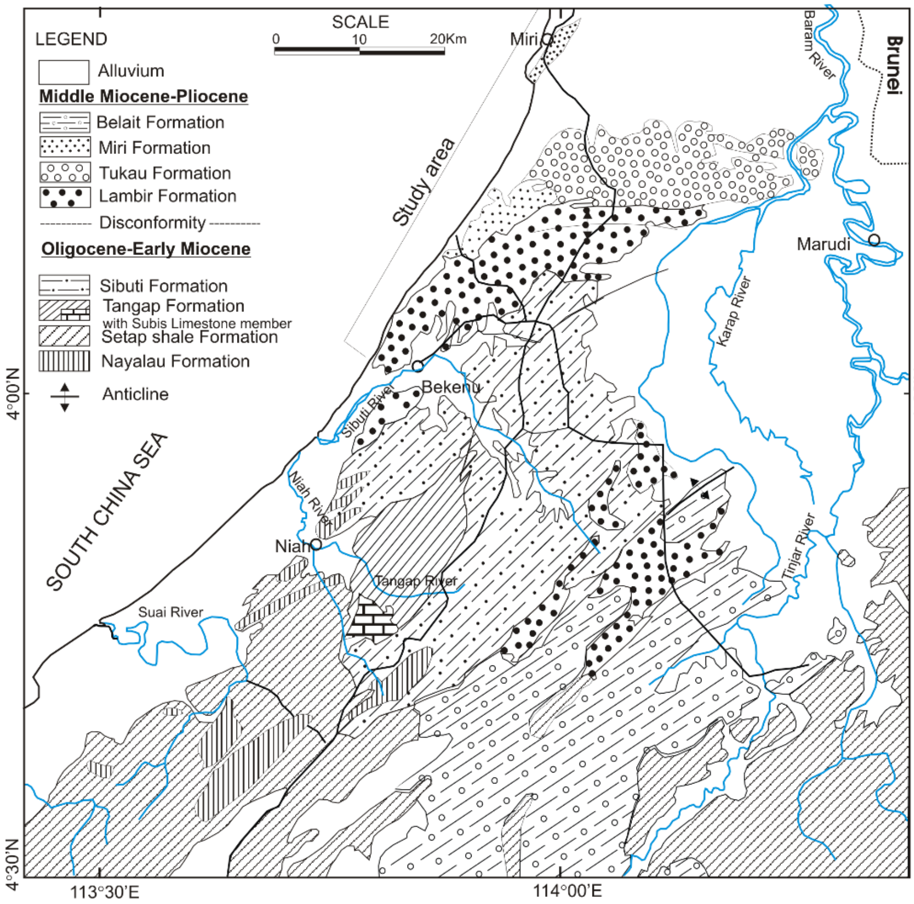

Figure 1.1 Geology map of the NW Borneo

1.5 Recent Developments

Human developments in the coastal zone have been rapidly increasing over the last several years due to the discovery of oil fields. Enormous developmental activities such as the construction of Marina Bay, luxurious residential complexes, a recreational waterfront area, ocean-view apartments, squatter houses along the Miri River and breakwater structures are some of the major man-made activities evident in the coastal area of Miri in the past few years. The major industries are located in the Kuala Baram area (north of the city), the Piasau Industrial Estate area (in the central part of the city), Krokop and close to the Miri River draining into the South China Sea near Luak Bay. Heavy and small-scale industries located all along the banks of the Baram and Miri Rivers contribute to the source of heavy metal pollution. Other industries such as fiberglass boat companies, concrete curling, tire industries, crude oil storage stations, ship building industries, timber processing mills and agricultural operations are commonly observed near the shoreline of the Miri coast. In addition, to these industries, several palm oil plantation estates and agricultural sites are located near the shoreline area of Miri. Previous studies also indicate that the beaches in this region are often vulnerable to oil contamination due to the presence of numerous oil platforms off the Miri coast as well as the movement of cargo vessels along the coast (Nagarajan et al. 2013).

A major contributor of untreated waste water comes from the squatter houses on the banks of Miri River. The untreated effluents released from these squatter colonies and industries either directly or indirectly flow into storm drains before reaching rivers and coastal waters (Tang and Lee 2010). After entering the coastal area, these pollutants cause harmful effects to aquatic organisms and affect the beach quality. The effluents released from these industries were observed through field visits and a survey program in and around the Miri coast (squatter colonies in the Miri River waterfront area and Permyjaya area; Lutong-Kualabaram Highway road). Most of the domestic and sewage effluents from squatter colonies in Pujut and Lutong areas mix directly with the Miri river (Mary 2014) and directly empties into the South China Sea.

1.6 **Deforestation**

Primary forests are destroyed by logging companies for timber production and for clearing the land to introduce rubber and oil palm plantations as a major commercial crop. Consequently, forest cover in peninsular Malaysia was reduced from around 73% in the early 1950s to ~51% in 1982 (Brookfield and Byron 1990). Logging is the main reason for deforestation in Sarawak, East Malaysia (Lambin and Geist 2008). After the primary forest has been cut and burned, the deforested lands are converted into a secondary use - oil palm plantations- which are commonly observed in and around Miri city. This land conversion process of cutting and burning, (clearing the forest by fire is a common practice in Borneo) leads to the release of metals along the Miri coast by atmospheric deposition. It has been observed clearly from several decades of satellite images, numerous acres of forest area have been converted into palm oil plantation sites in Borneo (Gaveau et al. 2014). Many deforested lands are situated adjacent to the Baram and Miri Rivers. The

Baram and Rajang Rivers contribute to the source of eroded sediments and suspended particles into the South China Sea (Utoomprurkporn and Snidvongs 1999). Siltation is an important source of marine pollution in Malaysia coming from both terrestrial and seabed areas (Chou 1994; Yap et al. 2002a). Siltation is mainly a result of inland mining of sand, land development in conjunction with deforestation particularly in the upper Baram region, harbor dredging which is clearly evident by the high turbidity in the Baram River, visible on satellite images of the area. In the upper catchment area of the Baram, rainfall is frequent all year which results in high rates of soil erosion in the deforested areas and particularly on steeply sloping land. This sediment runoff is carried by small streams which feed into larger rivers and finally drains into the South China Sea. In addition, inland soil erosion is caused by other types of human development, for example, an increased expansion of commercial lots and housing complexes in the Miri city area which increases sediment loads into coastal waters by higher runoff velocities (Tang and Lee 2010).

1.7 **Urbanization**

In an attempt to improve their livelihoods, people living in the highlands and rural villages have migrated to the Miri area. Most of the initial settlements by these new immigrants in this region were observed near the river banks and coastal areas. Upon discovery of oil resources in the early 19th century in Miri, there was an increase in migration from the rural areas which led to urban infrastructure developments all along the Miri coast. The construction of offshore oil and gas extraction plants and other industrial developments in the Miri region caused further degradation of the natural environment and resources along the coast. Previous studies also indicate that the drainage effluents and domestic sewage from the urbanized residential catchments of Miri, mix with storm water runoff and drain into the rivers and accumulates in the South China Sea, which leads to an increase in nutrient loading (Carrie and Darshana 2011; Carrie and Choo 2012).

1.8 **Tourism**

Miri city is rapidly becoming one of Sarawak’s most popular tourist destinations and is the gateway to many national parks such as Gunung Mulu National Park, Lambir National Park, Niah National Park and Loagan Bunut National Park. Beautiful beaches, exotic tropical rainforests, colorful coral reefs and underwater gardens are some of the attractions for divers and tourists from all over the world. Miri city has 12 diving spots which attract tourists to explore the beauty of underwater wonders Miri. Many areas of live coral are visible along the Miri coast (Jacqueline 2013). As the coastal areas are being developed, migration from the rural areas and neighboring countries have also increased. Inhabitants of local communities enjoy spending their leisure time on the beaches of Miri but, the beaches in this region are exposed to several types of pollution sources including both natural (riverine influence) and anthropogenic (offshore platforms) sources. Miri city is often marketed as "Resort city" and is a popular destination for seafood restaurants. The local population consumes significant amounts of seafood which is available all year. Since many beaches serve as tourist/recreation areas and seafood plays an important food source for local communities, concern about the environmental and ecological health of the Miri coast is justified.

1.9 Study area

The study area for the proposed research extends from the Kualabaram River mouth to Bungai Beach, which covers a coastline of approximately 74kms from end to end. This environment encompasses sandy beaches, rocky shores, sand dunes, cliffs and waterfront developed areas. All these tourist spots attract many local and international tourists. The study area (Figure 1.2) is classified into 10 beaches, A) Kualabaram Estuary, B) Fish Landing Center, C) Lutong Beach, D) Piasau Boat Club Beach, E) Miri River Estuary, F) Park Everly Beach, G) Tanjong Lobang Beach, H) Esplanade Beach, I) Kampong Baraya Beach and J) Bungai Beach. These study sites were chosen based on the connection between local communities and their interaction with the beach area.

1.10 Problem Statement

Due to an increase in logging activities in the upper Baram region, there has been an increase in erosion and sedimentation as well as the release of metals leached from shale. Deforestation and humification release humic and fulvic acids, increases the acidity of the soil condition and enables complexation and transport of metals bound to other organic surfaces. Soil acidification enhances the metal leach out process. Further, there is a deterioration of water quality by increasing sedimentation along the shoreline both due to industrial activities as well as natural input.

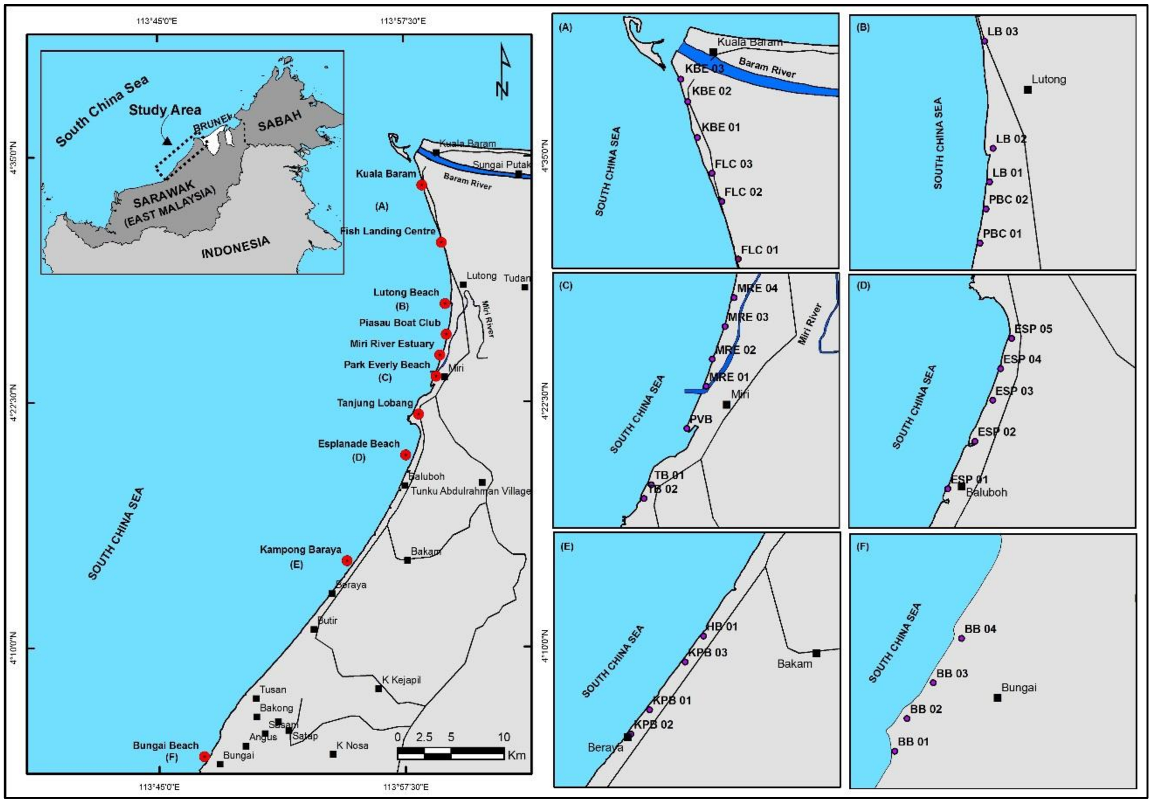

Figure 1.2 Location map of the study area showing the sample locations

How this continued erosion and sedimentation is going to affect the fragile marine ecosystem is unknown. Further, there is no baseline study to establish the background levels of various metals present along the Miri coast i.e. in seawater and marine life. Metal accumulation, remobilization and bioavailability are an important aspect of exploring the health of the coast. As analyzing the total metal concentration in the sediments does not provide a complete structure of the source and geochemical process of the environmental situation, sequential extraction and speciation studies are necessary to evaluate the ecotoxicological risk associated with the biota. If contaminated aquatic organisms are consumed this will cause severe and harmful health effects in humans, if quantities exceed the maximum permissible levels.

1.11 Aim

To investigate the comprehensive ecological risk assessment of trace element/metal contamination in the seawater, sediment and aquatic organisms of the Miri coast.

The Specific Objectives of this Study are as follows

1. To examine the degree of trace/heavy metal contamination, enrichments and potential toxicological significance in seawater, sediment and fish from coastal regions near Miri, based on international (The United States Environmental Protection Agency - USEPA) and Malaysian environmental guidelines.
2. To study the mobility and dynamics of operationally determined chemical forms of elements/metals in the surface sediments and their ecological risk on the biota through metal speciation studies.
3. To assess the environmental quality of seawater and sediments from the coastal regions of Miri using multivariate statistical analyses and to identify the major source of the pollutants.
4. To determine the uptake and bioaccumulation level of trace/heavy metals in commercially important marine life from the Miri coast.
5. To predict the shoreline changes and sediment deposit along the Miri coast based on Remote Sensing and Geographic Information System (GIS) to assess the coastal morphological changes and its impact on the coastal geomorphology.

The objectives of this research have been planned and implemented to determine the bioavailable toxic elements in seawater and sediments and their effect on marine life. Does the Baram and Miri River have any influence in controlling the seawater and sediment chemistry of the study area? If this coast is contaminated by trace/heavy elements, to what extent is it contaminated and is it necessary to know the current status and mobility of the toxic metals. These bioavailable (mobile) metals are easily accumulated in the aquatic biota and may cause harmful effects to other organisms and humans. So, is it essential to find out which sources, either natural or anthropogenic, are responsible for these elements in the water and sediment column? In addition, how are manmade and natural forces affecting the land use and land cover changes in the study area and what are the environmental impacts of these changes?

1.12 Significance of the Research

This is the first time, an integrated study have been used in order to address the geological processes controlling the coastal ecosystems of Miri, Sarawak. The linkage between the different compartments (seawater, sediments and marine biota) are well addressed by linking geological and biological processes between the sampled medium/compartments. Geochemical analysis of sediment samples through BCR sequential analyse facilitates the understanding of the bonding, mobility, bioavailability, fractionation and toxicity of trace/heavy metals from one medium to another. Geochemistry of sediments help to determine and evaluate the local sources of contamination and will also provide information regarding the critical sites in this coastal area. Outcomes acquired from testing commercial aquatic organisms provide invaluable information concerning the accumulation of trace/heavy metals in the organs of the fish as well as the potential risk from human consumption. Remote sensing and Geographical Information System offer detailed information regarding the shoreline changes made by human and natural forces over the past 50 years in order to determine the major events of erosion and accretion in the coastal area. A detailed study on a variety of marine species is supportive of the finding showing an accumulation pattern of toxic metals in the organs of the samples and is helpful in identifying the bioindicator marine species for metal accumulation and additional ecological monitoring studies. This information might be useful to the government and policy makers in order to sensitize the public on the accrued health risks of consumption of fishes and shellfishes collected from the coastal region of Miri. Also, since there was no earlier detailed study available, this study's data can be considered as a back ground values for the future environmental related studies.

1.13 Thesis Outline

The objectives above were addressed by targeting various insitu and laboratory experiments during the monsoon and post-monsoon season. In the following **Chapter 2**, a review of the literature was presented on various methodologies used for the extraction of trace/heavy metals in the seawater, geochemical extraction of trace metals in sediments and digestion protocols for aquatic organisms used at the international and national level are discussed in this chapter. **Chapter 3** describes the research methodologies applied in this study. It includes sample collection, storage, processing and analysis with the standard protocols employed in this study. Precision & accuracy, instruments used are discussed.

There is also a discussion on the effects of filtration techniques applied in this study and the results obtained from the physio-chemical parameters, as well as the differences in the ionic and nutrient variations in seawater for the monsoon and post-monsoon season. The analytical results using liquid-liquid extraction methodology for trace/heavy metal extraction from seawater samples for both seasons are reported in **Chapter 4**. The results of bioavailability and mobility of trace/heavy metals from the beach sediments using modified BCR sequential extraction techniques and the contamination of metals in different tourist beaches are discussed in **Chapter 5**. Statistical analysis of the results was carried out to study the correlation matrix and partition coefficient of trace/heavy metals in water and sediment column. This chapter also reports the soil quality assessment studies using contamination factor, a geo-accumulation index and the eco-toxicological effects based on ERM and ERL values.

Chapter 6 examines the effects of trace/heavy metals present in commercially available aquatic organisms such as fish, shrimp, crabs and bivalves. An inter-elemental correlation among the trace metals and the size of the aquatic organisms was carried out using statistical analysis. A comparison between the human health risk assessment and a hazardous index was also discussed. **In Chapter 7**, land use/land cover (LULC) effects in Miri city and the shoreline changes for the past 51 years were discussed. In addition, the findings of the study using remote sensing and geographical information system are discussed in this chapter. **Chapter 8** is a summary of the insights obtained from this thesis. Conclusions and recommendations for further research are also addressed in this chapter.

Chapter 2 **Literature Review**

This chapter provides a literature review on various methodologies used for the extraction of trace/heavy metals in the seawater, geochemical extraction of trace metals in sediments and digestion protocols for marine biota from national and international studies.

2.1 Introduction

Environmental pollution is one of the most important problems facing the world today. One of the responsibilities of the environmental scientist and geochemist is to focus on the toxicity of hazardous wastes released from natural and anthropogenic sources into the environment as well as documenting the impacts on humans and aquatic organisms from these toxic wastes. Numerous analytical studies have been carried out on natural water bodies, both freshwater and marine ecosystems, sediments and aquatic organisms to assess their environmental risks in these environments. In support of the aim and objective of the current research, a critical literature review was carried out to acquire information on various relevant aspects such as trace/heavy metals in the water, sediments and their accumulation in aquatic organisms. The evolution of extracting trace/heavy metals and their interaction between sediments and water columns, the various methodologies adopted, and risk assessment techniques for the environmental monitoring assessment studies are reviewed at both national and international levels ascertain the research gap in the proposed study area are then summarized in this chapter.

2.2 Outline: Environment Pollution

Environmental pollution is caused by the discharge of contaminants into the air, water or land, which may cause acute or chronic effects to the aquatic organisms and humans. Pollution occurs through metal corrosion, atmospheric fallout, soil erosion of metal ions from deforested land and other industrial sources. Trace elements/metals present in the water and sediment column enters the marine organism and humans by the process of the food chain. The dissolved and particulate form of metals easily enters into the aquatic organism through the process of respiration and the feeding mechanism. Figure 2.1 is a flowchart showing the role of trace/heavy metals in the environment from origin to accumulation in the tropical level of food and organism.

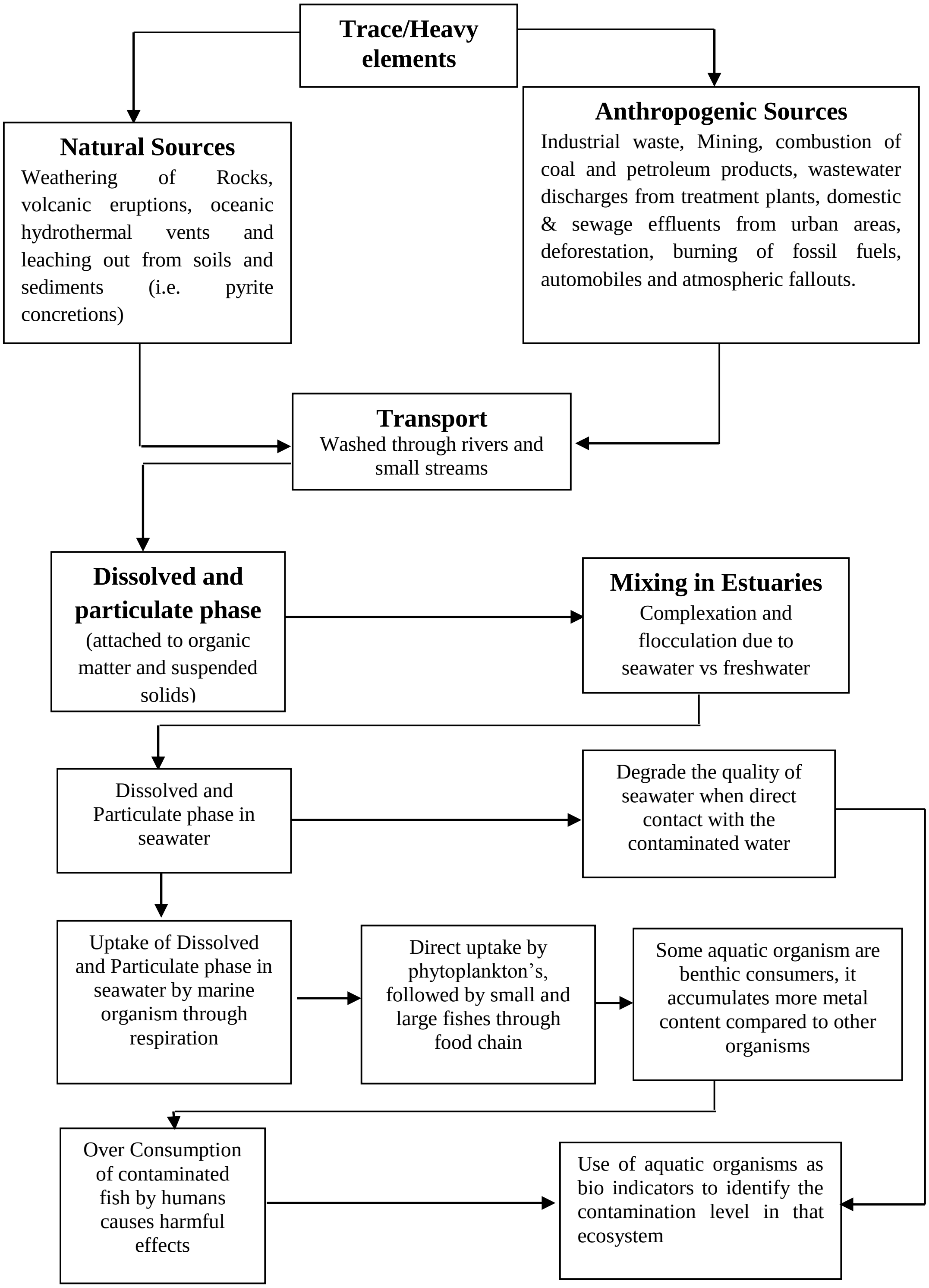

Figure 2.1 Origin, transport and accumulation of trace elements/metals in an ecosystem

2.3 Zones of Accumulation

According to Meyerson et al. (1981) there are three reservoirs in which metals may be accumulated in the marine environment (i.e.) seawater, sediment and biota. However, since the seawater are continuously exchanging due to tidal currents they cannot be considered as an accumulation zone. As a result, metals present in dissolved form must pass out to ocean except for a lesser amount which can be trapped as interstitial water and deposited in sediments. This leads the sediment and the marine biota as prospective zones of accumulation (Turner and Burt 1985).

2.4 Trace metals in Seawater: Global Scenario

Seawater is a chemically complicated system because many kinds of inorganic and organic chemical species are dissolved in it (Hirose 2006). The development of analytical techniques to observe trace metals in seawater was first refined in the 1970s and 1980s by (Boyle and Edmond 1975; Landing and Bruland 1980; Jones and Murray 1984; Kremling 1985). Trace metals exist in seawater as both dissolved and in particulate forms. According to Humborg et al. (1997) concentrations of trace metals can be modified regionally through volcanic activity, weathering of rocks, fluvial contribution and the geological nature of that particular study area. Hunter and Boyd (1997) suggests that trace metals concentration depends on the general physicochemical condition of the seawater (pH, salinity, redox and turbidity) and suspended particulate matter composition. Any investigation of dissolved and particulate trace metals in seawater is analytically challenging due to the low-level concentration in seawater and the potential interference of the matrix effect (Chen and Teo 2001) as well as other difficulties in the analysis process (Jiménez et al. 2002). This type of analysis requires special attention to collecting, filtrating and analyzing of trace metals concentration in seawater samples (Jan and Young 1978; Hunter and Boyd 1997; Crompton 2006).

Dittmar (1884) first reported the general composition of ocean water, which had been collected on an expedition around the world on the H.M.S. Challenger. In the 1920s, the process of analyzing physicochemical parameters and nutrients in seawater was developed. McKee (1928) introduced the determination of hydrogen ion, followed by Ball and Stock (1937) who measured the pH in seawater using a glass electrode. Nutrients (phosphate, ammonia, nitrite and nitrate), physicochemical parameters and major ions (sodium, potassium, calcium, magnesium) and the oxidation-reduction potential were investigated by Atkins (1923); Greenberg et al. (1932); Mitchell and Rakestraw (1933); Revelle (1934); Rakestraw (1936); Cooper (1937); Gripenberg (1937); Cooper (1938); Dietz et al. (1942). Before analyzing a group of trace metals, individual elements like arsenic, iron, manganese, fluorides and zinc in the seawater were first examined by Rakestraw and Lutz (1933); Thompson and Houlton (1933); Cooper (1935); Thompson and Wilson (1935); Atkins (1936); Webb (1938). During the 1950s, due to an outbreak of Minamata disease in Japan, the focus of investigating toxic metals in seawater emerged worldwide. The distribution of trace metals in seawater was studied for many years; however due to poor analytical techniques and unreliable sampling much of the published data was inadequate for understanding the role of these elements in the geochemical and biological cycles of the ocean (Brewer 1969).

During the 1970s, marine chemists imporved their understanding of the concentration, distribution and chemical behavior of trace metals in seawater. This was due to improvements in the advancement of modern analytical techniques and instrumentation developed in the 1970s. The investigation of trace elements/metals requires pre-concentration and separation before detection and there were many methods of preconcentration and purification processes proposed by the marine chemists in the 1970s. Different methods have been proposed to study seawater chemistry and to investigate the distribution and processes of trace elements/metals. Some of the case studies analyzing trace elements/metals in seawater from global ocean waters using different types of preconcentration and extraction methods are described in Table 2.1 to Table 2.5.

Table 2.1 Analysis of trace elements/metals in seawater from the global ocean waters using Chelating resins

Authors	Methodology	Findings
(Abdullah et al. 1972)	Extraction using chelating resins	Observed that due to anthropogenic inputs there was an increase in concentrations of Cd, Pb, Cu and Zn in the western coastal waters of England and Wales.
(Dassenakis et al. 1996)	Chelating resin columns and analyzed in FAAS	Trace metals were studied in seawater; sediments and particulate matter in the southern part of the Euripus Straits in central Greece observed a significant increasing trend in the analyzed metals due to the increase in anthropogenic sources.
(Wang et al. 2002)	Chelation method	Studied the heavy metals (Cu, Pb, Zn, Cd, Co and Ni) in coastal waters of Hong Kong and found that some locations recorded higher concentrations of heavy metals which were mainly derived from the vicinities of the study area.
(Censi et al. 2006)	Chelating resin columns	Evaluated the distribution of selected heavy metals (V, Cr, Co, Ni, Cu, Zn and U) in the NW Gulf of Thailand, observed the enrichment of heavy metals in SPM were mainly related to the lithogenic origin and an authigenic portion. V, Cr, Co, Cu and Zn showed an affinity for the colloidal fraction while Ni and U occured in the dissolved fraction.
(Wang and Wang 2007)	Chelating reagent and organic solvent extraction were used and analyzed in FAAS	Characterized the spatial distribution of dissolved Pb, Hg, Cd, Cu and As in the Bohai Sea. Examined the concentration of dissolved elements indicated decreasing values from the bays to central areas. Vertical distribution of all the dissolved metals was uniform except Hg as it showed an increased concentration towards depth. The input of pollutants from the land was the main influencing factor of dissolved metals.
(Al-Farawati et al. 2011)	Chelated resins and solvent extraction is used and analyzed in Cathodic stripping voltammetry	Dissolved Cu, Ni and Zn concentration in the coastal waters of Jeddah, eastern Red Sea were analyzed and observed; the increased concentration of Zn was due to industrial and human activities from sewage effluents.

Table 2.2 Analysis of trace elements/metals in seawater using carbamate, solvent extraction and ion-exchange method

Authors	**Methodology**	**Findings**
(Boyle and Edmond 1975)	Coprecipitation with cobalt-pyrrolidine dithiocarbamate and methylethyl ketone to extract from seawater and analyzed in FAAS	Analyzed Cu concentration in the surface seawater samples collected from the south of New Zealand, observed enrichment of copper is due to upwelling of Antarctic surface water and extension in the deep waters of the ocean.
(Danielsson et al. 1985)	Carbamate extraction	The concentrations of Cd, Cu, Fe, Ni and Zn were determined for 105 water samples from the NE Atlantic Ocean and observed that analyzed metals showed seasonal variations during the spring condition, it showed relatively high concentrations of Cd and Zn in the surface water.
(Díaz et al. 1990)	Pre-concentrated by complexing with APDC and extraction into freon-TF, followed by back-extraction and analyzed in AAS	Reported a baseline data for metal concentration (Hg, Pb, Cd, Fe, Ni, Cu and Zn) in the coastal waters of Santa Cruz de Tenerife, the Canary Islands and identified the source of seawater pollution using statistical analyses.
(Fileman et al. 1991)	Solvent extraction method and analyzed in GFAAS	Analyzed dissolved and particulate trace metals (i.e.) Mn, Fe, Co, Ni, Cu, Cd and Pb in surface waters over the Dogger Bank, Central North Sea and observed an elevated concentration of trace metals in both phases after an effect of the storm.
(Apte and Day 1998)	Solvent extraction and analyzed by GFAAS	Observed dissolved metal concentrations of Cu, Cd and Ni in the Torres strait and Gulf of Papua and identified the enrichment of these metals in the continental shelf area due to river input, which flows through a mining area, whereas in offshore waters these metal concentrations are close to background concentrations.
Udayakumar et al. (2011)	Solvent extraction	Analyzed the spatial and temporal variations in concentration of dissolved metals in surface waters off the southwest coast of India, identified enrichment of Cu, Zn and Ni due to anthropogenic influence.
(Zhang et al. 2015)	Preconcentration by ion-exchange method	Characterized the dissolved heavy metals Cu, Pb, Zn, Cr, Cd and As in the east and west Guangdong coastal waters, South China and observed metal concentrations varied spatially and seasonally due to anthropogenic activities.

Table 2.3 Analysis of trace elements/metals in seawater using direct analysis in ICP-MS

Authors	Methodology	Findings
(Accornero et al. 2004)	Filtered samples were directly analyzed in ICP-MS	The concentrations of some heavy metals (Zn, Cu, Mn, Pb, Ni and Cd) were measured in surface coastal waters of the southern Adriatic Sea and found to be low compared with Italian and Mediterranean coastal areas. Observed that Pb and Cd in the study area derived from atmospheric inputs and other elements from harbor and river outlets.
(Manfra and Accornero 2005)	Direct determination in ICPMS	Analyzed heavy metals (Zn, Cu, Mn, Pb, Ni and Cd) concentration in coastal marine waters of the central Mediterranean sea, observed metal enrichment is due to industrial and domestic effluents.
(Cuong et al. 2008)	Directly analyzed in ICP-MS	Identified the vertical profiles of heavy metals in the water column of Singapore's coastal environment, showed an enriched concentration of metals in the bottom water compared to the subsurface water due to the biogeochemical cycling processes associated with gravitational settlement and decomposition of dead organic matter.
(Padhi et al. 2013)	Filtered samples were directly analyzed in ICP-MS	Observed the seasonal and temporal distribution of dissolved trace metals (Co, Cd, Cr, Mn, Cu, Ni, Pb and Zn) in the coastal waters of Southwestern Bay of Bengal, India and the values were lower than the background values. Metals were primarily regulated by in-situ regeneration and remineralization.

Table 2.4 Analysis of trace elements/metals in seawater using DPASV technique

Authors	Methodology	Findings
(Benon et al. 1978)	Differential pulse anodic stripping voltammetry (DPASV) technique	Investigated Cu, Pb, Cd and Zn in the seawater collected from the Gulf of Fos, France near Marseilles. Observed the metal source comes from the numerous industrial and urban activities.
(Mart et al. 1982)	Differential pulse anodic stripping voltammetric (DPASV) technique	Made a comparative study of heavy metals (Cd, Pb, Cu, Ni and Co) in offshore and coastal areas of western Mediterranean and the North Sea to prove the influence of pollution sources along the shoreline.
(Fowler et al. 1984)	Differential pulse anodic stripping voltammetric (DPASV) technique	Analyzed chemical speciation of dissolved and particulate trace metals (Cu, Zn, Cd, Hg and Pb) in the coastal waters of the Gulf and Western Arabian Sea and observed that water samples collected nearby the industrial area and port area showed a higher concentration and are influenced by anthropogenic sources.

Table 2.5 Analysis of trace elements/metals in seawater using Liquid-liquid extraction method

Authors	**Methodology**	**Findings**
(Govindasamy and Azariah 1999)	APDC – MIBK extraction procedure by Brooks et al. 1969 and analyzed in FAAS	Analyzed seasonal variation of heavy metals in coastal waters off the Mahabalipuram and Pondicherry coast and identified direct discharge of industrial and sewage wastes into the coastal region and runoff by monsoonal rainfall are responsible for the increase in metal concentration in the study area.
(Selvaraj 1999)	Liquid-liquid extraction method and analyzed in ICP-AES	Analyzed total dissolvable Cu and Hg concentrations in inner shelf waters, off Kalpakkam, Bay of Bengal, India and observed bottom waters show higher concentrations of the analyzed metals, due to anthropogenic input from the coastal industries.
(Beltrame et al. 2009)	APDC-IBMK extraction	Studied dissolved and particulate heavy metals distribution in coastal lagoons, Argentina. Observed large input of heavy metals due to intensive agriculture and drainage basin system of the study area.
(Jonathan et al. 2011)	Liquid - liquid extraction method	Analyzed the concentration of dissolved trace metals (DTMs) in beach water and acid leachable trace metals (ALTMs) in sediments indicated that the enrichment of metals due to anthropogenic sources and increased tourist activities at the crowded beaches at Acapulco, Mexico.

2.4.1 **Review on National Scenario**

Several researchers (Shazili et al. 2006; Yap et al. 2009; Suratman et al. 2009; Othman et al. 2012; Lim et al. 2012; Soo et al. 2014) studied the impacts of water quality in Malaysia but focused mostly on the freshwater ecosystems compared to coastal environment. (Dragun et al. 2009; Yunus et al. 2011; Yap and Pang 2011; Lim et al. 2012; Idriss and Ahmad 2012) suggested that due to rapid population growth, urbanization and industrialization have contaminated the land and the aquatic environments in Malaysia. (Mohamed 1993; DOE 1998) observed domestic sewage, palm oil mills, rubber factories, industrial wastewater and piggeries are the principal contributors of pollutants in the estuaries/rivers/seas of Malaysia. The rivers of Malaysia are mainly polluted by industrial wastes, which subsequently pollute the coastal environment as rivers act as carriers of pollutants. Meanwhile, the Ministry of Environment (1995) reported two out of three rivers in the country are polluted, which subsequently carry a significant amount of pollutants from the interior to the sea.

Only a few studies were focused on trace metals in seawater compared to studies of trace metals in sediments and aquatic organisms due to the much lower trace levels in the open ocean (Jiménez et al. 2002; Shazili et al. 2006). Some researchers have addressed the quality of coastal water either based on general geochemistry or through microbial analysis (Law and Othman 1990; Ichikawa et al. 1999; Ibrahim et al. 2003; Hamzah et al. 2011; Praveena et al. 2011). Yap and Pang (2011) assessed water quality in the Malaysian coastal waters by using multivariate analysis from the southern coast of Peninsular Malaysia and found that Ni and Pb were the major dissolved metals in some selected sites due to anthropogenic input. Ngah et al. (2012) and their research group monitored the marine pollution trend on tourist beaches of Peninsular Malaysia from 2000 to 2006 and reported total suspended solids (TSS), E.coli and trace/heavy metals such as Pb, Cd and Cu were above the safety standards set by DOE in 1998.

The higher levels of these trace/heavy metals are mainly derived from land use development in the coastal zone, untreated domestic waste effluents and oil spill incidents. Shazili et al. (2006) stated that in Malaysia, numerous studies on trace metal analysis in both dissolved and particulate form have concentrated on freshwater bodies and estuarine systems but very few studies have focused on metal concentrations in seawater due to the greater difficulty in measuring the metals at ppb levels. According to Adiana et al. (2014) their database, which was collected from www.scopus.com, from 1968 to 2012, showed less than 10% of all studies on heavy metals have been focused on the southern part of the South China Sea (SCS). The determination of dissolved and particulate form of trace metals in Malaysian coastal waters are listed in the following Table 2.6.

Table 2.6 Analysis of trace elements/metals in seawater from the Malaysian coasts

Authors	Methodology	Findings
(Utoomprurkporn and Snidvongs 1999)	Solvent extraction method and analyzed in GFAAS	Studied trace metal concentration in dissolved and particulate form off coastal waters from Sabah, Sarawak and Brunei, identified the increase in vertical profile of Cd near offshore drilling platforms and high concentrations of Cu, Pb, Ni, Fe, and Cd might have derived from the riverine inputs and the variation in spatial distribution of metals was due to the effect of local littoral water currents and wind patterns from the Indonesian archipelago.
(Adiana et al. 2011)	Chelex 100 resin columns and analyzed in ICP-MS	Analyzed Cd, Mn and Pb in the water column from the South China Sea off the South Terengganu coast, Malaysia and observed all metals were measured in dissolved phase but the dominant amount was recorded in the particulate phase.
(Looi et al. 2013)	Filtered samples were directly analyzed in ICP-MS.	Analyzed the metals concentration in tropical estuaries and coastal waters along the Straits of Malacca. Detailed measurements were made on Physico-chemical parameters, major ions and metal concentrations of the water samples and revealed that pollution sources originated from anthropogenic and minerals-related activities.
(Praveena and Aris 2013)	APHA, 1995	Conducted a baseline study in tropical coastal waters off Port Dickson, Malaysia. Examined the physicochemical characteristics and nutrient concentrations varied due to tidal variations.
(Sany et al. 2013)	Filtered samples were directly analyzed in ICP-MS	Identified the temporal and spatial distribution of heavy metals (As, Cd, Cr, Cu, Ni, Pb, Hg, and Zn), in water and in sediments of Port Klang, Malaysia. The main sources of heavy metal in Port Klang were industrial wastewater discharge and busy port activities.
(Adiana et al. 2014)	Chelex 100 resin columns and analyzed in ICP-MS	Analyzed the effects of northeast and southwest monsoon on trace metal distribution in the SCS off Peninsular Malaysia, observed higher levels of particulate metals in the deeper water samples during the monsoon season as a result of resuspension of bottom sediments and an increase in the metal concentrations in the study area due to anthropogenic activities.

Several researchers (Everaarts and Swennen 1987; Ismail et al. 1993; Lim et al. 1995; Yap et al. 2002b; Shazili et al. 2006; Suratman et al. 2009; Sany et al. 2013; Udechukwu et al. 2015) have concentrated on the total metals content associated with water, sediment or biota in the Peninsular Malaysia. Nevertheless, (Yunus et al. 2011; Yap and Pang 2011; Lim et al. 2012; Idriss and Ahmad 2012) focused on selected elements like Cu, Cd, Pb and Zn and concluded anthropogenic activities and effluent discharges through rivers were the main sources of trace metals in the coastal waters of Malaysia. (Utoomprurkporn and Snidvongs 1999; Adiana et al. 2011) examined higher levels of metals were noticed in the intertidal regions, and spatial distribution studies and established the level of dissolved trace metals in the offshore samples was nearly equal to the normal background level concentration, whereas in a particulate fraction the metal level was higher compared to the dissolved form.

The summary from national and international studies in seawater falls into two main areas of discussion. Firstly it traces the concentration and distribution of trace/heavy elements in seawater are controlled by several processes such as delivered by river sources, wind-blown dust, volcanic eruptions, hydrothermal vents and circulation at mid-oceanic ridges. Secondly it describes the numerous methods adopted by current investigators and any bearing this may have on the comparison of results. According to Benner (2002) most of the dissolved organic matter in seawater is 40-60 µM in the surface water, which has not yet identified. The concentration of bioactive trace metals (Cu, Zn and Fe) in the order of nM or less in the open ocean. The chemical speciation of trace inorganic and organic constituents in oceanic water samples has been studied for more than four decades, (Sillen 1961; Dyrssen and Wedborg 1974; Stumm and Brauner 1975). Until the 1970s, the subject of study had been confined to the interaction of metal ions with inorganic ligands, such as halogens, carbonate and hydroxide. However, these studies on inorganic speciation are evidently insufficient to understand the ecological roles of trace metals in the marine environment. The purpose on chemical speciation is to clarify the chemical forms of trace metals in seawater and their controlling processes from both chemical and geochemical aspects.

Some authors (Karbassi et al. 2008; Stolpe and Hassellöv 2010; Jung et al. 2012) studied only the total metal content, but the particulate phases are frequently separated by filtration at 0.45µm. These studies focused only on the dissolved trace metals but haven't explained the elements bind with suspended particles/particulate forms. Trace elements in other forms such as adsorbed species onto clay minerals, Fe/Mn hydrous oxides and colloids cannot be considered to be in truly dissolved form – as these are considered to be carrier phases for the trace elements. When samples were filtered using 0.45µm filter, almost half of the trace elements associated with the colloids were lost. Elements associated with these colloidal and suspended particles may have a higher chances to affect the health of the aquatic organisms through the respiration process and filter feeding mechanism. Hence, the present study aims to find the mobility and bioavailable toxic trace metals in sediments and their accumulation in aquatic organism, a 11µm filter is considered for the filtration process (due to greater suspended particles in seawater from the riverine influence) the filtrate includes the elements associated with dissolved as well as colloidal form which have the ability to accumulate in the marine biota.

2.4.2 Analytical Methods

Preconcentration techniques such as using ammonium pyrrolidine dithiocarbamate (APDC) and isobutyl methyl ketone (IBMK) extraction (Brooks et al. 1967; Koirtyohann and Wen 1973) which was later modified by Botté et al. (2007). Carbamate extraction (Danielsson et al. 1978), solvent extraction (Landing and Bruland 1987; Martin et al. 1990), extraction onto chelating resin columns (e.g. Chelex -100, 8-HQ chelating resin) (Riley and Taylor 1968; Kingston et al. 1978; McLaren et al. 1985; Obata et al. 1993), liquid-liquid extraction (Mentasti et al. 1989; Malvankar and Shinde 1991; Jonathan et al. 2011), ion-exchange techniques (Abdullah et al. 1976; Bae and Murray 1998), co-precipitation (Morse and Arakaki 1993; Vircavs et al. 1994), sorption on various adsorbents such as activated carbon (Gupta and Chen 1978; Sugasaka et al. 1981; Soylak et al. 1997), electrochemical deposition (Batley and Matousek 1980), Amberlite XAD resins and other sorbents (Soylak et al. 1996; Ramesh et al. 2002), cloud point extraction (Mesquita da Silva et al. 2000; Chen and Teo 2001; Safavi et al. 2004) and solid phase extraction (Narin and Soylak 2003) have all been extensively applied with reference to seawater analysis.

2.4.3 Improvement in the Instrument facilities

In most of these separation methods, the analytes retained on the column and resins are eluted with the matrix mixtures of HNO_3 and HCl, and then followed by trace elements/metals quantification using an atomic absorption spectrometer (AAS) or a graphite furnace atomic absorption spectrometer (GFAAS) or an inductively-coupled plasma mass spectrometer (ICP-MS). The most common method today of trace metals analysis in seawater involves the combination of one of the above techniques with GFAAS. The first reliable method of direct analysis of seawater for some of the trace metals (Fe, Mn and Zn) by GFAAS was proposed by scientists in the 1980s (Sturgeon et al. 1979; Berman et al. 1980; Beauchemin and Berman 1989). In the last two decades, online column preconcentration processes have been introduced by amending the previous standard procedures using recently developed chelating resins and these resins have higher affinity for metal ions (Beauchemin and Berman 1989; Dressler et al. 1998; Hirata et al. 2001; Karami et al. 2004; Lohan et al. 2005; Rahmi et al. 2007; Sohrin et al. 2008; Lee et al. 2011).

These modified methods are to allow trace element analysis with a simpler procedure using the latest advances in instrument facilities. But the direct determination of metals in seawater samples by FAAS, ICP-OES or ICP-MS is not always possible due to matrix interferences and very low concentrations of elements/metals. Therefore, (Danielsson et al. 1982; Wells and Bruland 1998; Hirata et al. 2001) suggested a pre-concentration/separation step is the best approach for trace element analysis in seawater even though the elements are present in low concentrations. For studying the speciation of trace elements in seawater, the differential pulse anodic stripping voltammetric (DPASV) technique is used worldwide and is one the oldest techniques being used successfully today (Forsberg et al. 1975; Hasle and Abdullah 1981; Donat and Bruland 1990; Muller 1996; Locatelli and Torsi 2002; Economou 2010; Ensafi et al. 2010; Zhuang et al. 2011).

2.4.4 Advantages of Liquid-liquid extraction method

"Liquid-liquid extraction is widely used as a pre-treatment technique for separation and preconcentration of both organic and inorganic analytes from aqueous samples" (Pena-Pereira et al. 2009). This technique is the most extensively studied and widely used for the analysis of trace elements/metals in seawater in FAAS. According to Komjarova and Blust (2006), this traditional ammonium pyrrolidine dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) agents in liquid-liquid extraction method showed excellent results for a multiple-elemental analysis. In the present work, based on the instrument facilities available locally and to overcome the difficulties of detectability of FAAS in the analysis of trace elements/metals using complexation with APDC and IBMK, for the separation and preconcentration, the liquid-liquid extraction procedure for the analysis of trace elements/metals in the seawater was chosen. This extraction method was also chosen because it minimized the problems of contamination and loss of analytes.

As there is little data and few baseline records available on trace metals content in the coastal water system of Miri, establishing an extensive background study on dissolved and particulate forms of trace metal concentration in the seawater is required to determine their origin as well as the differences among the seasonal variations (monsoon and post monsoon seasons) along the coast of Miri. Since the Miri offshore region is a vital source for Malaysian Oil production as well as an important destination for tourism in Sarawak, the data on trace metal concentration and the quality of seawater should be monitored regularly. Thus, the aim of the present study is to provide information on geochemical process, background value concentration, seasonal variation, partition coefficient of metals between sediment and water column and possible sources of metal contaminants along the Miri coast.

2.5 Trace/heavy metals in Sediments: Global Scenario

According to Krauskopf (1955) the level of trace and heavy metal concentration is always greater in sediments compared to the water column. This is due to adsorption of cations by organic matter in the sediment layers. The presence of contaminates and the water quality of a system, is reflected in the sediments because metals which were bound to sediment particles are released back into the water column by changes in the environmental conditions such as pH, redox potential, acidification and an increase in organic ligand concentration (Förstner 1985). Therefore, sediments and soils can be regarded as either a sink or a source for trace metals in the aquatic environment which may lead to bioaccumulation of toxic elements in the organisms through the food chain and cause adverse health effects to human (Salomons and Förstner 1984; Gleyzes et al. 2002).

Calmano et al. (1993) suggested in an aquatic ecosystem, trace/heavy metals are distributed amongst various aquatic compartments such as water, sediment, suspended solids and biota and generally occur in dissolved or particulate forms. The majority of metals may be partitioned onto particulate matter by several mechanisms such as clay minerals, particle surface absorption, co-precipitation, Fe-Mn oxy/hydroxides, complexation with organic substances (e.g. humic acids), ion exchange and biological materials (e.g. algae and bacteria). According to Gibbs (1973) there are five phases in which trace/heavy metals are associated with sediments 1. Bound to Exchangeable, 2. Bound to carbonate phase, 3. Bound to reducible phase, 4. Bound to organic matter and sulphides and 5. Bound to residual phase (detrital). The scattering of trace/heavy metals in different phases of sediment indicates different behaviors with respect to the changing environmental conditions i.e. their mobility, toxicity and bioavailability (Tessier et al. 1979; Salomons and Förstner 1980; Rauret et al. 1988; Szefer et al. 1995). Thus, to study and provide the complete picture of environmental contamination, analyzing total metal concentration is not a suitable measure because it does not necessarily reflects its bioavailability to living organisms. Hence, identification of trace/heavy metals in various phases helps to determine the geochemical processes controlling the concentration of sediments and to evaluate their eco-toxic potential and the risks induced. The case studies conducted in various coastal environments using different sequential extraction protocols are discussed in Table 2.7 to Table 2.9.

Table 2.7 Speciation of trace/heavy metals using 5 stage extraction technique

Authors	Methodology	Findings
(Kiratli and Ergin 1996)	5 stage sequential extraction and analyzed in FAAS	Distributions of heavy metals Fe, Mn, Co, Cr, Ni, Cu, Zn and Pb and their chemical partitioning were studied in oxic and anoxic surface sediments obtained throughout the Black Sea. Higher concentrations of Fe, Co, Ni, Cu, Zn and Pb were associated with oxidizable fraction and this phase was the major carrier for the anoxic basin.
(Sáenz et al. 2003)	5 stage sequential extraction and analyzed in GFAAS	Analyzed speciation of heavy metals in recent sediments of three coastal ecosystems in the Gulf of Cadiz, Southwest Iberian Peninsula, identified metals enriched through mining activity (pyrite) and industrial sources.
(Takarina et al. 2004)	5 stage sequential extraction and analyzed in ICP-AES	Analyzed the geochemical speciation of heavy metals Cr, Cu, Ni, Pb, Zn, Fe and Al in the coastal sediment of Semarang, Indonesia. Observed that the coast was contaminated by Cr, Pb and Ni due to the Babon river influence.
(Wang et al. 2010)	5 stage sequential extraction and analyzed in FAAS	Investigated the distribution and speciation of Cd, Cu, Pb, Fe and Mn in shallow marine sediments from Jinzhou Bay, China, observed the sediments had several folds contaminated due to nonferrous smelting activities. Cd concentration showed 39% to 61% in exchangeable fractions.
(Alomary and Belhadj 2007)	5 stage sequential extraction and analyzed in ICP-OES	Analyzed distribution of bioavailability of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in Algerian Mediterranean Sea sediments. The concentration of heavy metals was lower than the Upper Crust value, however, some sites were affected due to anthropogenic activities. The order of bioavailability of heavy metals studied was Pb > Cr > Cd > Ni > Zn > Cu > Fe.
(Olu-Owolabi et al. 2013)	5 stage sequential extraction and analyzed in FAAS	Analyzed bioavailability and mobility of As, Cd, Cr, Fe, Mn, Ni, Pb and V in sediments collected from crude oil prospecting zone in the coastal area of Ondo state, Nigeria. Sediments in this area and river mouth showed higher bioavailability and toxicity risk than other sites.
(Fernandes and Nayak 2014)	5 stage sequential extraction and analyzed in FAAS	Investigated the concentration, distribution and speciation of metals (Fe, Mn, Cu, Pb, Co, Zn and Cr) in sediment cores of intertidal regions along Mumbai coast, India. Metals showed good correlation with grain size and organic matter. Metals were higher in residual fractions and posed a low risk to biota except Mn.

Table 2.8 Speciation of trace/heavy metals using BCR sequential extraction technique

Authors	Methodology	Findings
(Yuan et al. 2004)	BCR sequential extraction and analyzed in ICP-MS	Analyzed 12 elements in the marine sediments from the East China Sea. The concentration of V, Cr, Mo, Sn, Fe, Co, Ni, Cu and Zn were high in residual fraction, while Mn, Pb and Cd content were in non-residual fractions. Top soils showed an increase in the concentration of elements and suggested reducing the anthropogenic discharges in this region.
(Ianni et al. 2010)	BCR sequential extraction and analyzed in ICP-OES	Analyzed total content and speciation pattern of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in coastal and off-shore sediments from Ross Sea (Antarctica). Only Cd and Pb were present in significant amounts in non-residual fraction and thus, bio-available to benthic organisms.
(Okuku et al. 2010)	BCR sequential extraction and analyzed in ICP-MS	Analyzed Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn in the sediment samples collected from the East African Coast. Results of sequential extraction indicates the metals are natural in origin. Only Cd, Co and Mn were more concentrated in labile fractions, whereas 62% of Fe and Zn were present in residual fraction and less bioavailable to the organism.
(Qiao et al. 2013)	BCR sequential extraction and analyzed in ICP-OES	Studied distribution and speciation of heavy metals (Cd, Cu, Zn, Mn, Ni, Co, Cr and Fe) in sediments from the coastal area of Shantou Bay, China which underwent rapid urbanization. Cadmium, Zn and Mn were observed in an acid-soluble fraction, Cu and Pb in organic matter and reducible fraction respectively and Co, Cr, Ni and Fe are associated with residual fraction. PCA analysis revealed that heavy metals in non-residual fractions due to anthropogenic sources.

Table 2.9 Speciation of trace/heavy metals using modified BCR sequential extraction technique

Authors	Methodology	Findings
(Rivaro et al. 2005)	Modified BCR sequential extraction and analyzed in ICP-OES	Observed speciation of heavy metals (Fe, Mn, Cr, Ni, Cu, Cd, Pb and Zn) in marine sediments of Albanian coast. Except for Fe, Cd, and Zn all remaining elements were present in the labile fractions due to mining and industrial wastewater discharge and riverine inputs.
(Morillo et al. 2004)	Modified BCR sequential extraction and analyzed in GFAAS	Identified the speciation of heavy metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Mn) in marine sediments from the southwest coast of Spain. Zn, Cd and Cu concentration were greater in exchangeable fractions and this was due to the river influence. Higher percentages Fe, Cr and Ni were found in residual fraction.
(Cuong and Obbard 2006)	Modified BCR sequential extraction and analyzed in GFAAS	Analyzed chemical speciation of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in coastal marine sediments from two coastal regions of Singapore. Except for Cd, all remaining metals showed high percentages in acid-soluble fraction due to anthropogenic discharges and runoff from the city of Johor.
(Alshemmari et al. 2012)	Modified BCR sequential extraction and analyzed in ICP-OES	Analyzed speciation of trace metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) in marine sediments from Sulaibikhat Bay, Kuwait. Observed metals were greater in residual phase compared to acid leachable phase. The mobility of metals in the exchangeable fraction decreased in the order of Cd > Zn > Cu > Co > Pb > Ni > Cr. Slight increase in the metal concentrations were due to sewage and domestic waste discharges.
(Chakraborty et al. 2015)	Modified BCR sequential extraction and analyzed in GFAAS	Performed sequential extraction to determine the concentrations of non-residual metal complexes in the mangrove sediments from Divar Island, India. Observed that Cu and Ni were mainly associated with Fe/Mn oxy/ hydroxide and organic phases in the sediments. The organic phases acted as a buffer to control the speciation and bioavailability of Cu.

2.5.1 Review on trace/heavy metals in sediments: National Scenario

In Malaysia, many researchers (Table 2.11) have broadly studied the total metal concentration of coastal and estuarine sediments, of Malaysia, however very few studies have been reported in the East Malaysian regions (Shazili et al. 2006). Also in Peninsular Malaysia, less attention was given to the Sequential Extraction Protocols (SEP) compared to the total metal extraction technique. Some researchers (Lim and Kiu 1995; Idriss and Ahmad 2012; 2013) applied this SET protocol to riverine and estuarine sediments, sludge sediments (Nemati et al. 2011), paddy soils (Jamil et al. 2013), mining areas and urban sediments (Ashraf et al. 2012), coastal and offshore sediments (Yap et al. 2002a; 2003; Shazili et al. 2012) of Malaysia, to study the geochemical processes of trace/heavy metals associated with different phases. The methodology and findings of the Malaysian studies adapted the SEP and total digestion protocols are discussed in Table 2.10 and Table 2.11

Table 2.10 Studies focused on speciation of trace/heavy metals in coastal sediments of Malaysia

Authors	Methodology	Findings
(Nemati et al. 2011)	Modified BCR sequential extraction and analyzed in ICP-MS	Analyzed speciation of trace elements (V, Pb, Cd, Co, Ni, Cu and Zn) in river sediments from Sungai Buloh and Straits of Malacca, Malaysia. Observed low risk in sediments for V, Cr, Cu and Pb with risk assessment value < 10%
(Shazili et al. 2012)	5 stage sequential extraction and analyzed in ICP-OES	Observed the effects of pre and post monsoon seasons and speciation of heavy metals in the sediments of the South China Sea Off the Pahang coast, Malaysia. Identified the NE monsoon had an effect on redistributing of sediments as well as on the distribution of metals within the different chemical fractions.
(Idriss and Ahmad 2012)	BCR sequential extraction and analyzed in ICP-MS	Investigated the effects of organic matter and sediment pH on the concentration of Cu, Cd, and Pb in sediments of Juru River, Penang, Malaysia. Observed analyzed metals are greater in the residual fraction followed by the organic matter phase.
(Idriss 2013)	BCR sequential extraction and analyzed in ICP-MS	Investigated the effect of organic matter and sediment pH on the concentration of Cr and Ni in sediments of Juru River, Penang, Malaysia. The analyzed metals are not significantly correlated with oxidation fraction.
(Nagarajan et al. 2013)	Acid leachable trace metals and analyzed in GFAAS and ICP-OES.	Studied the partially leached trace metals in the tourist beaches of Miri city, Sarawak. Observed that Co, Cr, Cu, Ni and Zn concentrations are higher compared to other regions, indicating an external input apart from the natural process.

Table 2.11 Studies focused on total digestion of trace/heavy metals in coastal sediments of Malaysia

Authors	Methodology	Findings
(Law and Singh 1986)	Total digestion and analyzed in AAS	Conducted a study on the distribution of Mn, Fe, Cu, Pb and Zn in the water and sediment of Kelang estuary, Malaysia. Identified the metal level in sediment was greater compared to the water column at the mouth of the estuary.
(Din 1992)	Digested with aqua-regia, analyzed in FAAS and ICP-MS	Analyzed heavy metals (Fe, Mn, Al, Cd, Cr, Ag, Au, Cu, Zn, As, Pb and Sn) in sediments from estuarine and coastal regions of the Melaka Straits. Observed Al can be used as a reference element to normalize granular variability in trace metal analyzes.
(Ismail et al. 1993)	Total digestion with HNO_3 and HCl and analyzed in FAAS	Analyzed the sediments from the West coast of Peninsular Malaysia and provided the background level concentrations of heavy metals. Also suggested the increase in metal levels was due to anthropogenic influences and industrial activities.
(Ismail 1993)	Total digestion with HNO_3 and $HClO_4$ analyzed in FAAS	Analyzed heavy metals (Cd, Cu, Pb and Zn) in the sediments from the Bintulu coast and observed contamination was recorded at moderate levels due to the influence of industrial activities in this area.
(Alkarkhi et al. 2009)	Digestion with nitric acid and analyzed in FAAS	Analyzed heavy metal concentrations (Cu, Zn, Cd, Fe, Pb, Cr, hg and Mn) in sediments of selected estuaries of Malaysia. Used multivariate statistical analyse (factor and cluster analysis) for the interpretation of large data and observed anthropogenic sources were responsible for the increased levels of metals.
(Ong and Yunus 2009)	Digested with aqua-regia and analyzed in ICP-MS	Analyzed concentrations of Pb and Cu in the bottom sediments from the South China Sea, Malaysia. Pollution indices calculations identified natural processes are more dominant than anthropogenic inputs.
(Zulkifli et al. 2010)	Total digestion with HNO_3 and HCl and analyzed in ICP-MS	Analyzed concentrations of V, Cr, Co, Ni, Cu, Zn, As, Ag, Cd, Pb and U in the intertidal surface sediments of Peninsular Malaysia. Observed metal concentration in the surface sediment derived from both natural and anthropogenic activities. Proposed to develop the new Interim SQG values for Malaysia.
(Sany et al. 2013)	Total digestion with HNO_3 and HCl and analyzed in ICP-MS	Investigated the temporal and spatial distribution of heavy metals (As, Cd, Cr, Cu, Ni, Pb, Hg and Zn) in water and in sediments of Port Klang, Malaysia. Identified the main source of pollution in this area is due to anthropogenic activities from the port and industrial discharges.
(Udechukwu et al. 2015)	Total digestion with HNO_3 and $HClO_4$ analyzed in FAAS	Evaluated the mobility and contamination of Cd, Cu, Ni, Pb, Zn and Fe in the intertidal surface sediments of the Sg. Puloh mangrove estuary, Malaysia. Observed Pb and Zn exceed the guideline values due to the results of industrialization and urbanization.

The coastal stretch of Peninsular Malaysia is likely to receive trace/heavy metal impacts from both natural and anthropogenic activities (Ismail et al. 1993; Yap et al. 2003). Previous studies (Shazili et al. 2006; Zulkifli et al. 2010) clearly showed Cu, Cd, Zn and Pb at increased levels in the intertidal regions compared to the offshore sediments. The increased levels of metals adjacent to the shoreline were mainly derived from the industrial sources, agro-based industries, municipal and sewage disposals, offshore oil refineries and port activities. River inputs also play an important role in delivering the trace metals contaminants into the Malaysian coast, which is clearly observed through the literature survey (Table 2.10 and Table 2.11).

The literature summary from the worldwide studies in sediments focusing the factors governing the mechanism of adsorption and desorption of metals from sediments. The main controversial issue with authors such as Sholkovitz (1979), Thorn and Burt (1983) and Morris et al. (1982) is the effect of salinity. In their view the adsorption of metals onto sediments is enhanced by the influence of salinity whereas according to Eaton (1979) and Salomons et al. (1981) supporting the view that salinity enhances desorption. In addition to salinity, the other issues such as the effect of pH, redox potential, the conservative/non-conservative behavior of metals, particle size, organic content and turbulence (exchange between intertidal and overlying water) enhances the metal migration and adsorption/desorption process. Chapman and Wang (2001) suggested in freshwater, pH is the controlling factor whereas in marine or estuarine environment salinity is the controlling factors affecting the partitioning of contaminants between sediments and water column. Taylor (1979) discusses the trace/heavy metals concentration in deposited sediments along the North-East coast of England, concluded that the geology of an area may be a more important factor than the anthropogenic input in deciding the metal content of marine sediments.

Studies conducted by Liang and Wong (2003); Guevara-Riba et al. (2005); Riba et al. (2010) concluded the mobility of trace/heavy metals in the estuarine and marsh sediments are due to the effects of salinity and pH. According to Trefry and Presley (1976) apart from the possible sources, the textural characteristics, organic matter contents, mineralogical composition and depositional environment of the sediments can also influence the trace element level in sediments. Similarly (Snodgrass et al. 2008; Zheng et al. 2008; Besser et al. 2009) revealed the adverse effect of trace/heavy metals in sediments to the health of aquatic ecosystem. Hence it is an essential task to assess environmental health risks posed by trace/heavy metals in order to develop pollution control strategies and approaches to environmental quality management in a coastal area (Long et al. 1995). (Cuadrado and Perillo 1997; Loska and Wiechuła 2003; Zhang et al. 2009; Nobi et al. 2010) suggested a collective approach which integrates the grain size effect, geo-accumulation index, contamination factor and enrichment factor can be appropriate in order to achieve a more precise assessment of trace/heavy metal accumulation from anthropogenic source and also the subsequent environmental impact on sediments.

Yang et al. (2012) recommended the environmental significance of metal contamination can be measured in two ways: (1) evaluations based on the comparisons of the effects-based Sediment Quality Guidelines (SQGs) for each contaminant and the collective effects of contaminants in sediments and (2) use of sequential extraction procedures in order to get valuable information about the origin, mode of occurrence, mobility and transport of metals under changing environmental conditions. Long (2006) proposed some of the SQGs such as the effects range-low (ERL), effects-range median (ERM), threshold effects level (TEL), and probable effects level (PEL) are based upon both theoretical methods that rely upon equilibrium partitioning models and empirical methods that depends upon analyses of matching, field-collected chemistry, and biological effects data. According to (Žemberyová et al. 2006; Sundaray et al. 2011) assessment of sediment quality by using the total metal concentrations will provide inadequate information regarding the adverse ecological effects, as the bioavailability, mobility and potential toxicity of metals in the environment depends strongly on their chemical forms or type of the binding of the element.

2.5.2 Problems and Limitations of the Sequential Extraction Protocols (SEP)

The elements/metals bound to different chemical fractions are extracted by using the 5 stage sequential extraction procedure suggested by Tessier et al. (1979). This procedure has been followed by many researchers since the 1980s. For the fractionation of trace elements, sequential extraction is a well-established approach (Ure and Davidson

2002). However, many researchers have used different chemical reagents and followed different extraction steps (Salomons and Förstner 1980; Kersten and Förstner 1986; Martin et al. 1987; Shan and Chen 1993; Gwendy 1996; Usero et al. 1998). Difficulties have been reported with non-specificity of chemicals and regents (Whalley and Grant 1994). So, in order to overcome the lack of uniformity in the procedures, the Standards, Measurements and Testing programme of the European Union (SM & T-formerly BCR) adopted a standardized protocol known as the BCR three-step sequential extraction protocol (Ure et al. 1993). Later this procedure was slightly modified by Rauret et al. (1999). The revised protocol involves use of an increased concentration of hydroxylammonium chloride and a lower pH. This allows for a more efficient dissolution of the soil/sediment matrix in the reducible fraction, most probably the elements bounds to iron oxyhydroxide phase (Mossop and Davidson 2003). In the present work, the suitability and applicability of this procedure was tested. Many researchers (Table 2.9) have successfully applied this modified BCR sequential extraction protocol to investigate bioavailability, mobility and toxicity of trace/heavy elements in coastal areas.

In Miri, most of the industries are located along the banks of the two major rivers (Miri and Baram) and Miri River crisscrosses the city and drains into the SCS. There are many small drainage channels which bring in domestic, industrial and agricultural effluents onto the coastal beaches of Miri (Nagarajan et al. 2013). In addition, several offshore oil refinery plants and regular shipping transports are commonly observed. These two phenomena make the intertidal area of the Miri coast an interesting topic for scientific studies because of the reported increase in the productivity and survival rates of aquatic organisms in this region. In Miri, there are a limited number of reports on the status of trace elements, particularly with reference to intertidal sediments and marine biota. Previous studies by (Nagarajan et al. 2013) in the tourist beach sediments of Miri focused only on the acid leachable fraction but haven’t explained the detailed geochemistry of elements and their enrichments. Therefore in order to identify the toxicity, mobility and possible sources of metal contaminants, the modified BCR (SEP) is the best approach.

The risk assessment studies conducted in Malaysia were focused in different kind of ecosystems such as freshwater/lake, mangrove, coral and estuarine systems but much attention have been given to the riverine ecosystem only. Except few researchers (Table

2.10), most of them are concentrating on the total metal contents and comparing with the international standards. Less importance has been paid to speciation studies particularly on the coastal ecosystem, which provides the information on mobility and toxicity of bioavailable trace/heavy metals. In Malaysia, the environmental status of an aquatic ecosystem, was being studied by focusing on either one of the ecological compartment i.e. water or sediment or any one bioindicator organism. The risk assessment indices and multivariate statistical analysis, in order to explain the environmental risks associated with trace/heavy metal concentrations received diminutive attention. An integrated approach, encompassing the concurrent analysis of the different compartments of a coastal ecosystem such as water, sediment and aquatic organisms collected simultaneously at the same time will give a comprehensive understanding of the environmental status. The overall geochemical processes which influence the metal distribution from water to sediment and vice versa along with the bioaccumulation and consecutive biomagnification on marine biota have been investigated in the present study.

2.6 Accumulation of trace/heavy metals in Aquatic organisms

Fish occupy the highest trophic level in aquatic systems. They also have high economic value, thus, fish are suitable as water quality indicator organisms. Fish are a good bioindicator because they have a potential to accumulate trace/heavy metals and other organic pollutants (Linde et al. 1996; Chen and Chen 1999; Usero et al. 2004; Yilmaz 2009; Ahmad and Shuhaimi-Othman 2010; Copat et al. 2012). When fish are exposed to high concentrations of trace elements in water they may take up substantial quantities of these elements. Trace metals can enter the water then, into the body of fish through various routes and can be accumulated at different rates in the various organs of fish. Fish accumulate trace metals in the tissue through absorption and humans can be exposed to trace/heavy metals via the food chain, which can cause acute and chronic effects in humans (Dallinger et al. 1987; Altındağ and Yiğit 2005). The average daily fish consumption in Malaysia is 15.8 g per person (Laurenti 2007). Marine fish are important protein sources in the Malaysian diet, and which constitutes about 60 to 70% of all protein consumed in Malaysia (Lihan et al. 2006; Zuraini et al. 2006). Trace/heavy metal accumulation in aquatic organisms and the acid digestion protocols followed by both national and international coastal waters are discussed in Table 2.12 to Table 2.15.

Table 2.12 Accumulation of trace metals in aquatic organism and digestion using HNO_3 acids collected from global and Malaysian coastal regions

Author	Methodology	Device	Metals Analyzed	Findings
(Babji et al. 1979)	Acid digestion followed by manuals in (Coleman-Instruments 1971)	AAS	Zn, Pb, Cd and Hg	Analyzed heavy metal's contents in the coastal fisheries of Peninsular Malaysia. Observed the metal levels in the analyzed fish species were low compared to International standards and recommended the government to fix the standard limits for the dumping of waste into the environment.
(Wong et al. 2001)	Acid digestion using HNO_3	AAS	Cd, Cr, Cu, Ni, Pb, and Zn	Analyzed HM in the marine fish from Hong Kong. Observed that essential metals (Cu and Zn) were higher in liver and gonad tissues, whereas remaining metal levels were lower in the edible tissues and safe for human consumption. Metal concentration varied among different species. Different tissues show different accumulation patterns.
(Kumar and Achyuthan 2007)	Ashed at 450˚C and then digested using HNO_3	FAAS	Cu, Co, Cr, Ni, Cd, Pb and Zn	Collected marine organisms such as fish, prawn, crab and mussel from Pulicat lake to Chennai harbor, in India observed that the concentration of HM was lower than the permissible limit. Using the bioconcentration factor, it was clearly identified the metal level in the tissues had accumulated through the food chain rather than the water column and or sediment.
(George et al. 2011)	Acid digestion using HNO_3	Flame AAS	Fe, Co, Ni, Cu, Zn, Cd and Pb	Analyzed TM in marine shrimp collected from the Kochi coast, Kerala. Findings reflected the elevated metal levels in the shrimp species were due to the process of the food chain and the habitat conditions of estuarine and shelf waters. Also observed inter-elemental relationships in shrimp by statistical analysis.
(Biswas et al. 2012)	Microwave digestion using HNO_3	ICP-MS	Cu, Mn, Zn, Fe, Cr and Pb	Analyzed HM in nine edible fish species collected from the coastal region of Kalpakkam, India, and observed differences in the accumulation pattern of HM in different species depended upon the lifestyle pattern and physiological regulatory mechanisms of individual species.

Table 2.13 Accumulation of trace metals in aquatic organism and digestion using HNO_3 and $HClO_4$ acids

Author	Methodology	Device	Metals Analyzed	Findings
(Denton and Burdon-Jones 1986)	Acid digestion using HNO_3 and $HClO_4$	AAS	Zn, Cu, Cd, Ni, Pb and Hg	Studied trace metal contents in muscle and liver tissues of 50 marine fish species from the Great Barrier Reef. Observed Hg in fish is dependent on their size and trophic level. Levels of all metals in muscle tissue were well below the Australian standards and safe for human consumption.
(Ismail et al. 1995)	Acid digestion using HNO_3 and $HClO_4$	AAS	Cu, Cd, Pb and Zn	Conducted preliminary survey on trace metals in 10 marine prawn species from various Malaysian coast and reported metal content in the prawns species were low compared to Malaysian Food Regulation 1985.
(Kalay et al. 1999)	Acid digestion using HNO_3 and $HClO_4$	AAS	Cd, Pb, Cu, Cr, Ni, Zn and Fe	Investigated HM in fish tissues collected from the NE Mediterranean Sea. Among the analyzed metals Cd and Pb exceeded the permissible limits of WHO/FAO.
(Canli and Atli 2003)	Acid digestion using HNO_3 and $HClO_4$ acids.	AAS	Cd, Cr, Cu, Fe, Pb and Zn	Analyzed HM in six fish species from the NE Mediterranean Sea, measured the relationship between fish size (length and weight) and metal concentration were negative. Liver tissues showed a higher concentration of metals followed by gills and muscles.
(Bat et al. 2013)	Acid digestion using HNO_3 and $HClO_4$	FAAS	Cu, Pb, Zn, Ni, Cd, Mn, Fe and Co	Analyzed HM in brown shrimp from the Black Sea coast of Turkey during different seasons and suggested this species could be used as a good bio-indicator.
(El-Moselhy et al. 2014)	Acid digestion using HNO_3 and $HClO_4$	AAS	Cd, Cu, Fe, Mn, Pb and Zn	Studied bioaccumulation of HM in three organs of 14 benthic and pelagic fish species collected from three marine fish landing centers in Egypt and observed the concentration of metals in muscles was lower compared to other organs.
(Yap et al. 2014)	Acid digestion using HNO_3 and $HClO_4$	AAS	Cd, Cu, Ni, Pb and Zn	Examined HM in different tissues of Bivalve *Polymesoda erosa* from the west coast of Peninsular Malaysia. Observed gill tissues accumulated higher Cu and Zn, whereas the shells contained non-essential metals (Cd, Pb and Ni).

Table 2.14 Accumulation of trace metals in aquatic organism and digestion using HNO_3 and H_2O_2 acids

Author	Methodology	Device	Metals Analyzed	Findings
(Edwards et al. 2001)	Acid digestion using HNO_3 and H_2O_2	Digital Voltam meter	Cd, Pb and Cu	Analyzed metal levels in seston and marine fish muscle near industrial and metropolitan centers in South Australia, and observed significant levels of Pb in seston and fish muscle due to anthropogenic input from mining. However, mean flesh level of Cu and Pb did not exceed the Australian standards for human consumption.
(Elnabris et al. 2013)	Acid digestion using HNO_3 and H_2O_2	AAS	Cu, Pb, Cd, Mn, Ni and Zn	Analyzed HM in the muscle tissues of six commercially important fish species off their Gaza strip, Palestine and evaluated the possible risk associated with their consumption. Observed great variations among heavy metal levels in the muscle tissues of six species.
(Rahouma et al. 2013)	Acid digestion using HNO_3 and H_2O_2	ICP-MS	Zn, Mn, Pb, Cd, Cr and Cu	Analyzed HM in *Acetes* indicus, from Malacca, Johor and Terengganu coastal regions, Peninsular Malaysia. Found to be safe for consumption and public health.
(Bashir et al. 2013)	Acid digestion using HNO_3 and H_2O_2	ICP-MS	Fe, Zn, Al, As, Cd and Pb	Analyzed trace metals in tissue organs of two commercial fish species in Kapar and Mersing coastal waters of Peninsular Malaysia. Observed Fe accumulation in all the organs and metals accumulated in the order of livers > gills > muscles.
(Ahmad et al. 2015)	Microwave digestion using HNO_3 and H_2O_2	AAS	Hg	Studied Hg level in 46 species of commonly consumed fish species in Peninsular Malaysia. Observed that Hg level was higher in demersal fish compared to pelagic due to feeding habitats.
(Hosseini et al. 2015)	Acid digestion using HNO_3 and H_2O_2	AAS	Cd, Co, Cu, Ni, Pb, Fe and Hg	Analyzed HM in four commonly consumed fish species in Iran, observed the liver and skin showed higher metal concentrations than the muscles but the levels were under the suggested limits of the WHO (2000).

Table 2.15 Accumulation of trace metals in aquatic organism and digestion using mixture of acids

Author	Methodology	Device	Metals Analyzed	Findings
(Hossaina and Khan 2001)	Acid digestion using H_2SO_4, HNO_3 and $HClO_4$	AAS	Cu, Pb, Zn, Ni, Cd, Mn, Fe and Cr	Reported the TM concentration in shrimp and lobster from the Bay of Bengal, Bangladesh. The concentration of metals in muscle tissue was lower and do not pose a health hazard for consumers.
(Yunus et al. 2010)	Acid digestion using HNO_3, H_2SO_4, HCl and H_2O_2	ICP-MS	Pb, Cu and Zn	Analyzed HM in fish from Pahang River Estuary, Malaysia and observed metals were below the permissible limits. Stomach accumulated more heavy metals than muscle tissues.
(Alama et al. 2012)	Acid digestion using HNO_3, $HClO_4$, and HCl	ICP-MS	Cu, Cd, Zn, Pb and Cr	Analyzed three different types of marine organisms collected from Malacca Strait, Malaysia. Observed accumulation of HM in *A. granosa* was greater due to its feeding nature and mode of lifestyle. Also suggested that those species can be used as a good bioindicator.
(Saei-Dehkordi and Fallah 2012)	Acid digestion using HNO_3 and H_2SO_4	Potentiometric analyzer	Cd, Pb, Cu and Zn	Analyzed HM in fish species from the Persian Gulf and identified that demersal fish accumulated higher metal levels compared to pelagic. This study also revealed seasonal variation also influences the concentration of metals in the fish species.
(Rahouma et al. 2012)	Acid digestion using HNO_3	ICP-MS	Zn, Cd, Pb and Mn	Examined the level of HM in the shrimp *Acetes indicus* from Malacca and Kedah coast, Peninsular Malaysia and found all the analyzed metals were below the permissible limits.
(Kamaruzzaman et al. 2012)	Acid digestion using HNO_3, H_2SO_4, HCl and H_2O_2	ICP-MS	Cd, Pb, Cu and Zn	Studied bioaccumulation of heavy metals in different tissue organs of *Scylla serrata* crab collected from Pahang, Malaysia, found metal concentrations exceeded the maximum permissible limits due to contaminants inputs from anthropogenic sources and the feeding nature of crab species.
(Velusamy et al. 2014)	Acid digestion using HNO_3 and HCl	GF-AAS	Fe, Mn, Cu, Hg, Pb, Cd and Zn	Analyzed HM in 17 commercially important marine fish species from Mumbai harbor, India. Observed significant correlation among the HM in the fish tissue but safe for human consumption.
(Jonathan et al. 2015)	Acid digestion using HNO_3, HCl and H_2O_2	AAS and FIAS	Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, As, Hg	Analyzed HM in 40 fish species from Mexico, observed size, metabolism and feeding habits were correlated with metal concentration.

Nitric acid, hydrogen peroxide, hydrochloric acid and perchloric acids are commonly used for the digestion of fish samples. Some researchers (Hossaina and Khan 2001; Kamaruzzaman et al. 2010; Saei-Dehkordi and Fallah 2012; Jayaprakash et al. 2015) used the addition of sulphuric acid for the digestion of fish tissues. Daziel and Baker (1983) used nitric acid and hydrogen peroxide (1:1) v/v according to FAO methods.

Vaidya and Rantala (1996) proposed using dry ashing and microwave digestion procedures for the dissolution of biological tissue samples and determining trace/heavy metals using nitric acid. Schuhmacher and Domingo (1996); Canli et al. (1998); Al-Mohanna and Subrahmanyam (2001); Dural et al. (2006); Viswanathan et al. (2013) used nitric acid and perchloric acid in 2:1 ratio for the digestion of one gram of fish tissues as per the UNEP (1984). Lim et al. (1995); Edwards et al. (2001); Hashmi et al. (2002); Bat et al. (2013); Hosseini et al. (2015) used nitric acid and hydrogen peroxide for the digestion of one gram of fish tissues according to FAO methods.

The literature summary has clearly shown the use of aquatic organisms as a bio-monitor to study trace/heavy metal pollution in the aquatic environment of Malaysia has received widespread attention (Table 2.12 to Table 2.15). The bivalves (*Polymesoda erosa* and *Perna viridis*) and gastropods were frequently used to study the status of the aquatic environment, whereas fish and shrimp were mainly used for studying the relationship with health concerns as a result of fish consumption in the local diet. Shazili et al. (2006) suggested in Malaysia, the analysis for Cu, Cd, Pb and Zn have received wide attention, whereas As, Hg and Sn received little attention due to difficulties in the analytical procedures.

Numerous works on bioaccumulation of trace/heavy metals in aquatic organisms have been conducted along the west coast of Peninsular Malaysia, whereas only a few studies have been reported in East Malaysian coastal regions. Kamaruzzaman et al. (2012) suggested that a detailed study was required to determine the sex and size related metal accumulations in the mud crabs. Accumulation of essential metals (Cu and Zn) are greater compared to non-essential metals (Cd and Pb). Demersal fish show a higher concentration of metals compared to pelagic fishes, due to the metabolism and feeding nature of the fish.

Metal concentration varied among different marine species. Different tissues in the organisms show different accumulation patterns. Among all organs, liver tissues show a higher concentration of metals followed by gill, gonad and muscle tissues. Seasonal variations will also affect metal accumulation levels. Many researchers (Ismail et al. 1995; Kalay et al. 1999; Irwandi and Farida 2009; Raja et al. 2009; Rahouma et al. 2013) have compared their acquired values with the acceptable national and international guideline values in order to address the toxicity level in aquatic organisms. Researchers (Pourang et al. 2005; Kumar and Achyuthan 2007; George et al. 2011; Velusamy et al. 2014) reported their results, using statistical tools and index calculations for bioaccumulation of metals in aquatic organisms.

According to (Balkas et al. 1982; Tariq et al. 1991) the contamination of marine environments by trace/heavy metals is a serious concern worldwide. It may accumulate up to a toxic concentration under certain circumstances (Güven et al. 1999), which can cause ecological damage (Harms 1975; Jefferies and Freestone 1984; Boening 1999). Has-Schön et al. (2006) advised because of their potential toxicity, environmental persistence and tendency to accumulate in water and sediments, it become severe poisonous for all organisms, when it exceeds the permissible limits.

Agreeing with Topcuoğlu et al. (2002) in aquatic environments, trace/heavy metals tend to remain in solution or in suspension and precipitate on the bottom or be taken up by organisms. The transfer of metals along food chain can be well understood by analyzing the metal concentrations in biota samples at the same locations. Hodson (1988) stated that in water, elements/metals may remain in solution as free ions or as soluble complexes of organic and inorganic anions. Insoluble complexes with organic particulates or inorganic anions, such as carbonates, precipitate to the sediments. Therefore, exposure of aquatic biota is most often via direct uptake of free ions from water, usually across respiratory surfaces, or directly across cell membranes of plants and bacteria. Some metals move through the food chain as the organic form (e.g. mercury), and others are taken up by benthos with ingested sediments (e.g. selenium). The uptake and elimination rates determines the accumulation patterns of contaminants in fish and other aquatic organisms

(Güven et al. 1999). Al-Yousuf et al. (2000) suggested the sex and the body length has the influence of metal accumulation in fishes.

2.6.1 Selection of Suitable Digestion Procedure

In the present work, the digestion protocol adopted by FAO methodology was chosen because the recovery percentages of trace/heavy metals are greater compared to the mixture of other acids digestion and ashing methods while analyzing the same tissue. Digestion with HNO_3 acid and H_2O_2 is safe and time-consuming compared with the other methods. The loss of volatile elements is prevented by this digestion procedure. Due to local laboratory safety protocols, perchloric acid digestion is not possible. Integrated studies on metal accumulation in water, sediment and aquatic organisms have been infrequently reported in the East Malaysian region. This present study assesses the bioavailability of metal level in all compartments, including seawater, sediment and aquatic organisms to infer the relationship between these compartments. Bioaccumulation of trace/heavy metals between the pelagic and demersal fishes are also examined in order observe the variation in metal accumulation pattern. In addition, the inter-elemental correlation between the fish size (length and weight) and the metal accumulation rate is also studied. This study will be the first study for the accumulation of trace metals in commercially important aquatic organisms of the Miri coast associated with the human health risk assessment indices.

2.7 Effect of Land Use/Land Cover (LULC) change in the coastal ecosystem

The Earth’s coastal regions are important to humans as evidenced by most of the world’s population are settled near coastal areas. Due to the presence of abundant natural resources (coral, mangrove forests and fisheries) there is a rapid increase in e development activities along the shoreline areas of many countries. A growing population demands, more food, habitat, expanding settlements and infrastructure along coastal areas and will continue to have an impact on the aquatic environment. If coastal environments are modified due to industrial and other developments or human activities, this generally results in significant environmental issues as observed in many coastal areas around the globe (Lo and Gunasiri 2014).

Land cover refers to the physical and biological cover over the surface of land; this includes vegetation, water bodies (river/lake/sea), bare soil and artificial structures. Whereas land use refers to the conversion of these surface areas for anthropocentric purposes including forestry, agricultural and other manmade buildings, as well as deforestation, urbanization and changes in permanent/artificial structures (Meyer and Turner 1994). The impact of LULC changes affect coastal ecosystems, particularly if there is a major riverine system located in the region because the river is an important source for delivering any sediments into the coastal regions. Sediments from deforested agricultural lands and hilly areas become eroded due to high rainfall and other natural factors (geomorphology, weather/climate, weathering, landslides or earthquakes etc.) then carried by small streams and rivers, finally discharging into the coast. The sediments from the river mouth are carried by the longshore and littoral ocean currents and are distributed all along the coast. These sediment discharges allow mobility of trace/heavy metals during the favorable environmental condition. In addition to riverine inputs, sediments are also eroded from cleared lands for development activities and finally reach the coastal environment through smaller streams.

Various land uses have a direct impact on hydrologic systems within a watershed (Omernik et al. 1981; Lenat and Crawford 1994; Paul and Meyer 2001). Land use changes are closely related to manmade activities, which results in carrying the anthropogenic substances from these areas via hydrologic systems through drainage or runoff processes. Water quality parameters in several aquatic systems have been affected due to changes in the land use pattern within the watershed (Tong and Chen 2002). Relationships between land use and ecological factor changes were noticed in many fields and which may lead to changes in environmental elements due to human activities. Karouna-Renier and Sparling (2001), investigated the relationship between ambient geochemistry, watershed land-use and trace metals (Cu, Zn and Pb) concentrations in three types of aquatic invertebrates living in stormwater treatment ponds. Lee et al. (2009) investigated the spatial configuration of land uses within watersheds in South Korea and examined the complex nature of the relationships between land use patterns and water quality.

He and Yin (2010) studied the temporal and spatial evolution of LULC changes and their environmental effects in coal mining areas of Beijing, China through the integration of GIS techniques and laboratory experiments and observed that Cr and Pb elements were relatively abundant in the environment and which contaminated the soil, surface water and groundwater. Derome and Lukina (2011) studied the interactions between LULC changes and environmental pollution in the Arctic and observed heavy metals present in the environment were derived from non-ferrous metal smelting and mining activities which were the main threat to the prevailing land cover. Sowana et al. (2011) studied the impacts on soil from heavy metal contamination imposed by coastal land use changes in Pattani Bay, Thailand. Hadibarata et al. (2012) contrasted the effect of land use changes on water quality with the presence of heavy metals (Cd, Pb and Zn) in the water and in green mussels in the Johor Strait, Malaysia. Huang et al. (2013) analyzed the influence of various land use types on water quality in the Chaohu Lake Basin, China from 2000 to 2008. The results indicate a significant negative correlation between forest land, grassland and water pollution but, the influence of cultivated land on water quality was found to be very complex. Kuusisto-Hjort and Hjort (2013) statistically analyzed the effects of different suburban land use types and trace metal contamination of suburban stream sediments in the Helsinki region, Finland. Correlation analysis revealed a moderate relationship between the land use parameters of the contributing catchment and the metal concentrations.

Xin et al. (2014) discussed the relationship between land use changes caused by human activities and heavy metal accumulation in mangrove wetlands in China through a correlation between landscape indices and metal contents. Ghorbani et al. (2015) investigated the effects of land use on the concentrations of some heavy metals (Cr, Se, As, Cd, Ni, Pb, Zn, Cu and Fe) in surface soils of Golestan Province, South Caspian Sea and observed the enrichment factor of Se and As in soils were higher than the other metals, however, their values showed that anthropogenic activities had no serious effects on the environmental quality of the studied area. Many studies have showed that metal concentration in the aquatic systems has increased in recent decades due to changes in land use patterns by manmade activities. However, an integrated study that links LULC change and trace/heavy metal enrichment in beach sediments has never been conducted in the East Malaysian region. Thus, the present research has been proposed to study the sediment distribution pattern, how the shoreline accretion and erosion activities changes with different time period, whether the effect of LULC changes enhances the enrichment of trace/heavy metals and alter the geochemical character and quality of the sediment and water in the Miri coastal region.

2.8 Bioavailability of Metals

Trace/heavy metals occur naturally in soil, but become toxic in an environment when the concentration exceeds the normal background values due to natural and anthropogenic processes. Metals are especially toxic, particularly when they are mobile, which can enter into the food chain by the process of bioaccumulation and biomagnification or can migrate greater distances. The toxicity of pollutants in the aquatic system depends upon the bioavailable fraction of contaminants available for absorption. Dissolved or weakly absorbed contaminants are easily bioavailable to aquatic organisms compared to structurally complex mineral bound contaminants (Chapman et al. 1998). Metals in sediments of an aquatic system may be associated with different chemical fractions (Tessier et al. 1979; Salomons and Förstner 1980) and these can be leached due to changes in physicochemical characteristics such as temperature, pH, redox potential and acidification (Campbel and Stokes 1985). Metals bioavailability also depends on the process of complexation along with organic matter (Censi et al. 2006).

pH is an important factor for controlling metal speciation, the solubility of mineral surfaces and bioavailability of metals in aqueous solutions (Chuan et al. 1996). pH interrupts solubility of metals and adsorption-desorption processes (Muller and Kester 1990). A decrease in pH of the aqueous system may lead to an increase in solubility of metals bound to minerals and suspended particles and becomes potentially bioavailable for aquatic organisms (Salomons 1995). Temperature variation is also an important factor in metal speciation because an increase in temperature may alter the biochemical nature of the metals and chemical reactions are highly sensitive to changes in temperature (McLusky et al. 1986; Stumm and Morgan 2012).

An increase in organic carbon-rich sediments can form a strongly reducing (anoxic) environment. A low redox condition in the environment can promote sulfate reduction and sulfide mineral deposition. Potential toxic metals such as Cd, Cu, As, Zn, Pb and Zn can be co-precipitated with pyrite and form insoluble sulfides and become nonavailable to biota. If oxygenated water enters that environment it will result in rapid reactions and release these metals bound to sulfides. Pyritization or de-pyritization of trace metals are an important process in governing the chemical form and the potential toxicity to organisms and controls the bioavailability of many trace metals in the aquatic environment (Morse 1994).

2.9 **Summary**

Miri is a fast growing city in Sarawak, Malaysia. Industrial activities have commenced and rapid urbanisation has occurred in this area. Concurrent with these developmental activities in urban areas, many changes occurred in forests as a result of timber exports. It has resulted in a significant change in the ecosystem paving the way for substantial reduction in forest cover and a significant increase in soil erosion in the Baram river basin. As a result, the river water turned completely turbid throughout the year, pointing to an increase in suspended sediments – both spatially and temporally. These kinds of changes will generally lower dissolved oxygen in the riverine water, increase the delivery of humus material (as more and more humus rich soil is brought down), and potentially interfere with the health of the riverine ecosystem. Once delivered to the sea, the riverine water and sediments have a profound impact on the quality of the Miri coastal area – as this is where the Baram River empties into the South China Sea. Apart from the Baram River, the Miri River, the Sibuti river and approximetly 30 other smaller streams *viz.*, Lutong, Esplanade, Bakum etc., deliver their water and sediments along the Miri coast. These streams carry domestic, industrial and agricultural discharges but their impact on the environment is not well established. These events have serious ramifications for aquatic biota living in the coastal area. Trace/heavy elements have a larger impact on aquatic biota as even at trace levels they can have a potential impact.

Acquiring information on the level of trace elements in biota, especially in fish, shrimp, crabs and bivalves is important for the reason they enter the human food chain – and are consumed by people dependant on seafood as a part of their dietaray needs. Under such a scenario, and in the wake of the fact no other detailed studies have so far been conducted on these important issues. Thus this study was proposed to answer the question whether the seafood in this region is safe to consume or not. There are two possibilites for exploring this situation: i) collection and analysis of aquatic organisms for trace elements, or; ii) making a detailed study on the environment where they live. Here an attempt has been made to explore both of these scenarios for the reason the following questions can be answered: i) whether the aquatic biota is contaminated with a specific metal at a level above national and international standards; ii) whether the species is safe for human consumption; iii) what are the possible reasons for the observed level of trace elements in the biota; iv) what geochemical processes are occurring within the coastal zone that may have an impact on the bioavailabiity of these trace elements to the biota; v) what are the sources of these trace elements and how these trace elements may have been mobilised from that environment; vi) whether such trace elements are natural or anthropogenic in nature and; vii) if anthropogenic whether changes have occurred as a result of urban development and land-use and land-cover changes and have an impact on the local marine life. To answer all these questions, one key question must be addressed: how much of the trace elements are bioavailable?

Based on a thorough literature review, few studies have been carried out in the Miri region, to assess the environmental conditions but there is a lack of information in studies associated with human health concerns. The focused study on fish species will dictate the potential risk to human and ecological health. Thus, this identified research gap may be partially addressed by the proposed present integrated study and additionally, this research would become a background study for any kind of environmental studies and future developments in this region. This integrated study would provide a complete profile and current status of bioavailable toxic trace elements associated with the marine biota along the Miri coast.

Chapter 3 **Research Methodology**

This Chapter describes the research methodologies applied in this study. It includes sample collection, storage, processing and analysis with the standard protocols employed in this research.

3.1 Selection of Sampling Sites

The study area for the proposed research extends from the Kualabaram estuary area to Bungai beach, which covers an area of approximately 74kms along the coast. In order to investigate the metal accumulation in seawater and beach sediments, the following standard protocols were followed. The sampling site must reflect the characteristics of a beach/location or of an entire water body respectively. Sampling sites were selected based on the relative source of possible pollution sites such as; industrial areas, construction sites, port activities, sewage effluents discharge sites, river mouths, fish-landing centers, crude oil storage plants, and recreational beaches. Each selected site in this study area has been exposed to different types of contaminants/pollutants from a point and non-point sources. The point sources refer to the direct discharge of industrial effluents into the aquatic environment without any treatment/partial treatment, while non-point sources refer to municipal and residential sewage wastes from households, and run-off from agriculture which are carried by small streams or confluences directly into the coastal environment.

In the study area, two major rivers (the Baram and Miri) flows directly into the South China Sea near Kualabaram and Miri town respectively. A high amount of sediment and suspended solids are carried from the upstream regions of the Baram River and discharged at the Miri coast. The Miri River contains less sediment inputs compared to the Baram River. These two rivers flow through many palm oil plantation sites and transport a significant amount of organic and agricultural wastes which is then discharged into the Miri coast. (Johannes 2000) The Department of Environment (DOE), examined the Miri River and reported 70% of point pollution originates from organic waste and the remaining pollution is due to non-point industrial waste. The main sources of these pollutants are the squatter colonies, auto workshops and sawmill factories located along the river’s banks. Also, a DOE Miri officer claimed that the squatter colonies located alongside the river have used the Miri River as a dumping zone (Jacqueline 2012). These colonies throw their organic and non-organic trash (non-biodegradable plastic, cans and household wastes) directly into this river and contributing to a worsening water quality problem. Due to the high level of peat in the soil, the water pH is around 3 to 4 in the Miri River which increases the chance of leaching bioavailable trace/heavy metals from the sediment and clay surfaces. The bioavailable trace/heavy metals in the water column eventually reach the Miri coast and increase the chances of accumulating in aquatic organisms and some metals may chemically flocculate in the sediments due to the mixing of freshwater and seawater. In the past local people fished in the waterfront areas of the Miri River and Baram River mouth zones. Frequently consumtion of the contaminated fish and shellfish may cause harmful health effects. It is thus necessary to check the water and sediment quality of the suspected areas.

Most of the local communities spend their leisure time in the coastal area, having picnics, bike rides, playing and recreating in the sandy beaches. Boating, swimming, diving, snorkeling and other water sports are some of the common activities observed along the Miri coast and all this human activity resulted in selecting these sites for our sample collecting. The research zone covers an area of approximately 74 Km along the coast including almost all the important tourist and commercial beaches. Traveling from a NE to SW direction, the areas selected for the present research have been coded as: KBE, FLC, LB, PBC, MRE, PVB, TB, ESP, HWB, KPB and BB.

3.2 Fieldwork and sample collection

For this research, field work and sample collecting was done for two seasons. The first sampling was done in December 2013 to represent the monsoon season and the second sampling was done in June 2014 to represent the post-monsoon (POM) season. Water and sediment samples were collected along the Miri coast from a selected 28 locations during the monsoon season and 31 locations during the POM season. Fieldwork datasheets were separately prepared for all sampling locations and for both seasons. Prior to the sampling process, containers for sampling were cleaned by soaking them in diluted HNO_3 (20%) and rinsed with deionized water.

3.2.1 Collection of water and sediment samples and field data collection

Water and sediment samples from the sampling locations were collected during both monsoon and POM seasons during low tides. Surface seawater samples (5L) were collected in acid-washed plastic jerry cans and transported immediately to the laboratory for analyzing of trace metals. For the analysis of nutrients, an additional 500ml of seawater was collected in separate plastic bottles from all the sampling points. Then surface sediment samples were collected in polyethylene plastic bags using clean plastic scoops to avoid contamination. The nutrients bottles and sediment samples were then immediately placed in an ice box until reaching the laboratory. and the samples were then stored in a freezer at 4 ° C. General physicochemical parameters such as salinity, temperature, conductivity, TDS, redox potential and resistivity were measured in situ (Figure 3.1) using a multiple parameter sensor (Orion 4 Star portable water quality analyzer -Thermo Scientific). The pH values were measured using an HACH pH meter. Turbidity was measured by using a turbidimeter (HACH 2100Q Portable turbidimeter). The DO was measured by using a DO probe (YSI Pro 20). All the portable analyzers were calibrated prior to the field trip. The collected samples from the different beach locations were bagged, labeled and returned to the laboratory on the same day.

Figure 3.1 Collection of water and sediment samples from the Miri coast and onsite analysis of physico-chemical parameters

3.2.2 Collection of marine organisms

Biological samples, i.e. fish, bivalves and crustaceans were collected from the fish landing center at Satu Bathu, located adjacent to the Miri - Kualabaram highway (Figure 3.2). The selection of marine organisms was based on the most commonly consumed and economically important seafood of the local population. A total of 174 seafood samples were collected during the study period from the fish landing centers. The selected marine life included seven species (Figure 3.3) of fish (*Carcharhinus leucas*, *Scomberomorus lineolatus*, *Sphyraena qenie*, *Setipinna tenuifilis*, *Psettodes erumei* and *Trichiurus lepturus*), five species (Figure 3.4) of shrimp (*Parapenaeopsis sculptilis*, *Litopenaeus vannamei*, *Penaeus merguiensis*, *Harpiosquilla harpax* and *Acetes indicus*), three species (Figure 3.5) of crab (*Portunus sanguinolentus*, *Portunus pelagicus* and *Scylla serrate*) and one species of bivalve (*Polymesoda erosa*). From each species, a minimum of 10 specimens was collected from the Fish landing center. Collected fish and shellfish (shrimp and crab) samples were packed in polyethylene bags, labeled, place in an ice box and transferred to the laboratory for analysis.

Figure 3.2 Panoramic View of fish landing center at Satu Bathu on the Miri coast

A) *Otolithes ruber*

(B) *Setipinna tenuifilis*

(C) *Scomberomorus lineolatus*

(D) *Sphyraena qenie*

(E) *Carcharhinus leucas*

(F) *Psettodes erumei (top)* and *Trichiurus lepturus*

Figure 3.3 (A-F) Fish species collected from the Miri coast

(G) *Parapenaeopsis sculptilis*

(H) *Litopenaeus vannamei*

(I) *Penaeus merguiensis*

(J) *Harpiosquilla harpax*

(K) *Acetes indicus*

Figure 3.4 (G-K) Shrimp species collected from the Miri coast

(L) *Portunus sanguinolentus* (M) *Portunus pelagicus*

(N) *Scylla serrata* (O) Bivalve - *Polymesoda erosa*

Figure 3.5 (L-O) Crab and bivalve species collected from the Miri coast

3.3 Sample Storage

After reaching the laboratory, seawater samples were filtered using Whatman No 1 filter paper and acidified to pH 2. The filtered water samples were stored in a refrigerator. A detailed explanation of why Whatman No.1 filter paper (pore size 11 um) was used is presented in **section.4.2.** The sediment samples were stored in a deep freezer until later analysis. The length in cm and weight in grams of the fishes and shellfishes were measured. The fish species name and feeding habitats were identified from taxonomy texts and the fishbase.org website. The average length, weight, scientific name, English/common name, habitat, and the feeding habits of the collected aquatic organisms were recorded.

3.4 Sample processing: Water, Sediment and Aquatic organisms

For the analysis of trace metals, the seawater samples were analyzed using the liquid-liquid extraction technique proposed by Mentasti et al. (1989). The concentration of trace metals in the water samples are expressed in µg/l. For the nutrients concentration (nitrate, ammonia and phosphate), the water samples were analyzed within 48 hours of the collection using HACH kits (method 8192, 8155 and 8048) and a UV-Spectrophotometer.

Prior to processing the sediment samples, which were first brought to room temperature, organic debris were removed and the sediments were washed with distilled water then dried in an oven at 60˚C for 24 hours. Afterwards sediment samples were homogenized by using the cone and quartering method and stored in a desiccator. The sediment samples were then ground to <63 µm using an agar mortar. The geochemical fractionation of metals was performed by using a three-stage modified BCR sequential extraction process proposed by Rauret et al. (1999). A series of chemical reagents were used in the different fractions and the extracts were analyzed in a Flame Atomic Absorption Spectrometer (FAAS).

After recording the respective sizes, the aquatic organisms (fish and shellfish) were thawed to room temperature then washed with distilled water. The fish samples were dissected and separated by muscle, gills, liver and gonad tissues. In the case of shrimp, whole body organs were used for the analysis after removing the shell. Crab samples were dissected into carapace muscle tissues, walking legs and gills. The bivalve samples were dissected into foot muscles, gills and gonads. All these tissues were dried at 80˚C until a constant weight was obtained or to complete dryness. After drying, the tissue samples were reduced to a powder using an agate mortar and then stored in plastic containers which were placed in the desiccator prior to further analysis. Moisture content for all the analyzed tissue samples was calculated using the difference between the initial weight and dry weight. The concentration of metals in the sediment and aquatic samples are expressed in µg/g.

3.5 Sample Digestion Process

3.5.1 Graphite Block Acid Digestion System

An ODLAB Graphite Block Acid Digestion System (Figure 3.6) was used for the total digestion of sediment samples. The main advantages of using this digestion system are, the construction is made of graphite material instead of aluminum to prevent trace/heavy metal contamination, the digestion time is less compared to other systems and recovery efficiency is greater. The block type production made by graphite maximizes the digestion efficiency and the Teflon coating reduces the corrosion effects and metallic contamination from the surface of the system as harmful corrosive acids and gasses are used. This system is able to digest 24 samples at a time and fewer potentially toxic fumes are released from this system. The acids used for the digestion are circulated between the digestion vessel and the collection tube until the digestion completes. After completion of the digestion process, the teflon vessels were cooled and the digestion mixture was filtered and transferred to a volumetric flask and adjusted to the desired volume using distilled water.

3.5.2 **Digestion of Aquatic Organisms**

Prior to the digestion process, the dried powdered tissue of the fish and shellfish were thoroughly homogenized and then subjected to digestion using concentrated nitric acid and hydrogen peroxide (1:1) according to FAO methods (Daziel and Baker 1983). 1g of powdered fish and shellfish samples were weighed in the digestion vessels, then a mixture of 10ml of conc. HNO_3 (69%) and H_2O_2 (30%) was added to the digestion vessel and kept overnight until various reactions occured. Then, the digestion vessels were heated on a hot plate to 130˚C until the volume of the mixture reduced to 2-3ml. After digestion, the samples with clear solutions were allowed to cool, filtered and adjusted to 50ml in the volumetric flask with distilled water. Finally the digested samples were analyzed in the FAAS. The entire process of digestion was carried out inside a fume hood.

Figure 3.6 Graphite Acid Block digestion system with Fume Hood

3.6 Instruments and Working procedures

3.6.1 Flame Atomic Absorption Spectrometer (FAAS)

A flame atomic absorption spectrometer (Perkin Elmer AAnalyst 400 with WinLab 32 Software Version 6.5) (Figure 3.7) was used for the analysis of heavy metals in the water, sediment and aquatic organisms. All measurements were carried out in an air/acetylene flame. The operating conditions for all elements were set and followed the recommended conditions, by the manufacturer. The instrument-specific condition is presented in Table 3.1. The wavelengths (nm) used for the determination of the analyses were as follows: Cd: 228.80; Cr: 357.87; Co: 240.73; Cu: 324.75; Fe: 248.33; Mn: 279.48; Ni: 232.00; K: 766.49; Pb: 283.31; Rb: 780.02 and Zn: 213.86 nm. The gas flow rate was about 1.10 Lit/min, slit width was between 0.1- 2.0 nm and lamp current between 10-20 mA.

Table 3.1 shows instrument specific condition of AAS

Element	Wave Length (nm)	Char. Conc[a] (mg/l)	Sensitivity Check[b] (mg/l)	Linear Range[c] (mg/l)	Slit width	Oxidant Flow: Air (L/min)	Acetylene Flow (L/min)	Light Sources[d] (Lamp)
Cadmium	228.80	0.01	0.5	1	2.7	10	2.5	EDLs & HCL
Copper	324.75	0.025	1.3	1.6	2.7	10	2.5	HCL
Cobalt	240.73		7	3.5	1.8	10	2.5	HCL
Chromium	357.87	0.078	4	5	1.8	10	3.3	HCL
Iron	248.33	0.04	2	3	1.8	10	2.5	HCL
Lead	283.31	0.18	8	10	2.7	10	2.5	EDLs & HCL
Manganese	279.48	0.016	1	0.6	1.8	10	2.5	HCL
Nickel	232.00	0.06	3	4	1.8	10	2.5	HCL
Potassium	766.49	0.02	1	1	2.7	10	2.5	HCL
Rubidium	780.02	0.05	2.5	2.5	2.7	10	2.5	EDLs & HCL
Zinc	213.86	0.006	0.3	0.75	2.7	10	2.5	HCL

[a] Characteristic conc. is the minimum absorbance value of the instrument

[b] Sensitivity check is the concentration giving approximately 0.2 Absorbance Units (AU)

[c] Linear Range is the maximum absorbance value with the relative noise

[d] Light Source is Electrodeless discharge lamps (EDLs) and Hollow Cathode Lamps (HCLs)

Figure 3.7 Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrometer (AAS)

3.6.2 UV- Spectrophotometer

UV portable spectrophotometer (HACH DR 2800) (Figure 3.8) was used for the analysis of nutrients (Nitrogen –Ammonia, Nitrate, Sulfate and Phosphate) in the surface seawater samples. All the chemical reagents and standards used for the analysis were supplied by HACH. The standard solution was freshly prepared from standard stock solutions and analyzed on the same day. The wavelengths (nm) used for the determination of the nutrients were: PO_4^3: 880 nm; NH_3-N: 655nm; NO_3-N: 507 nm and SO_4^{2-} : 450 nm.

Figure 3.8 HACH DR-2800 Spectrophotometer

3.6.3 Mechanical Shaker

The sediment particle sizes were analyzed using the mechanical shaker (Figure 3.9). The percentages of the following 4 groups of grain size were determined; (0.5-2mm) coarse sand, (0.125-0.5mm) fine sand, (4-63µm) slit and (<4 µm) clay.

Figure 3.9 Mechanical Shaker and different particle size of beach sediment

3.6.4 Orbital Shaker and Centrifuge

A SKF 3100 model shaker and Thermo Scientific centrifuge (Figure 3.10) was used for the BCR sequential extraction procedures. For each batch of sediment samples, the shaker was used for 16 hours a day at 200 to 300 rpm and continued for three days for the complete extraction process. The extract was then separated from solid residue by centrifugation. A Centrifuge instrument (Thermo Scientific - Heraeus Labofuge 400/400R Tabletop Centrifuges) was used to separate solid and liquid phases of the sediment samples during the sequential extraction process.

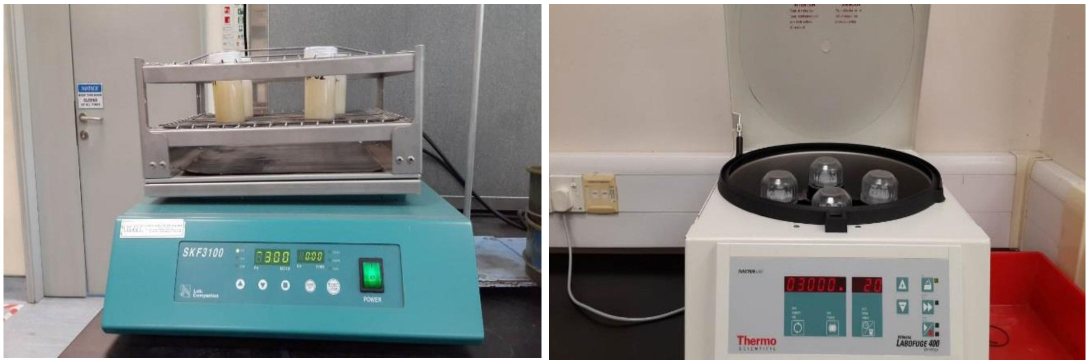

Figure 3.10 Orbital Shaker and Centrifuge used for the BCR Sequential Extraction

3.7 Accuracy and precision: for overall study

3.7.1 Apparatus and reagents

All the glassware and plastic containers used in this research were soaked in a solution of 20% HNO_3, left overnight and rinsed thoroughly with distilled water prior to use. All reagents were of analytical grade, purchased from Merck (Darmstadt, Germany) and Fisher scientific. The Safety Data Sheets (MSDS/SDS) for all the chemicals and instruments were reviewed before starting the experiments. Chemical wastes and reacted solutions were disposed of according to local, state and federal regulations.

3.7.2 Standards solutions

Standard stock metal solutions (1000 mg/L) were purchased from Merck (Darmstadt, Germany). A sub-stock solution of 100 mg/L and 10 mg/L was prepared by diluting the standard stock solution using (2%) of HNO_3 or distilled water according to the recommended conditions mentioned in the instrumentation protocols. The working standard solution of 0.1 mg/L, 0.5 mg/L, 1.0 mg/L and 2.0 mg/L was prepared by further diluting of the sub-stock solution.

3.7.3 Calibration Procedure

For checking the accuracy of the flame atomic absorption spectrometer, the calibration curves for each trace/heavy metal analysis were done to ensure and confirm accuracy and reliability. The calibration curves were made with standard solutions. Normally three to five working (0.1 mg/L, 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L) calibration standards were prepared by serial dilution of a sub-stock solution of 100 or 10 mg/L. These working standards were freshly prepared before the analysis started. The liner range calibration method was used and the correlation coefficient (R^2) for each metal was determined from the calibration curve and all R^2 which were greater than 0.995

3.7.4 Evaluation of analytical performance and quality control

The precision of the analytical performance was validated by measuring the certified standard reference material (CASS4 for nearshore seawater; MESS 3 for sediments, BCR 701 for sequential extraction of sediments and Lake Superior fish 1946 from NIST, USA for fish) were used to check the accuracy of the results. The overall mean recovery rates for trace/heavy metals ranged between 87% and 105%, and this was found to be satisfactory with the results of certified values. Analytical control was assured by preparing the reagent blanks and utilizing standard solutions as quality control at every five sample intervals. The reagent blanks showed no detectable contamination.

3.7.5 Geochemical Analyses

The analysis procedures were adopted from APHA (2005) for analyzing major ions (calcium, magnesium, carbonate, bicarbonate and chloride) in seawater samples. Potassium in seawater samples was analyzed in FAAS. Calcium carbonate and organic carbon in the sediment samples were determined by using the standard protocol by Gaudette et al. (1974) and (Muller 1969) respectively. Sequential extraction was performed using a three stage modified BCR protocol plus residual fraction proposed by Rauret et al. (1999).

3.7.6 Reagents used for Modified BCR Sequential Extraction Method

All reagents were of analytical reagent grade. Distilled water (Milli-Q Millipore) was used for all dilutions. Acetic acid (glacial, 100%), hydroxylammonium chloride, hydrogen peroxide (30 %), ammonium acetate and nitric acid (69%) were of supra pure quality (Merck, Darmstadt, Germany). Extractants were prepared according to the following procedure.

Solution A (Acetic acid, 0.11 mol/L): Add 25±0.2 mL glacial acetic acid to about 500 mL of distilled water in a 1000 mL polyethylene volumetric flask and made up to exactly 1000 mL with an addition of distilled water. 250 mL of this solution (0.43 mol/L acetic acid) was diluted to 1000 ml to obtain an acetic acid concentration of 0.11 mol/L.

Solution B (Hydroxylammonium chloride, 0.5 mol/L, pH 1.5): 34.75 g of Hydroxylammonium chloride was dissolved in 900 mL of distilled water. The solution was acidified with concentrated nitric acid to pH 1.5 and made up to 1000 mL.

Solution C (Hydrogen Peroxide 8.8 mol/L): Hydrogen Peroxide (H_2O_2) was used as supplied by the manufacturer i.e. acid-stabilized to pH 2–3.

Solution D (Ammonium Acetate 1.0 mol/L): 77.08 g of Ammonium acetate was dissolved in 900 mL of deionized water. The solution was acidified to pH 2.0 with concentrated nitric acid and made up to 1000 mL.

Solution E (Aqua regia): A mixture of aqua regia and HF. Aqua regia was prepared in the following proportion: (15ml HNO_3 + 5ml HCl + 2ml HF).

3.7.7 Modified BCR Sequential extraction procedure

The procedure for modified BCR sequential extraction is presented in Table 3.2. All extractions were carried out for 16 hours (overnight) at room temperature, using a mechanical orbital shaker. The extract was then separated from the solid residue by centrifugation for 20 min at 3000 rpm, and the resultant supernatant liquid was transferred into a polyethylene volumetric flask. The residue was back washed by adding 20 mL of deionized water, shaken for 15 min and centrifuged for 20 min at 3000 rpm. Subsequently, the supernatant was decanted.

3.7.7.1 Steps of sequential extraction

Step 1 (acid extractable/exchangeable fraction): 40 mL of 0.11 M acetic acid (solution A) was added to 1 g of sample in a centrifuge tube and shaken for 16 h at room temperature. The extract was then separated from the solid residue by centrifugation and the filtrate was separated by decantation as previously described.

Step 2 (easily reducible fraction): 40 mL of a freshly prepared Hydroxylammonium chloride (solution B) was added to the residue from step 1 in the centrifuge tube, and re-suspended by mechanical shaking for 16 h at room temperature. The process of separation of the extract, collection of the supernatant, and rinsing of residues was the same as described in Step 1.

Step 3 (oxidizable fraction): the residue in Step 2 was treated twice with 10 mL of 8.8 M hydrogen peroxide (solution C). First, 10 mL of hydrogen peroxide was added to the residue from Step 2 in the centrifuge tube. The digestion was allowed to proceed at room temperature for 1 h with occasional manual shaking, followed by digestion at 85 ± 2°C for another 1 h in a water bath. During the digestion, the centrifuge tube was loosely covered to prevent substantial loss of hydrogen peroxide. Subsequently, the centrifuge tube was uncovered and heating was continued until the volume reduced to about 2–3 ml. An additional 10 mL of hydrogen peroxide was then added to the tube, covered, and digested at 85 ± 2 ◦C for 1 hour. Heating was then continued uncovered as before until the volume reduced to 1–2 ml. Finally, 50 mL of 1.0 M ammonium acetate (solution D) was added to the cold mixture and shaken for 16 h at room temperature. The process of separation of the extract, collection of the supernatant, and rinsing of residues were followed as described in Step 1.

Step 4 (residual fraction): the residue from Step 3 was digested using a mixture of aqua regia and HF (solution E). HF was used for digestion of metals that are bound to silicate materials. The residue from the sediment samples were placed in the Teflon vessels and 20 ml of acid (15 ml HNO_3 + 5 ml HCl + 2 ml HF) was added and then heated in the graphite block acid digestion system. After completing the digestion process samples were cooled, filtered through Whatman filter paper and makeup to 100ml. Finally, the residue was analyzed in the Flame Atomic Absorption Spectrometer.

Table 3.2 Modified BCR three-stage sequential extraction scheme

Extraction step	**Fraction**	**Reagents**	**Target phase(s)**
1	Acid soluble	Acetic acid CH_3COOH (0.11 mol l^{-1})	Bound to exchangeable and carbonates iron
2	Reducible	Hydroxyl Ammonium chloride $NH_2OH.HCL$ (0.5 mol l^{-1}), pH 1.5	Bound to iron - manganese oxides
3	Oxidizable	Hydrogen peroxide 30% H_2O_2 (8.8 mol l^{-1}), 2h at 85˚C, followed by CH_3COONH_4 at pH 2	Bound to organic matter and sulphides
4	Residual	Aqua regia + HF	Metals bound in lithogenic minerals

3.8 Statistical Analysis

In order to understand the geochemical processes responsible for the observed variations in the elemental concentrations, factor analysis was carried out using Statistical Package for Social Sciences (SPSS, version 17). Factors were extracted using principal components and varimax rotation was also employed to determine uncorrelated factors. This is essential for identifying influencing factors affecting the trace metals concentration within the water and sediment column. Furthermore, it is critical to verify the data exhibit *normality* as many of the statistical tests assume the samples are from a normal population with the same variance (SPSS 1999). To test for normality of the data, the *Shapiro-Wilk* *test* was carried out, and some of the parameters have shown calculated p-value less than the chosen α - value of 0.05 for the given sample size. These parameters were considered unsuitable for further analysis as they exhibited non-normality behavior, necessitating application of log-transformation to the entire data set - as transformation solves violations of both normality and equality of variance (SPSS 1999). After log-transformation, the data was again checked for normality using the *Shapiro-Wilk test*, and outliers in each parameter were eliminated in order to achieve normally distributed data. The parameters that showed non-normal behavior after the elimination of outliers were omitted from further analysis. Since different parameters have different scales, all parameters were standardized and their z-scores were used for factor analysis. Then, factor analysis was carried out for seasonal water column and sediment quality data. Factors with eigen-values greater than 1 were considered for interpretation.

3.9 Land use/Land cover and Shoreline changes study

The Land Use/Land Cover (LULC) and shoreline changes along the selected stretches of Miri, for the past 51 years were assessed using the geographical information system (GIS). LULC changes were analyzed by comparing the area statistics of different LULC classes and shoreline changes by the overlay analysis in the GIS using different temporal shoreline maps derived from various sources. Methodology and datasets used in the change detection study are described in detail in the following section.

3.9.1 Data Source

In order to detect, identify and quantify the changes of shoreline and LULC changes over a period of 51 years, data sets from various sources were collected and used in the present study. The sources of data collected included topographical maps and satellite images. As with most change detection studies, a topographical map produced by the Malaysian Department of Survey and Mapping from 1963 was used as baseline information for the shoreline in this study area. Landsat satellite images of path 119 and row 057 covering an area between 113˚46’ E and 114˚02’ E longitude and 4˚10’ N and 4˚34’ N latitude were also used for this study. The Landsat data sets corresponding to the study area were downloaded from the Earth Explorer website (http://earthexplorer.usgs.gov/), which hosts a multitude of digital data sets. There was limited availability of cloud free and continuous data for the study area prior to 2000. The details of the datasets collected and used in the analysis are given in Table 3.3 and also shown in Figure 3.11

Table 3.3 Sources of datasets used in the analysis of its characteristics.

Data source	**Year**	**Scale**	**Bands**	**Date of Acquisition**	**Resolution (m)**
Toposheet	1963	1:50,000	-	-	-
LandSat - 2	1988	1:50,000	2,3,4	1/17/1988	60
LandSat - 5	1991	1:50,000	2,3,4	4/18/1991	30
LandSat - 5	2001	1:50,000	2,3,4	7/10/2001	30
LandSat - 8	2014	1:50,000	3,4,5	5/23/2014	30

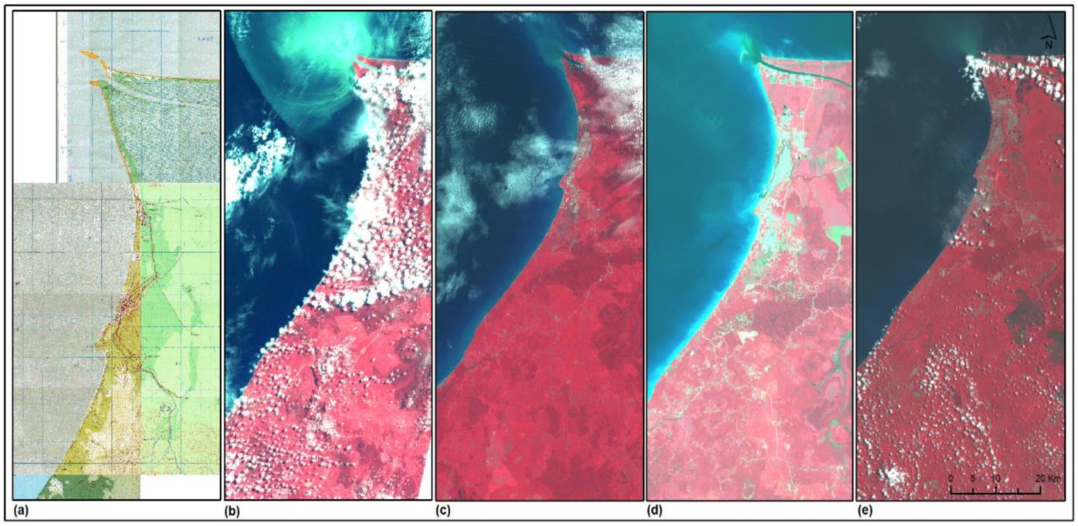

Figure 3.11 showing the temporal datasets used in the shoreline change detection. (a). Topographical maps-1963 (b) Landsat 2 image-1988 (c) Landsat 5 image -1988 (d) Landsat 5 image – 2001 and (e) Landsat 8 image 2014.

3.9.2 **Data Processing**

The historical dataset available of the study region (topographical sheets) was geo-referenced to create a seamless image of the study area. Initially, the known coordinates of the topo-sheet were entered as decimal degrees and the images were then projected in Rectified Skew Orthomorphic (RSO) with datum as Timbale 1948. The extent of the study area was fixed by designating a 10 km buffer from the shoreline which existed in 1963 and which covered an area of 713 km^2. The downloaded Landsat images were co-registered to the topographical sheets of the study area, in order to use in the LULC analysis. Basic image correction techniques were applied to the satellite images to minimize the errors associated with the reflectance values. The interpretation of historical

LULC from the topographical map and more recent LULC changes from the additional images was carried out as an on-screen visual interpretation and digitization process using ArcGIS 9.3 software.

For the shoreline analysis, the interval was fixed at every 10 years, but due to the absence of satisfactory and continuous Landsat images covering the period of 1972 to 1980, the first change year was kept as 1988. After 1988, satellite images were collected for years 1991, 2001, and finally 2014. The basic data (toposheet) was fixed as the master data layer and all the images were co-registered to the toposheet by cross matching using identifiable and detectable common points. Once the co-registration process was over, the individual data-sets were projected in Rectified Skew Orthomorphic (RSO) with datum as Timbale 1948 and used to interpret the shoreline area for the corresponding years. The generation of the shoreline area for the corresponding years started with the digitization of the toposheet based shoreline for the year 1963 in ArcGIS. The same technique was used to delineate the shoreline layers corresponding to the satellite images collected and this resulted in five different shoreline vector files based on the year (shape file format supported by the ArcGIS was used for the purpose).

In order to identify, determine and calculate the shoreline changes (area changes) between the different time periods, the merge tool available in the Arc Toolbox was used. The merging of different time shorelines has resulted in a new output of overlapping lines in some areas. Due to the variation or changes in shorelines in different time periods, the change calculation in the area was facilitated with converting merged output to polygons by using the feature to polygon conversion tool in the Arc Toolbox. This resulted in a polygon layer with different numbers of polygons in the overlapping regions and the automatic geometry calculation tool was used to attribute areas to each polygon created. Each polygon was assigned with erosion and accretion labels for better understanding.

3.10 Methodology overview

The overall methodology for the analysis of trace/heavy metal contaminants in water, sediment and aquatic organisms is shown in Table 3.4.

Table 3.4 Overall methodologies for this present study

S.No	ANALYSIS	METHOD	INSTRUMENT USED
A.	**SEA WATER**		
1.	Physico-chemical parameters Temperature, pH, TDS, ORP and Salinity		Water quality Analyzer Thermo Scientific Brand
	Dissolved oxygen		DO Meter (YSI Pro 20)
	Turbidity		2100Q Portable turbidimeter
2.	Major Ion Chemistry		
i)	**Anions**		
	Carbonate (CO_3) Bicarbonate (HCO_3) Chloride (Cl^-)	H_2SO_4 Titration (APHA 2005) Mohr's Titration (APHA 2005)	
	Sulphate (SO_4)	SulfaVer 4 Method (HACH kits)	UV- Spectrophotometer
ii)	**Cations**		
	Calcium (Ca^{2+}) Magnesium (Mg^{2+})	EDTA titration (APHA 2005)	
	Potassium (K^+)	Photometric	FAAS
3)	**Nutrients**		
	Nitrate Nitrogen (NO_3-N)	Cadmium Reduction Method	UV- Spectrophotometer
	Orthophosphate (PO_4^{3-})	Ascorbic acid	UV- Spectrophotometer
	Nitrogen-Ammonia (NH_3-N)	Salicylate Method	UV- Spectrophotometer
4)	**Trace/Heavy Metals**		
	Dissolved trace metals (DTMs)	Liquid-liquid extraction (Mentasti et al. 1989)	FAAS
B.	**SEDIMENT**		
1)	Sequential Extraction of heavy metals	Modified BCR extraction Method (Rauret et al. 1999)	FAAS
2)	Particle Size	(Sand, silt and clay ratio)	Mechanical size analyzer
3)	Calcium Carbonate	Titration method (Muller 1969)	
4)	Organic Carbon	Titration method (Gaudette et al. 1974)	
C.	**FISHES, CRUSTACEANS AND BIVALVES**		
	Trace/heavy metal accumulation	Acid Digestion by FAO (Daziel and Baker 1983)	FAAS
D. REMOTE SENSING AND GIS			
1)	Land Use/Land Cover and Shoreline changes	On-screen visual interpretation and digitization and Overlay analysis technique	ArcGIS 9.2 software package

Chapter 4 **Chemistry of Seawater**

This chapter describes on the effects of filtration techniques and the results obtained from the physio-chemical parameters, as well as the differences in the ionic changes, nutrients and trace metal variations in seawater for the monsoon and post-monsoon season.

4.1 Preamble to the Characteristics of Miri Coastal Water

The analytical results of seawater for physico-chemical parameters are presented in Table 4.1 and Table 4.2 for the monsoon and post-monsoon season respectively. In order better understand their variations, *Box and Whisker plots* were prepared and shown in Figure 4.1 to Figure 4.3. As can be inferred from these plots, the data is mostly skewed, and often have outliers and extreme values. This indicated the highly heterogeneous nature of the seawater which has been continuously perturbed and modulated by riverine input from two major rivers and numerous small streams delivering water and sediments to the coastal area. Such a perturbation has one common feature – the formation of discrete zones of typical characteristics.

The characteristics of discrete zones are perturbed as littoral currents, waves and tides bring water and sediment well away from these zones. Under such a scenario, the already existing balance between the partition of trace elements and the water and sediment columns are likely to be affected (Tessier and Campbell 1987; Santschi et al. 1990). Then, depending on the local environmental conditions, the trace elements either accumulate or remobilize and may affect bioavailability (Tessier and Campbell 1987). In such a highly dynamic coastal environment results are difficult to interpret but, at the same time, provide an opportunity to learn the various geochemical processes present in such a complex environment.

From the preceding discussion, it can be inferred, the computation of the *partition coefficient* of trace elements between water and sediment is an important component of the requirement for such an understanding. The calculated *partition coefficient* reflects the effect of perturbation of water column characteristics on sediment chemistry. When these partition coefficients are correlated it shall be possible to outline the related parameters and explore the relationships among them. Thus, the application of statistical analysis is another part of the effort towards understanding the impact of water column on sediment chemistry. Another dimension to the current problem is in the assessment of the levels of various trace elements in the water column. A thorough review of earlier works on trace elements in the water column and, how the present research differs from earlier methods, needs a detailed discussion. The discussion is in the next section.

Table 4.1 Physico-chemical parameters, nutrients and major ions in seawater samples collected during the Monsoon season

Parameters	**N**	**Minimum**	**Maximum**	**Average**	**Std. Deviation**
Temp ˚C	28	29.30	32.50	30.91	0.71
pH	28	6.80	7.70	7.40	0.19
DO (mg/L)	28	2.60	5.10	3.86	0.51
EC	28	12.70	42.10	37.36	7.64
Turbidity (NTU)	28	14.50	403.00	156.59	123.75
Salinity(‰)	28	7.40	27.20	23.85	5.19
Redox (mV)	28	-64.80	1.40	-42.23	16.07
NO_3-N (mg/L)	28	0	0.04	0.01	0.01
NH_3-N (mg/L)	28	0.06	0.35	0.14	0.08
PO_4^- (mg/L)	28	0.01	0.43	0.06	0.07
SO_4^{2-}(mg/L)	28	500.00	2700.00	1760.71	471.67
CO_3^-(mg/L)	28	0.00	18.00	7.49	3.47
HCO_3^- (mg/L)	28	42.70	106.14	86.75	16.70
Mg^{2+} (mg/L)	28	64.00	956.00	688.64	319.57
Ca^{2+} (mg/L)	28	24.00	393.60	144.51	102.36
Cl^- (mg/L)	28	5000.00	18200.00	15742.86	3441.84
K^+ (mg/L)	28	104.90	596.70	292.91	82.37

Table 4.2 Physico-chemical parameters, nutrients and major ions in seawater samples collected during the Post-Monsoon season

Parameters	**N**	**Minimum**	**Maximum**	**Average**	**Std. Deviation**
Temp ˚C	31	29.50	34.00	31.37	0.95
pH	31	7.58	8.04	7.94	0.09
DO (mg/L)	31	3.70	5.50	4.37	0.35
EC	31	22.97	46.40	43.94	5.28
Turbidity (NTU)	31	9.89	343.00	71.70	69.19
Salinity(‰)	31	13.90	30.30	28.53	3.72
Redox (mV)	31	-52.60	-28.40	-47.45	4.78
NO_3-N (mg/L)	31	0	0.04	0.02	0.01
PO_4^- (mg/L)	31	0.06	0.33	0.20	0.06
SO_4^{2-}(mg/L)	31	600.00	2500.00	1912.90	480.79
CO_3^-(mg/L)	31	0.00	18.00	8.70	4.79
HCO_3^- (mg/L)	31	73.20	152.50	111.76	17.06
Mg^{2+} (mg/L)	31	92.00	976.00	840.38	207.10
Ca^{2+} (mg/L)	31	88.80	355.20	157.70	50.25
Cl^- (mg/L)	31	8100.00	25100.00	17964.52	2823.89
K^+ (mg/L)	31	181.50	386.20	325.89	50.71

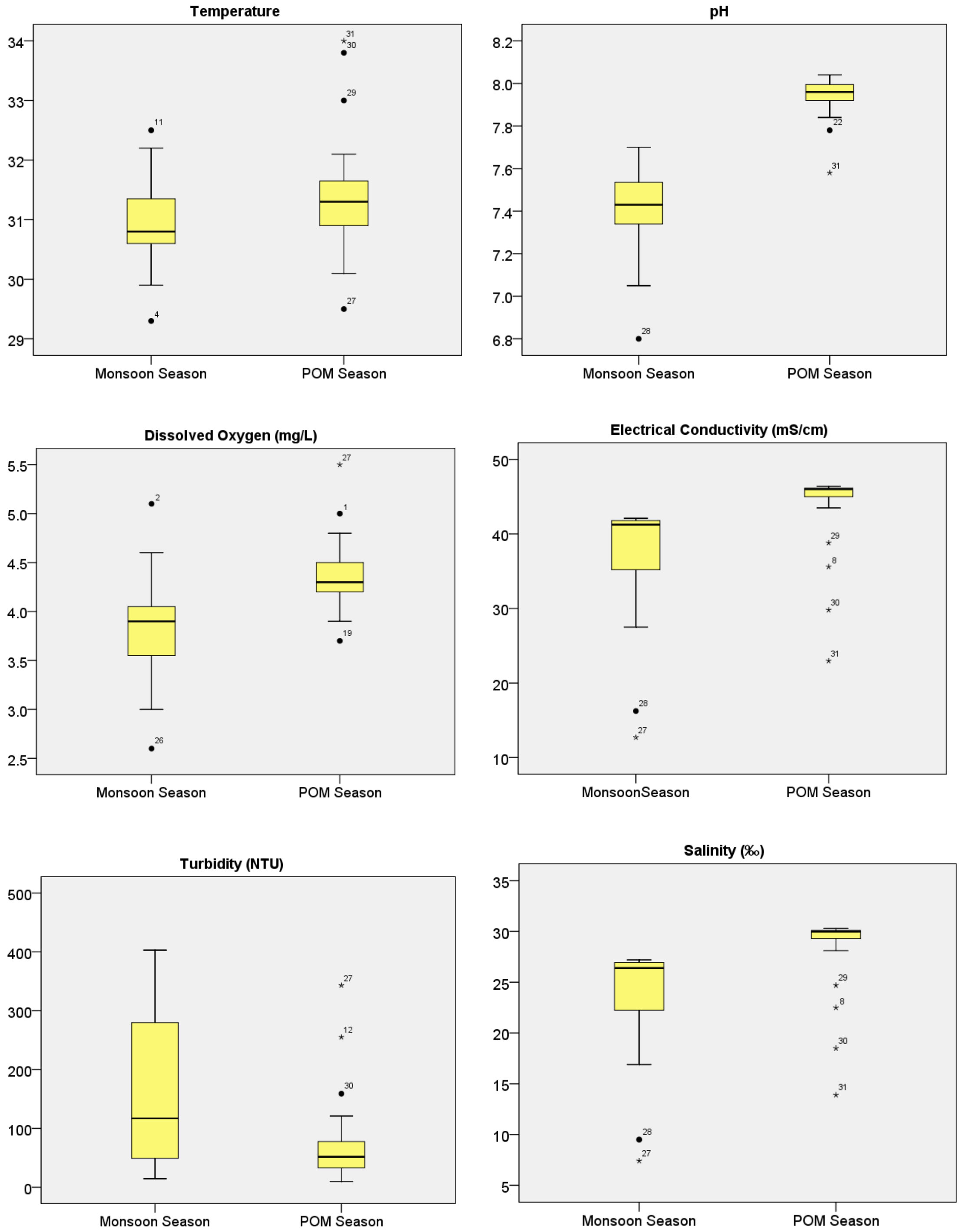

Figure 4.1 Variations in physico-chemical parameters of seawater collected in monsoon and post-monsoon season

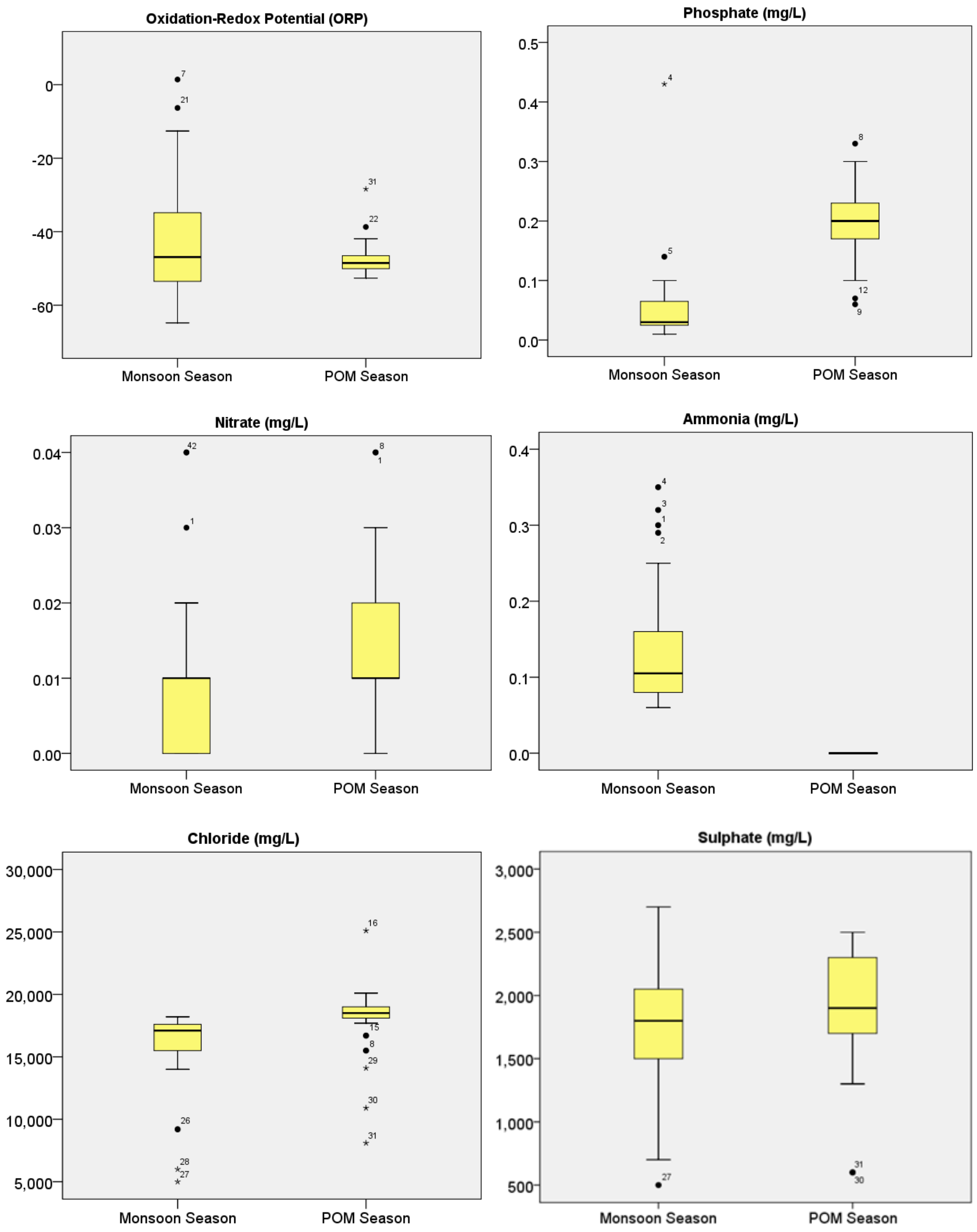

Figure 4.2 Variations in nutrients, chloride and sulphate in monsoon and post-monsoon season.

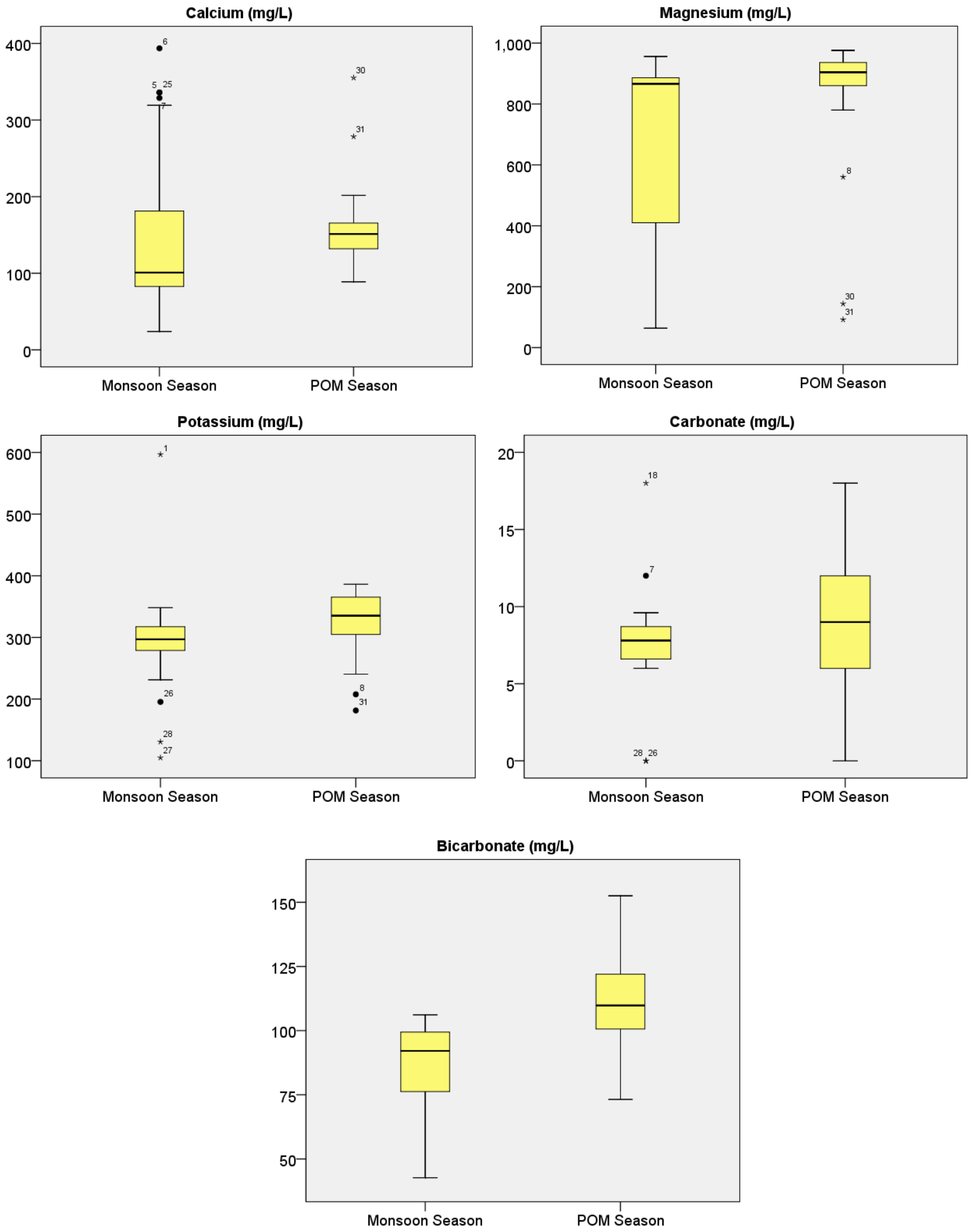

Figure 4.3 Variations in major ions concentration in monsoon and post-monsoon season

4.2 Considerations on Filtration of Water Samples

In view of the abundance of particulate trace elements in any coastal area due to the prevailing turbulent water column conditions, and their ability to easily exchange with the water column, the filtration process employed for seawater was modified from earlier works. The details are presented and the results are further discussed. The most important aspect of this discussion is that a part of the trace elements bound to suspended particles of various sizes can be mobilized and become bioavailable. There is a need to estimate the elements bound to the fine particles since these elements may be exchanged with the water column depending on the prevailing pH, Eh, and suspended sediment concentration (Balls 1988; Gao et al. 2015).

In circumstances when simple physical mixing of riverine suspended sediments with seawater can explain the observed variations in the variability of trace elements in suspended sediments (Nolting et al. 1990; Turner et al. 1991), several studies have clearly established trace elements adsorption onto fine particles and their remobilization due to desorption, organic complexation, and early diagenetic processes (Nyffeler et al. 1984; Horowitz, 1985; Tovar-Sánchez et al. 2004; Impellitteri et al. 2006; Mustafa et al. 2006; Garnier et al. 2006; Diop, 2014). This aspect of trace metal mobilization becomes more and more important as the size of the suspended particles becomes smaller. This is due to the fact that, when the size of the particles becomes smaller, the surface area increases for the given mass of the suspended sediment. This increase in the surface area has the potential to adsorb a greater quantity of trace elements and dissolved organic matter from the water column. This is due to the fact that under estuarine and seawater conditions, the riverine supplied iron and manganese flocculates due to the formation of their respective hydrous oxides. These hydrous oxides and riverine humic acids then form a coating on the fine mineral particles and become the most important active sites for metal adsorption (Zhou et al. 1994; Dyer et al. 2004; Nachtegaal and Sparks 2004; Fan et al. 2005; Boonfueng et al. 2006; Chesne and Kim 2014).

Once adsorbed, these trace elements may be released to the water column when the suspended sediments are exposed to the reducing conditions. Under normal coastal environmental conditions, where waves oxygenate the water column continuously, the possibility for such an anoxic or suboxic conditions is absent in the water column. However, in organic-rich coastal waters, especially in the tropical regions of the world (like Borneo) where the river originates in the deep jungle and brings a lot of organic debris to the sea, the redox potential in the water column may be highly influenced by these organic compounds. Irrespective of being bound to the fine particles, these elements may become bioavailable after mobilization to the water column. Thus, it is imperative to take into account the quantity of trace elements bound to the fine particles. In many of the earlier works water samples were filtered using a 0.45 μm membrane filter and the filtrate was used for the analysis. While it was a widely accepted procedure for the estimation of dissolved elements, there are some considerations on the selection of the pore size for the estimation of dissolved constituents as outlined below.

In several earlier works different filtration cut-off pore sizes *viz.*, 0.22 μm (Karbassi and Nadjafpour 1996; Nicolau et al. 2008), 0.40 μm (James et al. 1993; Lucia et al. 1994), 0.45 μm (Karbassi et al. 2008; Stolpe and Hassellöv 2010; Jung et al. 2012), 0.70 μm and 1.2 μm (Boyle et al. 1977) were used for the determination of dissolved trace elements. Such a wide range of employed pore size cut-off leads us to conclude there is no established cut-off for the determination of *truly dissolved* trace elements in water samples. Here the term *truly dissolved* means the elements in either *free form* as ions or, being complexed with organic (for example humic and fulvic acids) or, inorganic ligands (for example CO_3^{2-}, HCO_3^- and SO_4^{2-}). Trace elements in other forms such as adsorbed species onto clay minerals, iron/manganese hydrous oxides and colloids cannot be considered to be in truly dissolved form – as these are considered to be carrier phases for the trace elements. Any species that exists in solution may be considered as *truly dissolved*.

The difficulty in separating *truly dissolved* form of the species arises from the fact that when trace elements are being complexed with macromolecules such as natural organic matter (which have a wider range of molecular weight), finding a filtration technique that can pass through these molecules shall also pass a certain degree of carrier phase because of the overlap of the particle size and wider size distribution of the pores of the filtration medium. Further, the elements being adsorbed onto clays, iron and manganese hydrous oxides, and in colloidal form can be easily exchanged with the water column (Duarte and Caçador 2012) and by this process, they can become *truly dissolved*. Such a dynamism in trace elements mobility is brought about by changes in environmental conditions such as water column pH, redox potential, salinity, ionic interactions (of Ca^{2+} and Mg^{2+} ions) (Boyle et al. 1977; Mayer 1982), tidal fluctuations and turbulence, dissolved oxygen concentration, and biological activity. When samples were filtered using 0.45 µm (i.e., 450 nm) filter, almost half of the trace elements associated with colloids were lost (1 to 1000 nm) (Vold and Vold 1966) and then re-adsorbed to various natural adsorbents, although they can become easily re-mobilized again under the dynamic environment of coastal areas. Moreover, particle size analysis (Malvern Zeta Sizer) of 13 filtered (< 11 μm) water samples from the study area indicated the presence of colloidal particles (particle size range: 0.037-1.484 µm). Thus, albeit being widely accepted, filtration of water samples using 0.45 µm cannot be unequivocally accepted as a universal procedure for the determination of dissolved trace elements.

At the same time, consideration of the distribution of trace elements in suspended particles along the coastal waters and open ocean have demonstrated a wider variation in their concentration (Stolpe and Hassellöv (2010) and the references therein). It was also reported (Oursel et al. 2014) in the suspended load, almost all sand and coarse silt are deposited on seabed sediment, 65% of fine silt (3.9 to 15.6 μm) and almost all finer fractions (< 3.9 µm) of the particles are transported to the open ocean. In the study of trace elements bioavailability to the biota, such long distance transport of trace elements is likely to affect distant fish populations and may have important implications for their biogeochemical cycles.

Further, this work is aimed at assessing the biological toxicity of trace elements on biological organisms living in the water column. Studies on fish digestive systems have indicated an acidic pH in their stomach (Getachew 1989; Sturm and Horn 1998; Yúfera et al. 2004; Krogdahl et al. 2015) and trace elements in the colloidal fraction are most likely bioavailable. For example, (Tessier et al. 1983; 1984) have found that the levels of trace elements Cu, Pb, and Zn in the tissues of *Anodonta grandis* and *Elliptio complanata* are correlated not to the total metal concentration in the sediments – but to the easily extractable fraction. Luoma and Bryan (1979) have found a positive correlation between Pb accumulation in the tissue of *Scrobicularia plana* and a Pb/Fe ratio in the 1 N HCl extractable fraction. This is further discussed by Martin et al. (1987) and they concluded trace elements accumulation in benthic organisms is related to the mobile fraction of trace elements in the sediments. Thus, by filtering collected water samples using a 0.45 µm filter, artifacts were artificially introduced and the results were biased towards underestimation of the quantum of available trace elements to the aquatic biota. Further, filter-feeding organisms are also likely to consume colloidal particles. Thus, when considering bioavailability of trace elements, it is essential that their suspended load should also be taken into account.

Sheldon et al. (1972) discussed fixing an upper limit for the particle size to be considered for analysis, and further demonstrated the number of particles decreases with an increase in their class size. Later, Eisma and Kalf (1987) had shown in shallow areas of the sea, suspended particles of size peaked around at 5 and 15 µm, and the mineral particles were predominantly in the range of 2 to 5 µm. Oursel et al. (2014) have demonstrated fine fraction particles (< 3.9 µm) have most of the trace elements in high concentration – though sand and coarse silt fraction contributed a major part of the elements to the total concentration.

Such a discrepancy in the trace elements particle size distribution needs further discussion along the following lines: i) as the size of the particles increases, its population density (*i.e.*, the number of particles within the given volume of water) decreases dramatically. The low number of suspended particles in a particular size class is likely to affect the precision of the results as there should be a sufficient number of particles present in the water. In order to overcome this problem, the sample volume has to be increased and it may be impractical in some cases[1]. Further, the overall contribution of a mobile fraction of trace elements from larger particles is less compared to the finer particles (fine particles offer high surface/volume ratio for adsorption of trace elements); ii) the elements attached to the finer fraction (< 3.9 µm) can be transported to the open ocean from the coastal areas while, the larger fraction is likely to be deposited closer to the coastal areas; iii) the size fraction of suspended sediments between 0.002 and 30 µm in the ocean can be observed by satellite imaging of optical scattering of the water column (Kostadinov et al. 2009). Of this, about 77% of optical back scattering occurs within the particle size

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[1] for a detailed discussion reference can be made to (Sheldon et al. 1972)

range of 0.002 to 10 µm. Further to this, Tessier et al. (1984) have demonstrated the ingestion of suspended particles by the mollusc *Elliptio complanata* peaked at around 10-13 µm.

An optimally chosen filtration cut-off for fixing an upper limit for particle size analysis of a water column should consider the quantity of elements that can be mobilized from the suspended particle size class chosen for the analysis. Its metal content, and the ease with which the concentration in the water column can be estimated for extrapolation of results obtained from field investigations. ii) large-sized particles can be sustained in the water column only under highly turbulent conditions and their concentration may not be uniform throughout the water column, thereby limiting their role in determining the availability of trace elements to the biota living in the water column; iii) the percentage of a mobile fraction of elements bound to fine particles is comparatively higher when compared with large-sized particles due to the high surface/volume ratio of fine particles as well as due to their population in the given volume of water; iv) the < 3.9 µm particles are most likely ingested by fish and other fauna, and filtration of water samples using 0.45 µm would very likely underestimate the level of bioavailability of these trace elements; v) in the development of an algorithm for estimating the particle size distribution (PSD) of the suspended particles in the open ocean using satellite observations, Kostadinov et al. (2009) have found the abundance of picoplankton-sized (<2 µm) particles is roughly constant spatially and the abundance of microplankton-sized (2-20 µm) particles vary over many orders of magnitude. Sheldon et al. (1972) have shown the particle size distribution peaked at around 20 µm in the equatorial and north Pacific regions (between 5ºS and 20ºN). Krey (1967) indicated a mean equivalent spherical diameter of about 5-6 µm for particles in the surface waters of the North Atlantic and Gordon (1970) found particles < 7 µm are abundant. Reynolds et al. (2010) have reported a range of 0.265 to 8.709 x $10^{10}/m^3$ for particle number concentrations, and 0.67 to 168.4 ppm for the concentration of particle volume.

Considering the above discussion, it was thought that if 11 µm is taken as the cut-off for filtration of the water samples, it would allow most of the fine particles to pass through and may not introduce artifacts into the analysis due to a low number of particles in the given sampling volume of 1 L. The liquid-liquid extraction procedure (Mentasti et al. 1989) utilized in this work includes elements bound (i.e., only in the easily mobile fraction) to particles < 11 μm size. Thus, the measured water column trace element content is derived from both dissolved as well as particulate form, and the results may not agree well with earlier literature reporting on the level of dissolved trace elements (< 0.45 μm) in coastal areas from various parts of world (Apte and Day 1998; Utoomprurkporn and Snidvongs 1999; Cuong et al. 2008; Adiana et al. 2011; Jonathan et al. 2011; Padhi et al. 2013; Zhang et al. 2015). However, after careful consideration the cut-off of 11 μm will improve the accuracy of the interpretation towards trace elements ingestion by fish and other aquatic populations – as this work mainly focuses on the bioavailability of the trace elements.

4.3 Physico-Chemical Characteristics of the Water Column

Water column chemistry is an integral part of the biological system in the coastal areas since living organisms are in continuous contact with it, and receive essential support to stay alive especially, dissolved oxygen and food. Since the water column characteristics along the Miri coastal area is not quite stable, a continuous exchange of trace elements with the sediments attempting to reach equilibrium is taking place. Such a dynamic environment will have its own impact on trace elements speciation and affect its adsorption, complexation, precipitation and remobilization. For example, the pH and redox potential has the potential to influence trace element species existing in solution (Batley 1989; Caetano et al. 2003). Similarly, the major ion composition of the water column can influence the speciation of both trace elements (Millero and Hawke 1992) and their potential adsorbents *viz.*, Fe-hydrous oxides (Millero et al. 1995). Thus, it is imperative to consider seasonal variations in the water column chemistry and try to explore how it can have an impact on trace elements speciation. Given the limitations of the facilities at hand, such a study on trace elements in the water column was not possible. However, by studying the fractionation of sediments for various fractions of trace elements (viz., exchangeable, reducible, oxidizable and residual) and relating it to the water chemistry, there is still a possibility to quantify the amount of trace elements available to the biota. Such quantification, with knowledge of the amount of trace elements assimilated and accumulated within the biota, will provide vital clues to the existing environmental conditions.

In general, the water column chemistry along the Miri coastal area exhibits wide variations due to riverine input of fresh water and suspended sediments, salinity gradient, turbulence and resuspension of sediments arising from tidal influences, waves and littoral currents. The net effect of such an overall scenario is the prevalence of various geochemical interactions that serve to modulate the quantum of trace elements in the water and sediments. The effect of changes on water column characteristics and how the water column characteristics are related to variability in the observed concentrations of various trace elements are discussed under Section- 5.9.1. The reason behind such an exclusion of discussion under this section is because sediment-water interactions cannot be understood until a clear picture of trace elements variability in the sediments is explored through the calculation of the *partition coefficient* and then subjecting the data to statistical inference. Meanwhile, a discussion of water column characteristics is presented in the following paragraphs.

4.3.1 **Temperature**

Aquatic organisms adapt to a certain range of temperatures to survive (McMahon and Russell-Hunter 1977). Significant changes in the temperature may lead to physiological stress in living organisms forcing their migration from one place to another. Apart from this, temperature can affect the speciation of trace elements because most of the chemical reactions are highly sensitive to temperature changes (Elder 1988; Prosi 1989), and therefore their mobility and bioavailability. Further, in aquatic ecosystems, temperature can influence the level of dissolved oxygen due to solubility considerations and alkalinity (Singh and Mathur 2005; Trivedy and Goel 1986). The observed temperature ranges (monsoon: 29.3˚C and 32.5 ˚C; average - 30.9 ˚C; POM: 29.5 ˚C and 34.0 ˚C; average - 31.4 ˚C) are typical of the tropical environment. However, it should be noted that Esplanade Beach and the Kualabaram estuary recorded high temperatures in the monsoon and POM. Though the Kualabaram area is the confluence point for the Baram River, the highest observed temperature was due to the presence of a sand bar near the sampling location effectively blocking water circulation and mixing. Such features are not uncommon in the littoral zone (Barnes 1999). Whereas, in the case of Esplanade Beach, there was no such blockage, and littoral currents or low tides (Barnes 1999) may be responsible for the observed high temperatures.

4.3.2 pH

Small changes in water column pH also affect aquatic organisms since most metabolic and biological activities depend on a stable pH of their particular environment (Eggleton and Thomas 2004). Furthermore, pH can affect the solubility of various minerals in the sediments, the speciation of trace elements, their toxicity and their bioavailability (Chuan et al. 1996). The pH values of the Miri coastal waters range from 6.8 to 7.7 in monsoon and 7.58 to 8.04 in the POM season. During the monsoon, the prevalence of circumneutral environmental was observed. On the other hand, the coastal waters were slightly alkaline during the POM season especially off Esplanade Beach, Kampong Baraya, Tanjong Lobang and Lutong beaches, which are located some distance from a major river outlet.

4.3.3 Dissolved Oxygen

The diffusion of atmospheric oxygen, as well as photosynthetic production by marine phytoplankton’s and algae are the major sources of dissolved oxygen in the water column. Once diffused, an equilibrium state is achieved with the environment whereby the solubility of oxygen governs the level of dissolution in the water. The solubility of oxygen in water is dependent on temperature, ionic strength, partial pressure of oxygen, and ionic composition (Green and Carritt 1967; Garcia and Gordon 1992; Tromans 2000; Ming and Zhenhao 2010). Dissolved oxygen is important for meeting the demands of respiration by fish and in the microbial degradation of organic matter. Dissolved oxygen also plays a dominant role in controlling the redox potential (Eh) of the water column apart from taking part in several geochemical reactions such as sulphide oxidation and oxidation of ammonia into nitrite and nitrate (Sørensen et al. 1979; Francis et al. 2005; Francis et al. 2007; Beman et al. 2008; Buchwald and Casciotti 2010). Another critical role of dissolved oxygen is in the formation of iron and manganese hydrous oxides when dissolved iron and manganese are delivered to the estuarine region since they serve as potential adsorbents for trace elements (Gadde and Laitinen 1974; Stumm and Sulzberger

1992; Perret et al. 2000; Nelson et al. 2002). Apart from representing the quality of water, dissolved oxygen also lowers the level of dissolved trace elements in the water column – since under oxidizing conditions most of the trace elements are precipitated out (Du Laing et al. 2009). Thus, a higher level of dissolved oxygen favors overall improvement in the health of the water column and results in a healthier environment for aquatic species to grow and flourish. Conversely, if the oxygen level is low, the water body becomes unsuitable for optimal health of marine organisms and the environment becomes highly toxic (Heath 1995; Förstner and Wittmann 2012).

The measured dissolved oxygen concentration ranges from 2.6 to 5.1 mg/L in the monsoon season and 3.7 to 5.5 mg/L in the POM season. Higher levels of dissolved oxygen were observed in the Bungai Beach during the monsoon, and in the Fish landing center during the POM season. The possible reasons for such high levels of dissolved oxygen are mainly attributable to water column mixing and turbulence. During the monsoon, the delivery of humus material by rivers may exert a higher demand for dissolved oxygen due to the degradation process. Under such a situation, the NE segment is most affected as the largest rivers; Baram and the Miri are located along this segment. Whereas, in the southern part, the amount of humus material is comparatively less, making the water column clear and rich in dissolved oxygen. The average dissolved oxygen concentration in the POM season was higher compared with the monsoon season. Further, there is a positive correlation (r^2=0.585; $P < 0.01$) between salinity and dissolved the oxygen during the monsoon (Figure 4.4); such a relationship is absent during the POM. This implies during an influx of a large quantity of freshwater into the coastal area, the fresh water introduces a significant salinity gradient along the shore (possibly through littoral currents) which modulates the dissolution of oxygen in the water column.

However, during the POM such a mechanism may have been overwhelmed by other factors influencing oxygen solubility. The factors which may can have a significant impact on the level of dissolved oxygen in the water column are the rate of decay of organic detritus, the ionic composition, the intensity of waves and currents, the water column depth, and turbulence. Based on the available data it is not possible to point to one specific parameter responsible for the observed variations in the level of dissolved oxygen.

However, the positive correlation between boron and dissolved oxygen (0.468; $P < 0.05$) needs further discussion. Shirodkar et al. (2003) have opined the release of boron during organic matter oxidation in the seawater column could explain its enrichment in the surface layers. However, in their study boron was negatively correlated with dissolved oxygen and the lowering of dissolved oxygen was thought to result from the requirement of oxygen in the degradation process of organic matter. On the contrary, the positive correlation between boron and dissolved oxygen may imply some other processes. Apart from river input, the other sources of boron are of hydrothermal (Spivack and Edmond 1987) or convergent margins (You et al. 1993; You et al. 1995). Borneo Island is near the subduction zone (Hamilton 1979) and boron is most likely to have been derived from convergent margins. Then, the observed positive correlation with dissolved oxygen should be interpreted as the supply of boron to the Miri coastal area through oxygenated oceanic currents from the convergent margins. The data also showed that boron is positively correlated with salinity during both the monsoon (0.777; $P < 0.01$) and the POM (0.765; $P < 0.01$; Table-4.6). Thus, a marine source for boron should be construed.

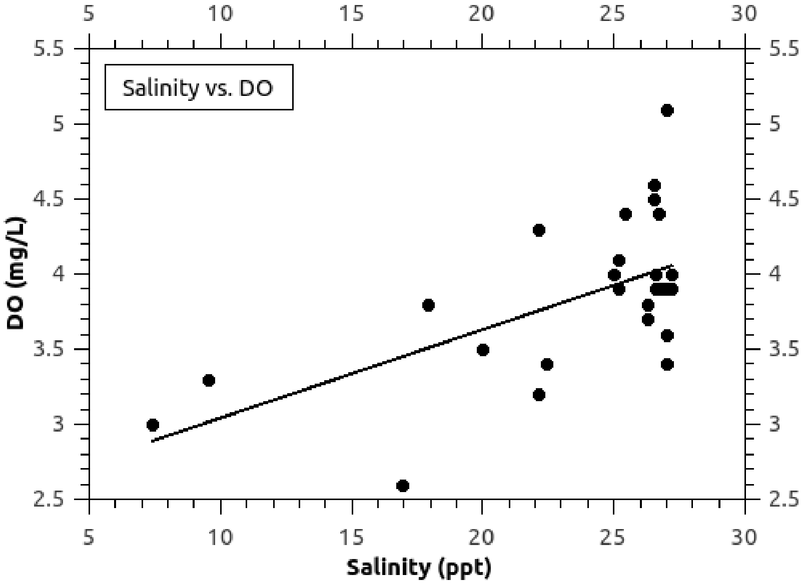

Figure 4.4 Correlation between the salinity and dissolved oxygen in seawater during the monsoon season

4.3.4 Electrical Conductivity (EC)

Compounds that dissolve into ions are known as electrolytes. Conductivity is a measure of the ability of water to pass electricity and, therefore, it is characteristic of the electrolytes in the solution. This ability of seawater to pass electricity is directly related to the concentration of ions in the water (EPA 2012) and originates from the dissolved species viz., sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). Electrical conductivity is also affected by the temperature of the water column. Since freshwater conductivity is less than that of seawater, electrical conductivity is an indirect measure of the ratio of the mixing of riverine freshwater with seawater – provided that the end member chemical constitution and conductivity are constant and well known. However, under normal conditions such constancy should not be expected. Thus, the measured electrical conductivity serves to make an overall judgment of dissolved species. The measured electrical conductivity ranged from 12.7 to 42.1 mS/cm and 22.97 to 46.4 mS/cm in the monsoon and the POM respectively. A lower conductivity value was observed in the Kualabaram region due to freshwater input from the Baram River. The most intriguing observation was the observed negative correlation between electrical conductivity and Zn

(-0.662; $P < 0.01$) only during the monsoon period (Table 4.5). For Ca, Pb, Cd, and Mn, a negative correlation was observed with electrical conductivity; but all of them were not so significantly correlated. Considering Ca, Pb, Cd and Mn are also negatively correlated with salinity, the observed negative correlation between Zn and electrical conductivity seems to arise from the mixing up of Zn-rich river water with Zn-poor seawater. Then, the absence of such a significant negative correlation between Zn and electrical conductivity may point to the removal of Zn during estuarine mixing (Karbassi and Nadjafpour 1996).

4.3.5 **Turbidity**

According to the USEPA (1986), the standard value of turbidity for seawater is 25 NTU. Turbidity is a measure of an optical determination of water clarity or murkiness. Suspended solids are composed of clay and silt particles, organic and inorganic materials and microscopic organisms such as, planktons and micro-algae (Lawler 2004). These suspended solids enter into the water column mainly through river runoff and originates from industrial effluent discharges and soil erosion. The increase in the turbidity level can affect the photosynthesis process and reduce the oxygen contribution from photosynthesis (Harding et al. 1986; Fichez et al. 1992; Hanelt 1992; Vincent et al. 1994; Zhang et al. 1999). Many fish and coral species are sensitive to the turbidity condition of a particular environment because this leads to the migration of fish species from one ecosystem to another (Cyrus and Blaber 1992; Vincent et al. 1996) and has the ability to suppress the growth of coral (Telesnicki and Goldberg 1995). On the contrary, for some species, turbidity can have a positive impact on their ecosystem (Blaber et al. 1995). Apart from the effect of turbidity on light penetration and photosynthesis, the chelation of toxic elements and growth factors with different size fractions of silt in the sediments may have an impact on the growth of fish larvae (Davis 1960).

The turbidity measurements along the coastal waters of Miri revealed great variations (the monsoon: 14.5 to 403 NTU; the POM: 9.89 to 343 NTU). Turbidity is positively correlated with Ca^{2+}, PO_4 and Zn and negatively correlated with Mg^{2+} in the monsoon period. The observation that turbidity, Ca^{2+}, PO_4 and, Zn are negatively correlated with salinity indicates a riverine source. This is quite acceptable since during the monsoon the river flow is high, and the water sample collected near the Baram river mouth (KBE-01) recorded the highest turbidity at 403 NTU. As the river plume extends into the South China Sea, turbidity should diminish. This can be inferred from the observed positive correlation between Mg^{2+} and salinity, and the negative correlation between Mg^{2+} and turbidity.

The concentration of magnesium is generally greater in the seawater than in the riverwater (Culkin 1965; Tsunogai et al. 1968). Therefore magnesium is positively correlated with salinity. When more and more seawater mixes with freshwater derived from a river, the magnesium concentration increases apart from a reduction in turbidity. Thus, there is a negative correlation between Mg^{2+} and turbidity. The wide variation in turbidity implied there is a very good possibility for photosynthetic activity, the fish population and species composition to be affected by turbidity. During the POM, the influence of the river supply decreases, and turbidity does not exhibit correlation with any other parameter except Fe (0.544; $P < 0.01$). Such a relationship between turbidity and Fe is due to the remobilization of Fe from the sediments, its reoxidation and the formation of iron colloids in the coastal waters (Boyle et al. 1977; Fischer 1999). However, at the Fish Landing Centre (FLC-02), the turbidity was the highest when compared to other localities. Probably this is due to the prevailing waves and currents, and the geomorphology of the shoreline.

4.3.6 **Salinity**

Salinity is the measure of the amount of salts dissolved in the sea water (Wetzel, 2001). The salinity ranged from 7.4 to 27.2 ‰ during the monsoon and 13.3 to 30.3‰ during the POM, respectively. Salinity varied significantly in the NE segment of the Miri coast during both seasons. This is due to the fresh water influence from both the Baram and Miri Rivers. Salinity values were lower in the NE segment (Kualabaram) and comparatively higher in the SW segment (Esplanade Beach). Salinity correlated with many water column parameters (Table 4.5 and Table 4.6). For example, SO_4^{2-}, HCO_3^-, Mg^{2+}, Cl^-, K^+, B are all positively correlated with salinity during both seasons. This implied all these ions are dominant in the seawater, and relatively depleted in the river water. However, Ca^{2+} is negatively correlated with salinity and this indicates a riverine source for calcium. The weathering of carbonate rocks from the Subis member of Tengap

Formation and the Sibuti Formation and transported by the Sibuti and Niah rivers are the source for Ca^{2+} in the river water. With regard to the trace elements, only zinc exhibited moderate negative correlation with salinity (-0.665; $P<0.01$) during the monsoon. However, such a relationship is absent during the POM season. The reason for such a relationship was already discussed under section 4.3.4.

4.3.7 Oxidation-Redox Potential (ORP)

Oxidation-reduction potential is the measure of the ability or strength of oxidizers or reducers in a solution. If the potential is positive then there is oxidizing taking place (i.e., a greater tendency to gain electrons). Whereas, a negative value represents the reducing nature (i.e., a greater tendency to loose electrons) in the environment. ORP is also known as Eh. In any given environment, the form of a metal species in solution is governed only by the pH and Eh. As the dissolved species tries to attain equilibrium with the sediment, minerals form under certain pH-Eh conditions and are also unique to the environment (Krumbein and Garrels 1952). Based on the prevailing environmental conditions, the already existing minerals may be solubilized. Though no attempt has been made here to elucidate the mineral equilibria (which is not within the scope of the study), a measured redox potential was used here to understand the possible processes which may occur within the given conditions. The redox potential value ranged from -64.8 to 1.4 mV during the monsoon and -52.6 to -28.4 mV during the POM.

4.4 Nutrients

Phosphorus is delivered to the marine environment as a result of natural weathering of phosphorus-bearing minerals in the rocks. The observed range of PO_4^- was 0.01 to 0.43 mg/L and 0.06 to 0.33 mg/L for the monsoon and the POM season respectively. The ammonia concentration was in the range of 0.06 to 0.35 mg/L for the monsoon season whereas in the POM season it was below the detectable range. The high concentration was observed off of the Bungai beach. Nitrate ranged from 0.0 to 0.04 mg/L during both the monsoon and the POM. Nitrate is the most mobile nutrient and the highest risk of water contamination (Watschke et al. 1999). The increase in nitrate concentration leads to the process of eutrophication and the growth of algal blooms that may reduce the photosynthesis process in the coastal environment.

The source of nitrate mainly originates from natural sources such as from atmospheric exchange, animal waste, decaying plants and from anthropogenic sources such as fertilizer waste from agricultural fields, wastewater discharge, septic tanks and domestic sewage (Paerl 1997; Wu and Wang 2007). Nitrate content in seawater is generally low, compared to fresh water. The analysis of nitrate levels in fresh water is quite simple but much more complicated in seawater due to the interference of chloride. In the present study, the nitrate content is very low in almost all sampled locations. The maximum concentration was observed as 0.04 mg/L for both seasons from the SW segment of the study area at Bungai Beach. Nitrogen is present as nitrate, nitrite and ammonia. Due to aquatic microorganisms, atmospheric nitrogen is reduced to ammonia and through the process of volatilization; ammonia will leave the aqueous solution.

4.5 Major Ions in Seawater

4.5.1 Chloride (Cl-)

The Cl^- concentration was in the range of 5000 to 18200 mg/L and 8100 to 25100 mg/L in the monsoon and the POM season respectively. The average concentration was higher in the POM season. The maximum concentration was observed in the SW segment of the study area for both seasons.

4.5.2 Sulphate (SO42-)

Sulphate ranged from 500 to 2700 mg/L in the monsoon and 600 to 2500 mg/L in the POM season respectively. Normal seawater contains about 2700 mg/L of sulphate (Hitchcock 1975). However, the average concentration of sulphate was higher in the POM season. The maximum concentration of sulphate was observed in the SW segment of the study area for both seasons particularly at Bungai Beach, whereas lower concentrations were found in the Kualabaram estuary area.

4.5.3 Alkalinity

Alkalinity is reported here as carbonate and bicarbonate alkalinity (as $CaCO_3$ mg/L). The carbonate level was in the range of 0 to 18 mg/L for both seasons. The bicarbonate level in the seawater was in the range of 42.7 to 106.14 mg/L and 73.2 to 152.5 mg/L in the monsoon and the POM season respectively. The lower concentration was recorded in the Kualabaram region for both seasons and the maximum concentration was observed at the Tanjong Lobang beach for the monsoon season and at Piasau Beach in the POM season. The average concentration of carbonate and bicarbonate level was higher in the POM season.

Both carbonate and bicarbonate exhibit positive correlation (r^2=0.852; 0.773; P<0.01) with salinity during the monsoon (Figure 4.5 Salinity-CO_3; Figure 4.6 Salinity-HCO_3). This indicates the major portion of alkalinity is derived from the seawater during this period. However, during the POM such a significant relationship could not be observed.

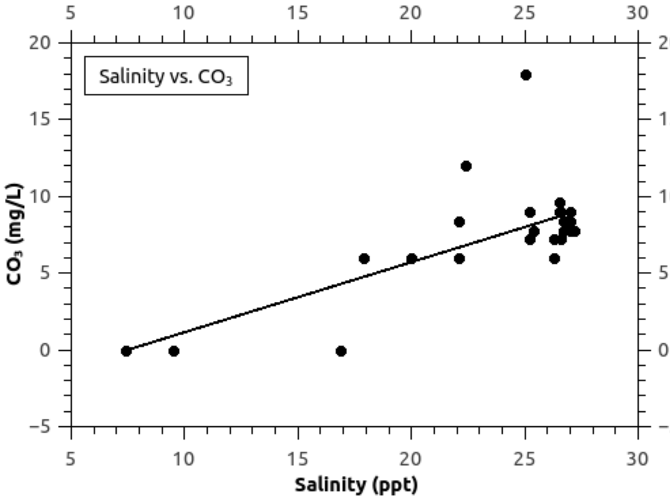

Figure 4.5 Correlation between salinity and carbonate in the monsoon season

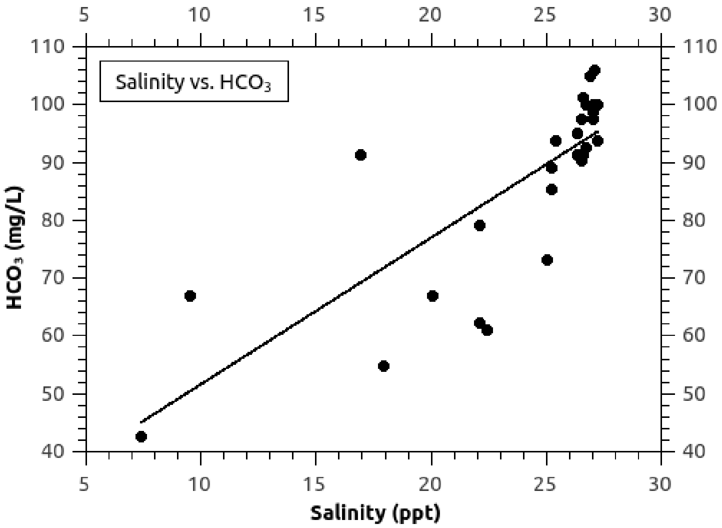

Figure 4.6* *Correlation between salinity and bicarbonate alkalinity in monsoon season

4.5.4 Magnesium (Mg2+)

Magnesium is the fourth most abundant ion in seawater (Dittmar 1884) and required by living organisms in trace amounts for their metabolic processes (Thompson and Wright 1930). The concentration of magnesium in the present study was in the range of 64 to 956 mg/L and 92 to 976 mg/L in the monsoon and the POM season respectively. The average concentration was higher in the POM season. Similar to other ions, Mg concentration was greater in the SW segment of the Miri coast, while lower concentrations were recorded in the NE segment.

4.5.5 Calcium (Ca2+)

Calcium content in seawater is lower compared to sodium and magnesium ions. Changes in salinity will cause fluctuations in the calcium level. Calcium originates naturally from rocks and discharged into the marine environment through rivers. Calcium is abundant in coral and marine sediments because of the skeletal deposition of dead organisms which is mainly composed of calcium carbonate. In the present study, calcium was in the range of 24 to 393.3 mg/L and 88.8 to 355.2 mg/L in the monsoon and the POM season respectively. The average concentration of calcium was higher in the POM season. The maximum concentration of calcium was observed in the samples collected near the freshwater mixing zones for both seasons.

4.5.6 Potassium (K+)

Potassium is the sixth most abundant cation in seawater. It has a constant relationship with chlorinity (Thompson and Robinson 1932). Potassium concentration in seawater is diluted by the influence of fresh water from rivers. In the present study, the concentration of potassium is in the range of 104.9 to 596.7 mg/L in the monsoon and 181.9 to 386.2 mg/L in the POM respectively. The average concentration was higher in the POM season.

4.6 Trace elements concentration in seawater

The range and average concentration of trace elements in the analyzed surface seawater samples for the monsoon and the POM seasons are presented in Table 4.3 and Table 4.4 respectively and are also represented by the box and whisker's plot in the Figure 4.7 and Figure 4.8. The sequence of trace metal concentration in the surface seawater samples for the monsoon season are in the order of B > Fe > Pb > Ni > Co > Zn > Rb > Cd > Cu > Mn whereas in the POM season are in this order B > Pb > Ni > Co > Zn > Cr > Fe > Cd > Cu > Rb > Mn.

Table 4.3 Trace metal concentration in the Monsoon season

Elements	N	Minimum	Maximum	Average	Std. Deviation
Cu (µg/L)	28	8.10	13.00	10.47	1.44
Zn (µg/L)	28	34.20	38.70	35.66	1.63
Pb (µg/L)	28	78.20	95.10	88.70	4.04
Co (µg/L)	28	44.00	52.50	47.95	2.08
Ni (µg/L)	28	63.90	77.20	70.82	3.37
Cd (µg/L)	28	10.60	14.40	11.28	1.05
Mn (µg/L)	28	3.70	9.90	6.76	1.75
Fe (µg/L)	28	431.40	569.90	491.17	30.77
Rb (µg/L)	28	19.00	32.50	28.24	2.88
B (mg/L)	28	1.80	5.80	3.89	0.98

Table 4.4 Trace metal concentration in the Post-Monsoon season

Elements	N	Minimum	Maximum	Average	Std. Deviation
Cu (µg/L)	31	9.50	16.70	13.81	1.88
Zn (µg/L)	31	54.70	59.90	57.81	1.27
Pb (µg/L)	31	138.90	158.70	149.12	4.62
Co (µg/L)	31	58.80	75.00	65.48	4.04
Ni (µg/L)	31	98.40	118.80	104.49	4.51
Cd (µg/L)	31	19.50	23.00	21.49	1.18
Mn (µg/L)	31	7.10	11.10	8.64	1.11
Fe (µg/L)	31	15.50	39.50	25.29	4.84
Rb (µg/L)	31	11.10	13.50	12.48	0.49
Cr (µg/L)	31	22.60	93.70	36.52	12.75
B (mg/L)	31	2.60	4.50	3.77	0.48

4.6.1 **Copper**

Copper concentration in the present study was in the range of 8.1 to 13.0 µg/l in the monsoon season and 9.5 to 16.7 µg/l in the POM season. The average concentration of Cu was higher in the POM season. Copper concentration was high in the Miri River estuary during the monsoon season and in Fish landing center in the POM season. Higher concentrations of dissolved Cu were recorded in the NE segment of the Miri coast for both seasons.

4.6.2 **Zinc**

Zinc concentration was in the range of 34.2 to 38.7 µg/l in the monsoon season and 54.7 to 59.9 µg/l in the POM season. The average Zn concentration was higher in the POM season. Higher Zn concentration was observed at the Fish Landing center and Esplanade Beach during the monsoon and the POM season respectively. The NE segment during the monsoon and the SW segment during the POM season showed a maximum concentration of Zn in the seawater.

4.6.3 **Lead**

Lead and its components are generally toxic, particularly to aquatic environments. Pb concentration was in the range of 78.2 to 95.1 µg/l in the monsoon season and 138.9 to 158.7 µg/l in the POM season. Lead concentration was higher compared to all other trace elements in the POM season. The maximum concentration was observed at the Fish Landing center in the NE segment of the study area for both seasons.

4.6.4 Cobalt

Cobalt is a naturally occurring element and is a dietary requirement of phytoplankton as an important micronutrient (Morel et al. 1994). Cobalt concentration was in the range of 44.0 to 52.5 μg/l during the monsoon and 58.8 to 75.0 μg/l during the POM season. The average Co concentration was higher in the POM season. Highest Co concentration was noticed in Bungai Beach and at the Fish Landing center in the monsoon and POM season respectively.

4.6.5 Nickel

Nickel is a dietary requirement for various organisms but becomes toxic at higher concentrations. Nickel concentration was recorded in the range of 63.9 to 77.2 μg/l in the monsoon season and 98.4 to 118.8 μg/l in the POM season, with the higher values from Esplanade Beach in the monsoon and from the Fish Landing center in the POM seasons. The average concentration was higher in the POM season.

4.6.6 Cadmium

Cadmium concentration was in the range of 10.6 to 14.4 μg/l during the monsoon season and 19.5 to 23.0 μg/l during the POM season. The maximum concentration was observed in the POM season. Cadmium concentration in the Kualabaram estuary area in the monsoon and at Piasau beach in the POM season was relatively higher compared to the other beaches.

4.6.7 Manganese

Manganese is an important micronutrient for microorganism, plants and animals (Underwood 1977). Among all the analyzed trace elements, Mn exhibited the lowest concentration for both seasons. It was in the range of 3.7 to 9.9 μg/l in the monsoon and 7.1 to 11.1 μg/l in the POM season, with the slightly higher average values in the POM season. The maximum concentration of Mn was found at Hawaii Beach and Piasau beach during the monsoon and POM season.

4.6.8 Iron

Iron is the fourth most abundant element in the Earth’s crust but dissolved Fe concentration in the open ocean seawater is very low. Fe is an essential micronutrient for plankton growth and also used for biochemical processes of many chemical reactions in the marine environment (Geider and Roche 1994). Iron concentration, was in the range of 431.4 to 569.9 µg/l during the monsoon and 15.5 to 39.5 µg/l during the POM season. The average Fe concentration in the monsoon was 20 times higher than during the POM season. Among the analyzed trace elements, Fe concentration was higher in the monsoon season. The maximum concentration was recorded along the Lutong Beach and at Fish Landing center in the monsoon and the POM season respectively. Fe concentration was enriched more in the NE segment of the study area for both seasons.

4.6.9 Rubidium

Rubidium is the 23rd most abundant element in the Earth’s crust. It is not required by living organisms for any kind of metabolic activities. Rubidium concentration was in the range of 19.0 to 32.5 µg/l in the monsoon season and 11.1 to 13.5 µg/l in the POM season. The average concentration was higher in the monsoon season. Higher Rb concentrations were recorded in the Esplanade Beach and the Fish Landing center during the monsoon and POM season respectively.

4.6.10 Chromium

Chromium is a naturally occurring elements in the Earth’s crust. Chromium concentration was analyzed and reported for the POM season only. Chromium ranged from 22.6 to 93.7 µg/l with an average value of 36.5 µg/l. The maximum concentration is recorded in the Fish Landing center and the NE segment of the study area showed greater concentrations of Cr compared to the SW segment.

4.6.11 Boron

Boron is a naturally occurring element in the Earth’s crust. It combines with oxygen and other elements in compounds called borates. Boron concentration in the present study was in the range of 1.8 to 5.8 mg/L in the monsoon and 2.6 to 4.5 mg/L in the POM season. The average Boron concentration was relatively similar for both seasons. Higher concentrations of Boron were recorded along Lutong Beach and at Piasau Beach during the monsoon and the POM season respectively whereas the lowest concentration was observed in the Kualabaram estuary area for both seasons.

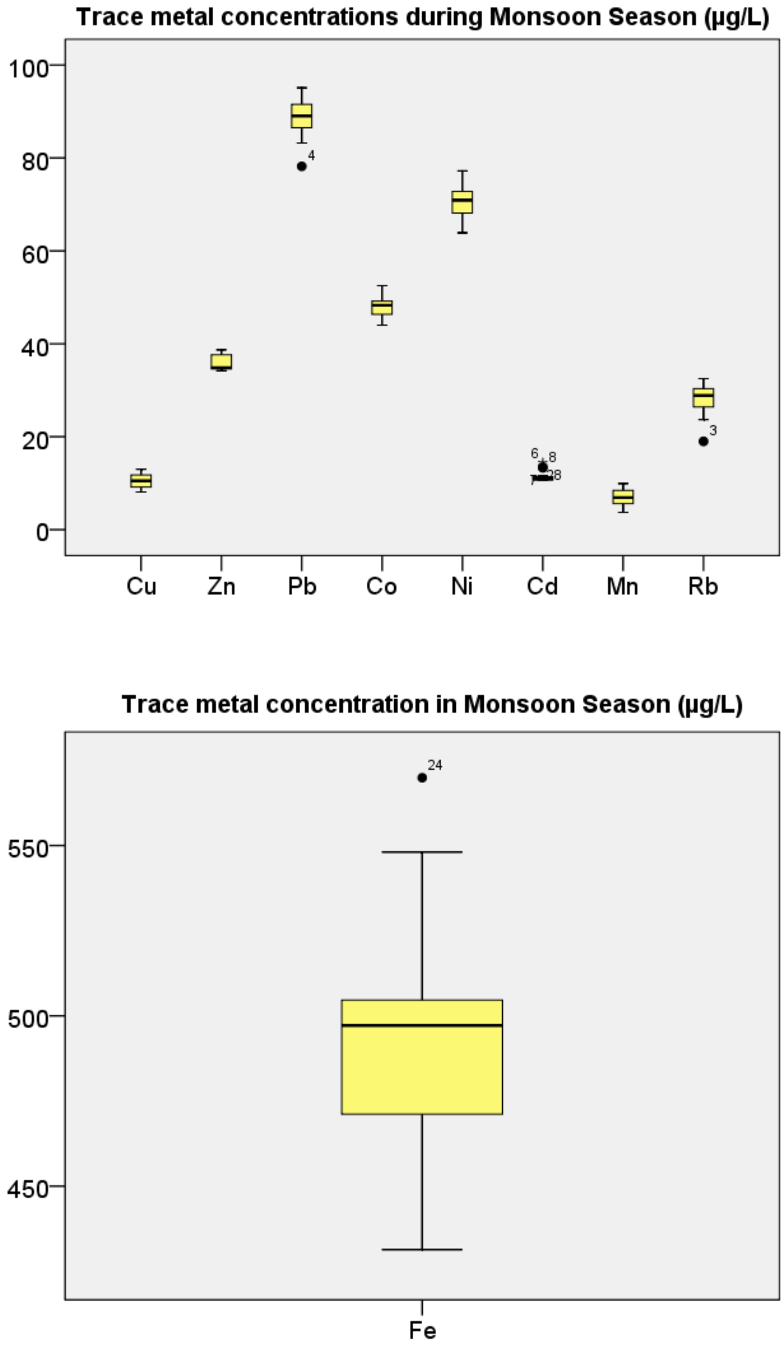

Figure 4.7 Trace metal concentrations during the monsoon season

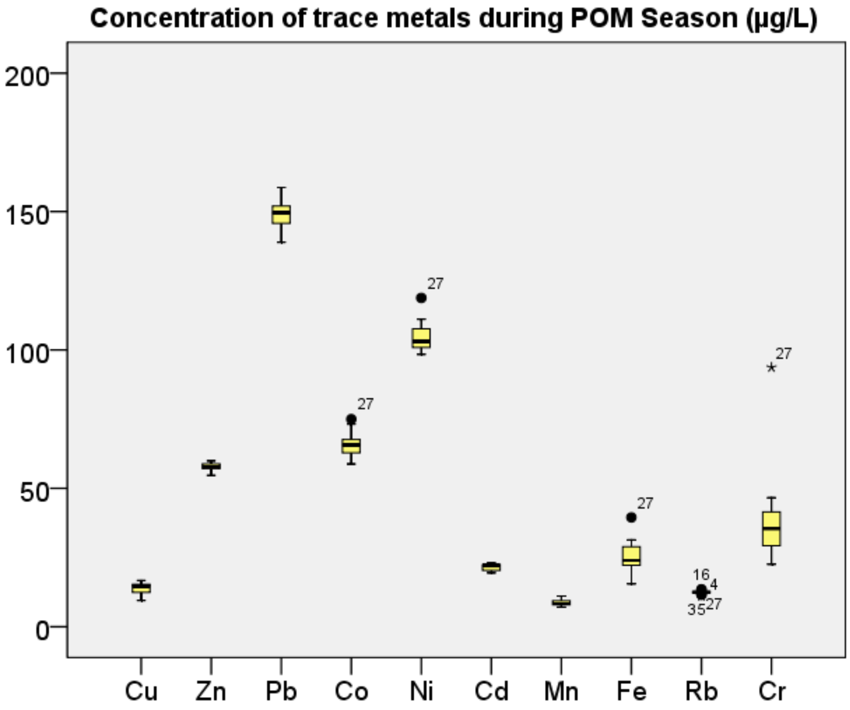

Figure 4.8 Trace elements concentration during the post-monsoon season

4.7 Discussion

4.7.1 Variation of physico-chemical parameters in the monsoon season

During the monsoon season, a wide variation in the physico-chemical parameters was observed between the NE and SW segments of the study area. The characteristics of seawater are mainly controlled by the large amount of fresh water input from the Baram River. Temperature, salinity, pH, DO, turbidity and EC are mainly controlled by the influence of the Baram and Miri River. Temperature, pH, DO, EC and salinity show a decreasing trend moving towards the NE segment, which is due to the mixing of fresh water with seawater from the two major rivers. Ocean current turbulence plays an important role in increasing the salinity concentration all along the Miri coast from the NE to the SW segments. Turbidity was affected due to the large amount of sediment and organic debris from the Baram River and thus the water looked brownish and turbid in colour. A slight acidic pH was recorded in the Kualabaram estuary mouth area, which indicated the riverine water condition was acidic in nature. An increase in pH value was clearly observed, which corresponded with an increase in the salinity condition of the seawater. The variations in pH was limited to the monsoon season, and was attributed to the freshwater input from riverine sources along the Miri coastal zone.

Like the physico-chemical parameters, major and minor ions such as chloride, sulphate, magnesium, potassium, bicarbonate and carbonate concentrations showed a decreasing trend as they moved towards the NE segment of the study area. Fresh water controlled the chemistry of seawater during the monsoon season, particularly in the NE segment. Calcium concentration was elevated in the seawater collected near the fresh water mixing zones. Normally, seawater is rich in chloride, sulphate, magnesium, potassium and bicarbonate levels but the concentrations of these ions were observed to be less than the normal seawater chemistry due to the mixing of freshwater from the Baram River.

Nutrients such as nitrate, ammonia and phosphate showed a higher concentration in the SW segment of the study area particularly at the Bungai Beach area due to agricultural activities. Chilli and palm oil plantations are commonly observed near the coastal areas of Bungai Beach and the enrichment by these nutrient parameters in the seawater is due to the runoff from the fields, where the use of fertilizers is common. During the monsoon season, fertilizers are leached out from the soil surface and discharged into the beach areas through small drainage streams.

4.7.2 Variation of physico-chemical parameters in the post-monsoon season

Compared to the monsoon season, the POM season shows a wider range of distribution of the physico-chemical parameters and some of the major and minor ions. All the analyzed parameters showed an increased level in the POM season. In most of the sampling locations pH was in alkaline condition. The DO level did not show much variation between the NE and SW segments of the study area. A decreased DO level was observed in the Kualabaram estuary area; this may be due to organic debris derived from the Baram River. DO, pH and salinity show lower values in the freshwater mixing zones particularly in the Kualabaram and Hawai Beach areas due to dilution by fresh water. According to the DOE (2006), the standard pH value for seawater is 6.5-8.5 and the values obtained for both seasons were within the permissible standard.

Major and minor ions such as chloride, sulphate, magnesium, potassium, bicarbonate and carbonate showed a decreasing trend moving towards the NE segment of the study area, but their average concentration is higher in the POM compared to the monsoon season. The decreasing level of ions in the NE segment of the study area was due to the mixing of the Baram river water, which can alter the natural proportions of local seawater by dilution or enrichment of some major and minor ions. Calcium showed an increasing concentration in the Kualabaram estuary area and indicates a riverine source. The sulphate concentration was observed to be at the maximum in the SW segment and the minimum concentration was recorded in the NE segment particularly in the freshwater mixing zone. The nutrients concentration during the POM season was very low compared to the monsoon season, due to little agricultural activities (near Bungai Beach) during the POM season.

Overall variations in the physico-chemical parameters of the seawater samples indicate the dynamic nature of the Miri coastal system, as the physico-chemical parameters are mainly controlled by the river input and ocean currents. In addition to this natural phenomenon, small drainage channels/stream inputs from the plantation and industrial sites also contribute to the changes of the physico-chemical parameters for both seasons. The input of freshwater stratifies the water column, creating a low salinity surface layer and resulting in the dynamics of estuarine behavior in the intertidal area (Sievers and Silva 2008; Ahumada et al. 2011). The fast moving surface water from the Baram River mixes directly with the open ocean in the NE segment and changes the physico-chemical variables of the seawater column particularly salinity, temperature, pH, Eh, DO and /or ionic strength, amongst others.

4.7.3 **Trace elements**

Seawater contains most of the elements in low concentration. Their solubility depends on the solvent characteristics and solubility constant for each elements, which determines its proportionality and abundance. These can be observed in both intertidal waters and in the surface water column (Davison et al. 1991; Fones et al. 1998; Pizarro et al. 2001). Metals enter into seawater through point and non-point source, and originate from natural processes and anthropogenic influences. Enrichment of elements/metals concentration in the seawater can be modified regionally through volcanic activity, leaching from shale and pyrite concretions, metheorization, erosion of the detritus phases of the rocky basement and fluvial contribution (Humborg et al. 1997). In addition to these sources, rivers deliver significant amounts of dissolved solids into the seawater and these can alter the physico-chemical parameters in the local seawater by dilution or enrichment of some major and minor ions (Libes 2011). Anthropogenic sources such as domestic and sewage effluents, industrial discharges and offshore petroleum platforms also may enrich the dissolved metal levels in the local seawater.

In this present study, except for Fe and Rb, the average concentration of trace elements is higher in the POM compared to the monsoon season. The enrichment of Fe and Rb concentration during the monsoon season was due to the riverine runoff from the Baram River. High concentrations of elements at near-shore sampling locations, especially in the Kualabaram estuary area, Kampong Baraya beach, Fish Landing center and Esplanade Beach are probably a result of river flush-out during a water tidal phenomenon, as each sampling location is located parallel and adjacent to these riverine input areas. Zn, Cd and Mn in the monsoon season and Cu, Pb, Co, Ni, Fe, Rb and Cr concentration in the POM season are higher for the samples collected near the riverine influence area.

Most of the analyzed elements except for Fe and Ni, showed higher concentrations at the Kampong Baraya beach in the monsoon season due to leaching of shale and pyrite concretions, but their maximum concentration was observed at the NE segment of the study area. Higher concentrations of Mn, Co and Rb were observed in the SW segment. The shale and pyrite concretions were commonly noticed in the Sibuti and Tukau Formations located near the beach areas of the SW segment. Elements in pyrite concretions are leached due to the oxidation process and mix with seawater by small streams. Many small drainage/streams which originate from these geological formations may leach and carry with them an increase of trace metals into the coastal environment. Nickel and Rb concentration are enriched in the Esplanade beach during the monsoon season because many small streams from households and construction fields directly mix with seawater near this beach area. Fe concentration was observed higher at Lutong beach during the monsoon season particularly near the crude oil storage areas whereas; lower concentrations were noticed in the Miri River estuary area. This may be due to the flocculation process where dissolved forms of Fe in the estuarine area of the Miri River settle to the bottom due to seawater chemistry. The flow of water in this river was low compared to the Baram River. Higher concentrations of Pb and Zn were observed at the Fish landing center in the monsoon season, this may be due to the use of petroleum fuels in boat engines (point sources). Enrichment of Cd concentration was observed in the Kualabaram estuary area and Kampong Baraya beach location.

Cu concentration in both seasons was higher in in the NE segment, showing a gradual increase in concentration moving from Bungai beach towards the Kualabaram estuary mouth during the POM season. Water currents during this season play an important role in the distribution of dissolved forms of Cu along this coast. During the POM season, except for Zn, all the remaining element/metal concentrations were higher in the NE segment. Among the analyzed elements, Pb showed the maximum concentration during this season.

Concentrations of Cu, Pb, Co, Ni, Fe, Rb and Cr were higher in the Fish Landing center during the POM season. Many industries such as the fiber boat industry, concrete curling, ceramics, farm houses and hatcheries are located near this area. In addition to these industries, a smaller river (Lutong River) which runs through the palm oil planation sites, housing areas, passing through industrial areas and finally draining into SCS near this sampling location. Higher Cd concentrations were observed at Piasau beach. Cd in marine environments generally exist as positively charged divalent ions, and thus can be adsorbed onto solid surfaces with negative electrical charges (Benjamin and Leckie 1982). The electrically charged solid surfaces are clays, organic matter, carbonate minerals and hydroxides of Fe and Mn. Cadmium is generally associated or adsorbed in solid particles and removed during the extraction process. Many researchers found a strong association between Cd and organic matter in the coastal environment (Rosental et al. 1986). The enrichment of Mn in marine environments takes place mainly as a result of the redox process, from mineral weathering and from atmospheric dust, originating from both natural and anthropogenic sources (Schenau et al. 2002). The higher concentration of Mn at Piasau Beach is due to the microbial degradation of organic matter, which then releases the soluble forms of Mn oxides into the coastal environment. Manganese is also derived from river run off because a slight increase in the concentration of Mn was recorded in the sampling locations near riverine area for both seasons.

4.8 Statistical Analyses

4.8.1 Correlation Analyses

The Pearson correlation analysis was performed for physico-chemical parameters and trace elements concentration in the seawater samples individually, and for both seasons. Correlations between trace elements may reflect information regarding their source of origin, their associations and the migration of these elements. A high significant correlation between two elements indicates these elements share similar pollution sources or they may share analogous transformation in certain circumstances (Vega et al. 1998; Sun et al. 2010).

During the monsoon, except for Zn, there was no significant correlation between trace elements and the physico-chemical parameters (Table 4.5). The metal Zn alone showed a negative correlation with physical parameters such as pH, DO, EC, salinity and positive correlation with turbidity. Zn also correlates negatively with major and minor ions except sulphate. Inter-elemental positive correlations were observed between trace elements/metals as Zn with Cd and Mn ($r = 0.650$; 0.595 respectively, $p < 0.01$), Pb with Mn and Rb ($r = 0.783$ $p < 0.01$, 0.578 $p < 0.01$ respectively), Cd-Mn ($r = 0.502$, $p < 0.05$), Mn with Fe and Rb ($r = 0.568$ $p < 0.\ 01$, $r = 0.598$ $p < 0.01$) and Fe-Rb ($r = 0.548$, $p < 0.01$). Co showed a negative correlation with Fe and Mn ($r = -0.700$, -0.654 respectively, $p < 0.01$).

One notable feature was Mn was positively correlated with Zn, Cd, Pb, and Rb. Remobilization of Mn from the coastal sediments due to an intense early diagenesis of organic rich sediments is an important process for its release to the open ocean (Elderfield 1976; Froelich et al. 1979; Heggie et al. 1987; Johnson et al. 1992; Naylor et al. 2004; Pakhomova et al. 2007). During such a remobilization trace elements *viz.*, Zn, Cd, Pb and Rb, which are adsorbed onto Mn-oxides, may also be released into the water column. Most of the Mn released in this way is reoxidized (Crerar and Barnes 1974; Klinkhammer and

Bender 1980; Hem and Lind 1991; Von Langen et al. 1997) resulting in the formation of colloidal Mn-oxides, which serve as potential scavengers for trace elements in the water column. Thus, the association of Mn with Zn, Cd, Mn, Pb and Rb is due to their adsorption onto colloidal Mn-oxides. Since the trace elements content in both dissolved and < 11 μm particulate form were measured together, there was a very good possibility of the presence of colloidal manganese hydrous oxides in the seawater samples taken for analysis. In the case of Co, it normally exists in dissolved form due to its desorption in the seawater (Li et al. 1984; Takata et al. 2010) whereas, riverine Fe and Mn flocculates under increasing seawater influence. This explains the observed negative correlation between Co *vs.* Fe and Mn.

During the POM season the following parameters were correlated (Table 4.6) and any associations are addressed: i) turbidity and Fe ($r = 0.544$, $P < 0.01$) due to resuspension of colloidal iron (Wen 2006); ii) HCO_3^- *vs.* Ni (0.540; $P < 0.01$), and Cd (0.471; $P < 0.01$) due to desorption from the sediments/complexation (Wong et al. 2013; Westrup et al. 2005); iii) SO_4^{2-} vs. Fe (-0.576; $P < 0.01$) due to sulphide oxidation (Wong et al. 2010); iv) K *vs.* Co (0.471; $P < 0.01$), K *vs.* Ni (0.454; $P < 0.01$), and K *vs.* Cd (0.644; $P < 0.01$) due to ionic interactions (Ćosović et al. 1982; Förstner 1986; Sadiq 1989; Millero and Pierrot 2001; Cenci and Martin 2004). Inter-elemental relationships are observed between Cu *vs.* Ni (0.461; $P < 0.01$), Cu *vs.* Cd (0.589), Cu *vs.* Rb (0.744), and Cr (0.678); Pb *vs.* Ni (0.482, $P < 0.01$); Co vs. Fe (0.577; $P < 0.01$), Co *vs.* Cd (-0.460, $p < 0.05$); Ni *vs.* Cd (0.638; $P < 0.01$), Ni *vs.* Rb (0.472; $P < 0.01$), Ni *vs.* Cr (0.-0.560; $P < 0.01$), Cd *vs.* Rb ($r = 0.539$, $p < 0.01$), Mn *vs.* Rb (0.488, $p < 0.01$), Fe *vs.* Cr (0.650, $p < 0.01$) and Rb *vs.* Cr ($r = 0.509$, $p < 0.01$). Such complex relationships among these elements require further investigation. This has been addressed using factor analysis under section 5.9.

Correlations between trace elements and physico-chemical parameters depend on the chemical properties and mobile forms of the elements, and are controlled by the variations of the parameters in situ (Ke 1991; Zhang et al. 2015). In the present study, almost all the trace element concentrations in the seawater samples originated from natural sources such as the weathering of parental rocks, leaching from shale and pyrite concretions in the Sibuti and Tukau formations and riverine influence. Ocean water currents and freshwater mixing responsible for the distributions of these trace elements all along the Miri coast due to the amount of water released by the Baram River which flows into the South China Sea. The slight increase of metal concentrations at certain sampling locations, specifically at the NE segment of the study area, was due to anthropogenic activities such as waste discharges from industrial areas, run-off from fiber boat manufacturing, effluents from small-holder farms, runoff from plantation sites all dumped into small streams and finally, by atmospheric deposition (Ip et al. 2007; Jonathan et al. 2011; Qiao et al. 2013; Zhang et al. 2015).

4.8.2 **Partition coefficient of trace elements**

In the study of trace elements, considerations based on their water column characteristics shall provide only minimal information with regard to their concentration and association with dissolved and particulate forms. In order to further understand the exchange of elements between water column and sediments, and to understand the environmental parameters regulating them, it is essential to compute the partition coefficient. Such a calculation was made and the data was further subjected to correlation analysis (Appendix A). To understand the processes controlling the geochemical mobility of trace elements, the correlation analytical results were combined with the factor analytical result of the sediments and discussed in detail in section 5.9.

Table 4.5 Pearson Correlation analysis for the monsoon season

	Temp	pH	DO	EC	Turb	Sal	PO_4	SO_4	CO_3	HCO_3	Mg	Ca	Cl	K	B	Cu	Zn	Pb	Co	Ni	Cd	Mn	Fe	Rb
Temp	1.000																							
pH	.179	1.000																						
DO	-.209	.197	1.000																					
EC	.072	.753	.585	1.000																				
Turbidity	-.339	-.496	-.229	-.413	1.000																			
Salinity	.071	.758	.585	1.000	-.413	1.000																		
PO_4	-.413	-.419	-.244	-.355	.509	-.360	1.000																	
SO_4	.240	.589	.389	.805	-.105	.802	-.144	1.000																
CO_3	-.006	.620	.643	.850	-.399	.852	-.310	.647	1.000															
HCO_3	.105	.573	.457	.774	-.352	.773	-.428	.594	.398	1.000														
Mg	.157	.704	.645	.907	-.537	.908	-.485	.657	.809	.769	1.000													
Ca	-.157	-.243	-.561	-.458	.528	-.460	.532	-.193	-.409	-.565	-.732	1.000												
Cl	.046	.717	.645	.981	-.401	.982	-.339	.787	.892	.691	.882	-.424	1.000											
K	.110	.596	.490	.900	-.207	.901	-.314	.851	.796	.672	.824	-.452	.891	1.000										
B	-.015	.583	.509	.777	-.211	.777	-.376	.588	.651	.659	.737	-.507	.753	.736	1.000									
Cu	-.241	-.277	.019	-.118	-.074	-.118	.117	-.117	.135	-.346	-.092	-.159	-.102	.020	-.031	1.000								
Zn	-.197	-.483	-.596	-.662	.519	-.665	.568	-.410	-.541	-.757	-.847	.860	-.646	-.627	-.589	.185	1.000							
Pb	.068	-.143	-.508	-.461	.113	-.463	.068	-.258	-.413	-.491	-.616	.661	-.434	-.491	-.392	-.114	.622	1.000						
Co	-.302	-.159	.353	.053	.128	.060	-.275	-.101	-.050	.260	.184	-.467	.032	.134	.155	.184	-.293	-.296	1.000					
Ni	-.004	-.079	.172	.016	.162	.019	-.244	-.030	.067	-.081	.014	-.082	.033	.041	.040	-.076	-.024	.095	.389	1.000				
Cd	-.241	-.376	-.393	-.433	.418	-.438	.432	-.228	-.233	-.570	-.611	.617	-.413	-.385	-.401	.208	.650	.387	-.458	.082	1.000			
Mn	.128	-.073	-.590	-.409	-.028	-.416	.246	-.269	-.370	-.445	-.557	.664	-.409	-.535	-.366	-.163	.595	.783	-.700	-.233	.502	1.000		
Fe	.520	.188	-.099	.079	-.288	.070	-.178	.112	.046	.087	.038	.092	.085	-.077	.178	-.466	-.086	.306	-.654	-.113	.052	.568	1.000	
Rb	.235	.188	-.348	-.110	-.259	-.111	-.002	-.059	-.101	-.151	-.153	.207	-.118	-.185	-.036	-.221	.139	.578	-.405	.123	.063	.596	.548	1.000

Table 4.6 Pearson Correlation analysis for the post-monsoon season

	Temp	pH	DO	EC	Turb	Sal	PO_4	SO_4	Mg	Ca	Cl	K	B	Cu	Zn	Pb	Co	Ni	Cd	Mn	Fe	Rb	Cr	HCO_3
Temp	1.000																							
pH	-.420	1.000																						
DO	-.473	.119	1.000																					
EC	-.669	.742	.240	1.000																				
Turbidity	-.486	.228	.368	.190	1.000																			
Salinity	-.664	.743	.233	1.000	.185	1.000																		
PO_4	-.118	-.169	.208	-.148	-.025	-.152	1.000																	
SO_4	-.497	.616	.205	.888	-.106	.890	-.181	1.000																
Mg	-.666	.715	.266	.968	.132	.967	-.115	.886	1.000															
Ca	.429	-.504	-.293	-.596	-.096	-.592	.190	-.507	-.724	1.000														
Cl	-.650	.597	.195	.933	.099	.932	-.107	.893	.909	-.509	1.000													
K	-.463	.565	.202	.819	.122	.823	-.179	.660	.755	-.417	.704	1.000												
B	-.634	.533	.468	.769	.340	.765	-.003	.547	.719	-.489	.617	.749	1.000											
Cu	.077	-.147	-.013	-.184	-.008	-.182	.169	-.339	-.193	.151	-.278	.260	.100	1.000										
Zn	-.080	.220	-.266	.173	-.184	.170	-.365	.346	.247	-.224	.260	-.037	-.237	-.298	1.000									
Pb	-.121	-.044	.135	-.011	.233	-.013	-.180	.003	.007	.049	-.018	-.065	-.100	.202	.181	1.000								
Co	-.196	-.167	.465	-.276	.420	-.285	.425	-.364	-.238	-.018	-.276	-.471	-.016	-.100	-.101	.114	1.000							
Ni	-.337	.322	.112	.295	.243	.296	-.228	.129	.265	-.145	.184	.454	.292	.461	.060	.482	-.267	1.000						
Cd	-.151	.288	-.081	.336	-.015	.344	-.263	.230	.316	-.125	.251	.644	.301	.589	.186	.262	-.460	.638	1.000					
Mn	.057	-.236	.126	-.044	-.036	-.039	-.063	-.053	-.071	.112	-.029	.143	.147	.330	-.042	.240	.069	-.035	.416	1.000				
Fe	-.146	-.271	.255	-.327	.544	-.339	.204	-.576	-.306	-.030	-.391	-.337	-.010	.221	-.320	.140	.577	.146	-.270	-.143	1.000			
Rb	-.036	-.150	.112	-.104	.049	-.101	.070	-.241	-.100	.053	-.102	.184	.061	.744	-.276	.429	-.034	.472	.539	.488	.178	1.000		
Cr	-.054	-.219	.285	-.199	.214	-.205	.189	-.374	-.226	.086	-.285	.081	.086	.678	-.360	.255	.196	.560	.173	-.012	.650	.509	1.000	
HCO_3	-.658	.556	.352	.715	.211	.712	.083	.513	.651	-.366	.629	.778	.771	.231	-.049	.013	-.128	.540	.471	.005	-.097	.137	.252	1.000

4.9 Comparison with Background Values and other literatures

"The natural background concentration of an element is commonly defined as the natural quantity of a given element in a certain material (in absence of external pollution), which is fundamental for the evaluation of soil and water pollution" (Zhang et al. 2015). In this study, the background concentrations of elements in the South China Sea were selected for geologic and geochemical concerns. Additionally, background concentrations in natural surface seawater, open pacific water and other coastal regions were also compared in order to evaluate the global comparability of our data (Table 4.7). The metal concentrations in this study significantly exceeded the background values for both seasons. This is due to analysis of dissolved and particulate metal concentration (< 11 µm) in the seawater. Geology of the study area and natural sources are important factors for the enrichment of trace/heavy elements along the Miri coast. Normally elements present in the dissolved form are very low compared to the particulate matter. When compared to the other literatures (Cuong et al. 2008; Adiana et al. 2011; Jonathan et al. 2011; Li et al. 2013b; Zhang et al. 2015) Pb, Co, Ni, Mn, Cr and Cd concentrations were significantly higher along the Miri coast. Copper, Zn and Fe concentrations were lower compared to the values reported from the Sabah, Sarawak and Brunei coast (Utoomprurkporn and Snidvongs 1999); Pondicherry coast, India (Solai et al. 2010); Acapulco coast, Mexico (Jonathan et al. 2011) and Guangdong coast, China (Li et al. 2013b).

Previous studies conducted by Utoomprurkporn and Snidvongs (1999) in the South China Sea covering the areas of Sabah, Sarawak and Brunei Darussalam suggested that Cd, Ni, Cu and Pb were mostly present in the dissolved form while Fe was in particulate form at most of the sampling stations because Fe is a geo-chemically controlled element. It was also observed the distribution of Cu, Fe, Pb and Ni in the South China Sea reflected some effects from the river inputs of Baram and Rajang Rivers. But the higher concentration of Cd was observed near the offshore oil/gas stations and the concentrations increased in a vertical direction near these offshore platforms. Jonathan et al. (2011) reported higher concentration of Fe in the seawater collected from the Acapulco coast, Mexico which was significantly higher than the present study concentration.

Table 4.7 Comparison of dissolved (µg/L) and particulate (µg/g) concentration of trace elements in seawater with those in some other regions in the world

Location	Cu	Zn	Pb	Co	Ni	Cd	Mn	Fe	Rb	Cr	Source
Range in monsoon Season (µg/L)	8.1 -13.0	34.2-38.7	78.2-95.1	44.0-52.5	63.9 - 77.2	10.6 - 14.4	3.7 -9.9	431.4 - 569.9	19.0-32.5	-	present Study
Average (µg/L)	10.5	35.7	88.7	48.0	70.8	11.3	6.8	491.2	28.2	-	present Study
Range in POM Season (µg/L)	9.5 -16.7	54.7-59.9	138.9 - 158.7	58.8-75.0	98.4 - 118.8	19.5-23.0	7.1 -11.1	15.5-39.5	11.1-13.5	22.6-93.7	present Study
Average (µg/L)	13.8	57.8	149.1	65.5	104.5	21.5	8.6	25.3	12.5	36.5	present Study
Terengganu coast, Malaysia (Dissolved µg/L)	ND	ND	0.03-0.49	ND	ND	0.002-0.19	0.04-2.71	ND	ND	ND	(Adiana et al. 2011)
Terengganu coast, Malaysia (Particulate µg/g)	ND	ND	10-4277	ND	ND	45-249	21-2885	ND	ND	ND	(Adiana et al. 2011)
Sabah, Sarawak and Brunei (Dissolved nM)	2.9-20.5	ND	0.02 - 1.50	ND	1.3 - 14.1	0.01 - 1.37	ND	47 – 2020	ND	ND	(Utoomprurkporn and Snidvongs 1999)
Northern Taiwan Coast (Dissolved nM)	0.37-1.74	10.3-74.9	0.09-0.43	ND	ND	0.03-0.14	8.5 -24.2	24.3-93.0	ND	4.35-6.86	(Fang et al. 2006)
East GD coast , China (Dissolved µg/L))	2.24	14.05	1.94	ND	ND	0.11	ND	ND	ND	1.2	(Zhang et al. 2015)
West GD coast China (Dissolved µg/L)	1.91	11.86	1.81	ND	ND	0.09	ND	ND	ND	1.27	(Zhang et al. 2015)
Coast of Saronikos Gulf, Greece (µg/L)	2.8	4.21	2.85	ND	1.48	0.28	1.19	ND	ND		(Ladakis et al. 2007)
Guangdong coast, China (Dissolved µg/L)	0.24-2.6	1.0-139	0.03-10.2	ND		0.04-0.91		ND	ND	0.31-0.86	(Li et al. 2013b)
Pondicherry coast, India (µg/L)	1.2 -10.7	6.1 -80.1	1.2 -47.5	ND	ND	0.2 -5.3	2.3 -51.3	ND	ND	0.5-10.5	(Solai et al. 2010)
Kalpakkam coast, India (µg/L)	3.50-4.95	26.55 - 44.26	1.2 -8.1	0.04-0.15	2.8 -5.35	0.24-0.52	1.34-4.11	ND	ND	0.15-0.55	(Padhi et al. 2013)
Acapulco, Mexico (µg/L)	1.61-48.52	5.77 - 410.10	0.40 - 44.97	ND	0.19-54.72	0.06-4.89	0.06-5.04	41-13,400	ND	0.01-0.59	(Jonathan et al. 2011)

Location	**Cu**	**Zn**	**Pb**	**Co**	**Ni**	**Cd**	**Mn**	**Fe**	**Rb**	**Cr**	**Source**
Singapore (total µg/L)	1.25-5.72	5.42-15.37	0.11-0.51	ND	0.46-2.10	0.02-0.08	ND	ND	ND	0.65 - 2.72	(Cuong et al. 2008)
Reloncavi Fjord, Chile (µg/L)	3.15	ND	0.74	0.04	1.43	0.14	3.17	20.15	ND	0.25	(Ahumada et al. 2011)
[a] The Background value (µg/L)	0.01-0.04	0.01	0.005-0.015	ND	ND	0.01	ND	ND	ND	ND	(Wu and Zeng 1983)
[b] The Background value (µg/L)	0.084	0.057	0.057	ND	ND	0.006	ND	ND	ND	ND	(Tao 2003)

[a] The background value of natural surface seawater; [b] The background value in the South China Sea

4.10 Summary

The physico-chemical parameters of the water column were perturbed by the influence of freshwater inputs from the Baram and Miri rivers, apart from several other smaller streams. The concentration of trace elements in the seawater exhibits different patterns during the monsoon and POM season. During the monsoon, Fe concentration was comparably higher and all other trace elements showed the opposite trend. Pearson's correlation analysis revealed levels of all trace elements in the water column was controlled by Mn-oxides. However, in the case of cobalt, desorption from the suspended sediments played a dominant role during the monsoon. Resuspension, desorption, complexation, sulphide oxidation and ionic interactions exert control over trace elements concentration in the seawater.

Finally after examining both seasons' results, natural sources and processes play an important role in the enrichment of these analyzed elements. In addition to the natural influence, anthropogenic sources at certain sampling locations, also contribute additional trace elements in the NE segment. Ocean currents, tidal differences, strong local winds, freshwater mixing and monsoonal effects were the main factors which controlled the temporal distribution of trace elements and physico-chemical properties of the seawater along the Miri coast. The SW segment of the coast was dominated by more natural processes, whereas the majority of the NE segment sites were controlled by riverine influences. The analyzed elements exceeded the background level concentrations in seawater. Ocean current turbulence led to resuspension of the surface sediments and a release of some elements from the sediment particles towards the water column. The observed increase in the concentration of Pb, for both seasons, suggested an additional input of this metal from the continent. Compared to ASEAN-Marine Water Quality Management guideline values all the analyzed trace metal concentrations exceeded their standard background value for both seasons, but the nutrient concentrations were below the maximum permissible level.

Chapter 5 **Geochemistry of Sediments**

This chapter explains the mobility and dynamics of operationally determined chemical forms of trace/heavy metals in the surface sediments and their ecological risk on biotic life through metal speciation studies.

5.1 Introduction

The Miri coast extends from the north-east to the south-west direction for about 74 kms. Based on particle size analysis the study area along this coast is divided into two segments – the northeastern (NE) and the southwestern (SW) segments. The NE segment is dominated by fine sand, and the SW segment is dominated by silt. The Kualabaram estuary (KBE), Fish Landing center (FLC), Lutong Beach (LB), Piasau Beach (PBC) and, Miri River estuary (MRE) fall under the NE segment, whereas, Park Everly Beach (PVB), Tanjong Lobang Beach (TB), Esplanade Beach (ESP), Kampong Baraya Beach (KPB), Hawai Beach (HWB) and Bungai Beach (BB) are in the SW segment (Figure 1.2).

Many industrial activities such as shipbuilding and dry-dock industries, timber processing and plywood/industrial wood companies, palm oil extraction facilities, fish landing centers, concrete curling and steel manufacturing, as well as crude oil storage facilities are all located along the NE segment of the Miri coast. In addition, the Baram and Miri Rivers deliver an enormous amount of water, suspended matters, sediments and associated humus and organic debris from the upper Baram region into the South China Sea (SCS). The SW segment of the Miri coast consists of tourist beaches which are mainly used for recreational, fishing and diving activities as well as other tourist activities. In addition, agricultural activities (mainly palm plantations) are also common adjacent to the SW segment of the study area.

The analytical results of the sediments collected during the monsoon and post-monsoon seasons are discussed in this chapter. A thorough discussion is presented of the general characteristics of the sediments and the distribution and geochemical fractionation of trace elements in various compartments of the sediments. The bioavailability and risk assessment of metal toxicity are then made based on national and international sediment quality guidelines.

5.2 General characteristics of sediments

The sediments were mainly composed of fine sand and silt; coarse fraction was less than 1% (Figure 5.1). During the monsoon the average percentage of fine sand was less (62%) than the POM period (73%). Silt, on the contrary, was more dominant during the monsoon (38%) than POM (27%). Silt was dominant near the river discharge areas notably, at the Baram and Miri river outlets. Coarse sand was only observed in the SW segment. The calcium carbonate content ranged from 0.52% to 2.51% with an average of 1.33% during the monsoon and 0.49% to 6.33% with an average of 1.78% in the POM (Figure 5.2). The organic carbon (OC) contents varied from 0.11% to 0.28% during the monsoon and 0.16% to 0.28% during the POM, with an average of 0.24% for both seasons (Figure 5.3). Higher OC content was observed at Piasau Beach for both seasons.

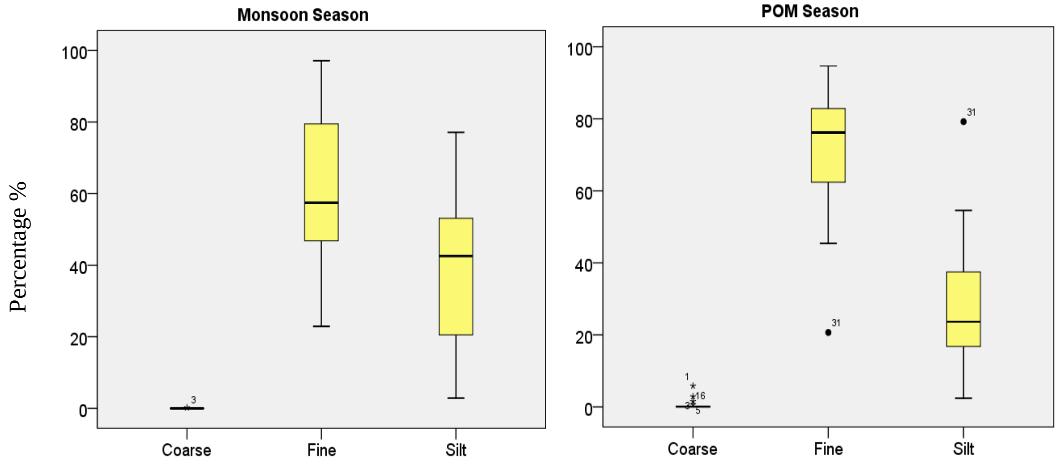

Figure 5.1 Particle size variation of beach sediments for both seasons

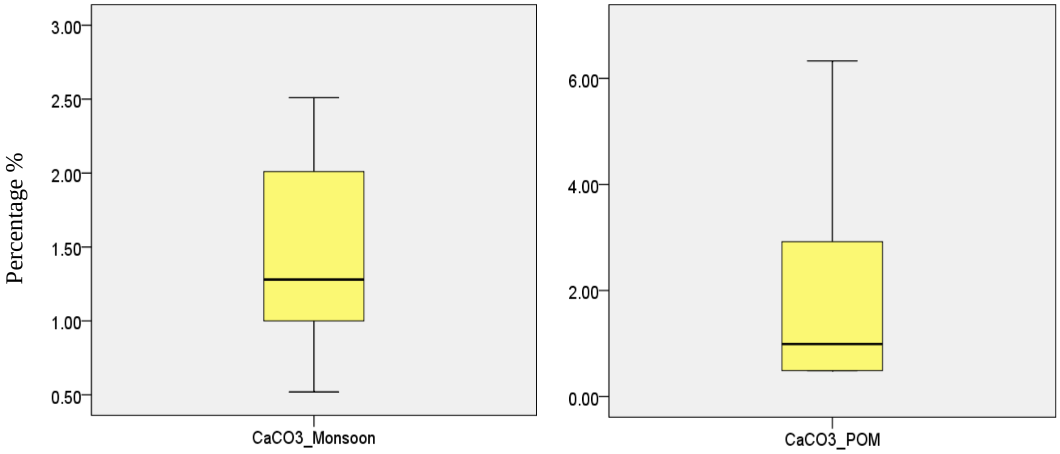

Figure 5.2 $CaCO_3$ concentrations in beach sediment for both seasons

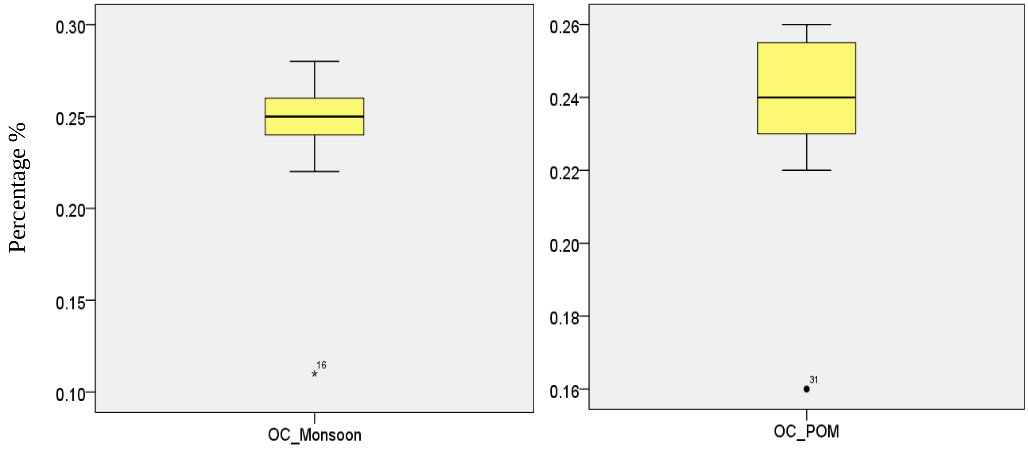

Figure 5.3 OC percentage in beach sediment for both seasons

5.3 Results of Total Digestion

The results of total digestion for the sediment samples collected in the monsoon season (December 2013; n=26); and POM (June 2014; n=31) are presented in Table 5.1 and Table 5.2 respectively. The distribution pattern of total trace elements/metals in the sediments are displayed in Figure 5.4 (Monsoon) and Figure 5.5 (POM). Among the nine metals (Cu, Cd, Cr, Co, Fe, Mn, Ni, Pb and Zn) analyzed, Fe concentration was observed as the highest and Cd concentration was observed as the lowest. The trace metal concentrations in the beach sediments can be shown in decreasing order: Fe > Cu > Zn > Cr > Mn > Ni > Co > Pb > Cd in the monsoon and Fe > Cu > Zn > Cr > Mn > Pb > Ni > Co > Cd in the POM respectively. Co and Ni concentration was recorded higher in the monsoon season and the remaining elements/metals (Cu, Pb, Cd, Zn, Fe, Mn and Cr) were slightly enriched in the POM season.

Table 5.1 Results of total digestion (µg/g dry weight) for sediment samples collected during the monsoon season (n=26) from the Miri coast.

Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr
BB 01	190.89	7.02	0.62	16.79	17.97	113.18	4300.44	40.72	41.01
BB02	160.8	6.96	0.68	15.12	17.42	96.04	4002.61	39.26	38.99
BB 03	184.81	9.67	0.63	12.71	16.49	107.55	3551.67	36.6	42.6
BB 04	242.26	11.69	0.9	9.25	13.67	149.23	3460.48	39.29	42.95
KPB 01	210.64	5.95	0.71	8.03	18.46	122.6	3476.4	34.26	31.76
KPB 02	200.02	5.89	0.61	12.32	20.13	117.19	3837.15	40.02	30.03
KPB 03	216.78	20.28	1.46	11.97	17.3	128.01	3514.6	39.63	34.52
HWB 01	218.9	8.08	0.47	15.02	20.9	127.68	3272.05	36.62	35.96
ESP 01	239.36	9.08	0.62	8.62	23.92	137.57	3856.95	41.14	36.4
ESP 02	231.04	7.66	0.66	9.86	23.74	139.29	3778.6	47.06	34.54
ESP 03	240.25	6.58	0.33	10.62	24.26	142.75	3981.4	37.77	43.11
ESP 04	240.31	9.41	0.5	16.38	27.84	146.75	3013.4	40.17	41.84
ESP 05	297.27	8.23	0.5	16.96	25.94	148.02	2793.15	32.2	42.19
TB 01	220.94	6.03	0.4	15.54	16.05	126.24	1900.15	21.26	44.75
TB 02	248.78	8.02	0.35	14.03	14.49	144.32	1817.54	20.64	47.26
MRE 01	193.86	11.02	0.15	10.38	20.24	111.16	5641.45	45.45	43.04
MRE 02	135.34	11.35	0.3	8.16	17.79	75.28	3112.25	27.65	40.15
MRE 03	140	10.65	0.3	7.27	18.57	82	2896.07	28.41	38.91
MRE 04	179.12	6.42	0.3	7.8	19.59	96.86	3063.58	30.96	41.95
PBC 01	188.1	8.17	0.1	15.02	14.93	105.76	3477.09	29.86	49.89
PBC 02	191.24	6.7	0.2	18.52	15.9	108.6	2842.57	28.7	47.02
LB 01	248.26	9.23	0.34	7.22	18.87	146.69	4281.7	33.06	50.33
LB 02	254.07	9.8	0.29	5.2	19.2	151.45	4319.35	31.48	50.51
LB 03	326.92	7.14	0.34	6.35	18.32	159.59	3877.15	30.09	47.49
FLC 03	221.74	8.54	0.48	5.54	20.13	119.78	5325.95	33.63	51.62
KBE 01	225.72	6.81	0.3	6.69	20.49	158.77	5789.45	41.34	58.8
Avg	217.21	8.59	0.48	11.21	19.33	125.48	3660.89	34.90	42.60
Min	135.34	5.89	0.1	5.2	13.67	75.28	1817.54	20.64	30.03
Max	326.92	20.28	1.46	18.52	27.84	159.59	5789.45	47.06	58.8
Std Dev	42.75	3.00	0.28	4.04	3.50	28.91	952.44	6.67	6.68

Table 5.2 Results of total digestion (µg/g dry weight) for sediment samples collected during the POM season (n=31) from the Miri coast

Sample ID	**Cu**	**Pb**	**Cd**	**Co**	**Ni**	**Zn**	**Fe**	**Mn**	**Cr**
BB 01	494.45	20.94	1.91	7.71	16.34	197.57	4093.05	41.46	51.56
BB02	520.93	21.84	1.17	10.51	18.58	219.83	6917.65	50	50.91
BB 03	597.2	15.95	1.12	9.72	18.64	250.38	4609.4	41.8	54.03
BB 04	545.66	34.67	0.99	9.8	16.57	225.58	4575.1	43.97	49.84
KPB 01	327.64	21.04	2.02	10.37	17.97	151	4114.75	46.58	40.19
KPB 02	285.48	22.34	1.83	5.43	15.85	136.36	4934.5	43.57	43.88
KPB 03	441	32.58	1.81	2.89	17.18	203.86	5103.85	50.2	50.31
HWB 01	321.42	18.71	1.81	4.04	16.57	137	3845.1	34.84	43.99
ESP 01	222.32	22.11	1.81	7.85	19.54	137.41	3108.55	37.78	39.34
ESP 02	205.88	21.49	1.4	5.75	17.59	123.33	3354.65	32.67	39.69
ESP 03	553.55	30.86	0.8	6.22	13.05	235.52	4453.15	49.74	48.19
ESP 04	210.46	21.42	0.84	9.36	13.45	127.74	3745.35	42.5	44.24
ESP 05	232.88	23.55	1.05	7.7	14.88	140.05	3102	36.25	45.16
TB 01	255.55	26.33	1.25	6.8	15.84	152.86	2123.2	30.97	43.19
TB 02	219.77	16.25	1.09	4.5	14.22	132.01	1874.4	23.53	49.25
PVR 01	144.05	14.17	0.52	8.53	19.59	91.48	5776.25	69.82	59.37
MRE 01	192.15	15.89	1.04	3.86	22.8	123.38	4789.85	31.78	60.77
MRE 02	109.98	17.34	0.98	3.76	16.58	81.97	3553.25	31.65	68.17
MRE 03	164.97	19.45	1.3	5.04	19.4	103.91	3897.3	33.57	69.91
MRE 04	214.77	14.2	0.91	3.3	16.39	136.99	3210.5	26.85	61.81
PBC 01	216.39	21.87	1.3	5.46	18.32	134.16	2570.55	25.22	47.01
PBC 02	216.09	32.04	1.14	4.65	17.71	115.55	2517.2	29.42	51.1
LB 01	201.45	9.62	1.24	4.62	20.24	137.05	2054.6	22.15	53.63
LB 02	206.72	14	1.33	5.19	22.65	130.31	5559.8	72.23	96.55
LB 03	335.76	14.38	1.35	4.87	19.38	189.01	3592.45	33.59	52.91
FLC 01	546.78	22.35	0.3	5.54	27.22	248.9	6339.95	83.68	98.54
FLC 02	348.84	12.06	0.39	6.62	20.03	175.26	4781.53	41.26	62.46
FLC 03	617.76	26.55	1.19	7.25	18.49	258.95	4415.5	30.86	58.41
KBE 01	177.02	8.57	0.48	8.36	19.04	107.88	4823.3	31.86	50.97
KBE02	390.61	44.73	1.27	8.8	22.68	194.51	5616.3	63.54	101.72
KBE 03	211.49	9.89	0.34	8.86	23.26	139.21	8609.05	47.81	66.43
Avg	313.84	20.88	1.16	6.56	18.39	159.32	4260.07	41.33	56.57
Min	109.98	8.57	0.3	2.89	13.05	81.97	1874.4	22.15	39.34
Max	617.76	44.73	2.02	10.51	27.22	258.95	8609.05	83.68	101.72
Std Dev	150.28	8.05	0.46	2.23	3.09	49.44	1478.90	14.63	16.31

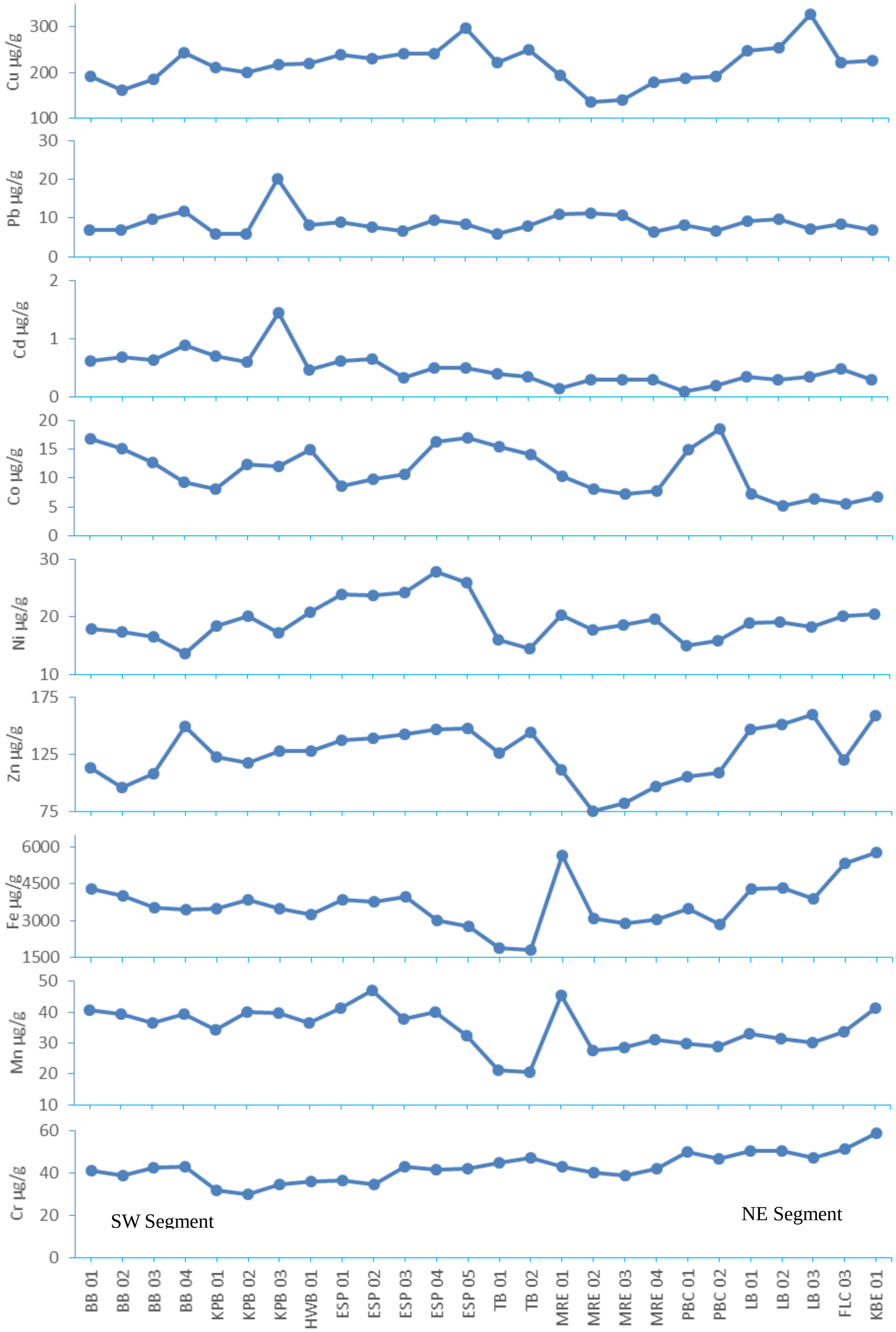

Figure 5.4 Distribution pattern of trace elements/metals in the sediments of Miri coast during monsoon season.

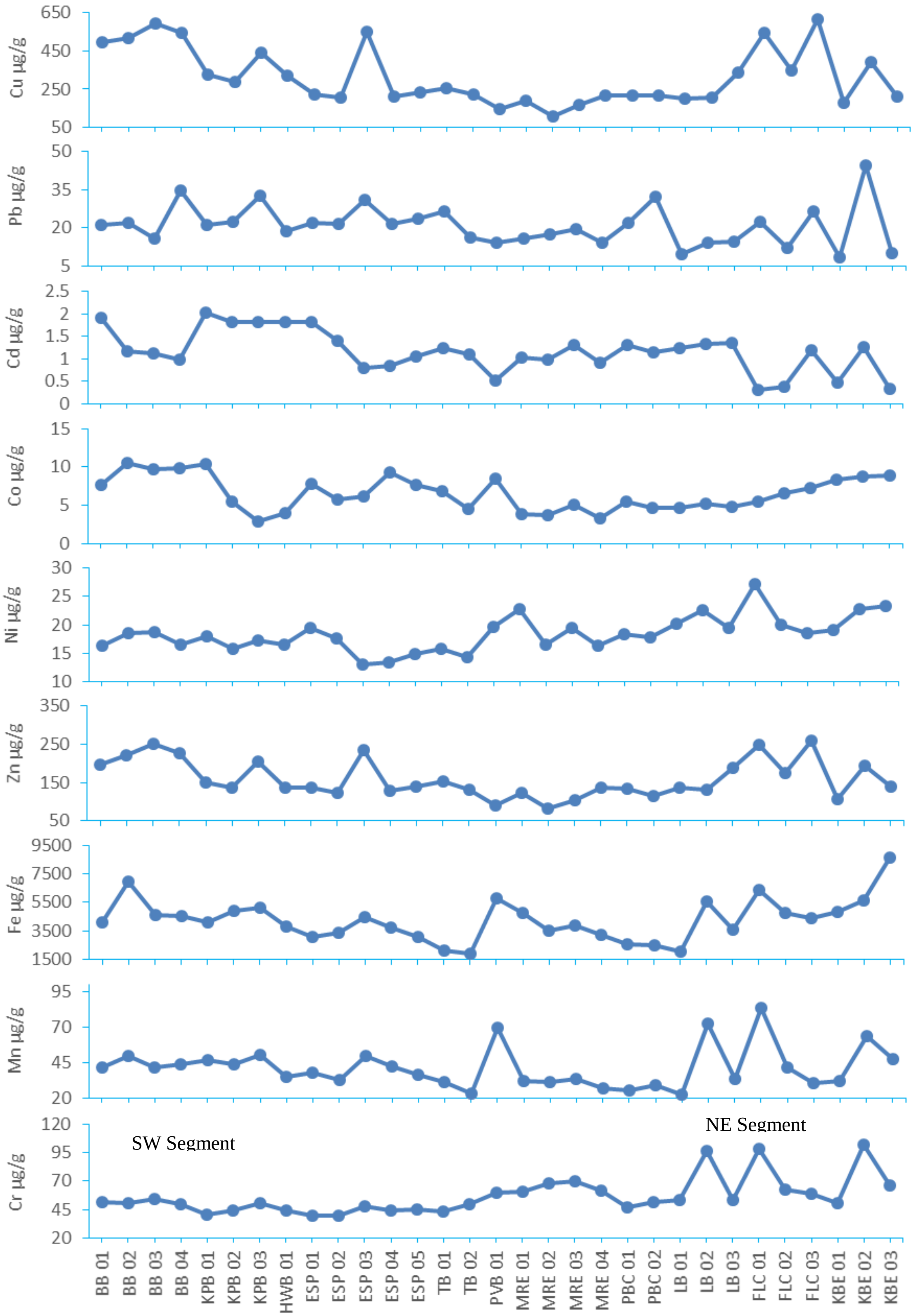

Figure 5.5 Distribution pattern of total trace elements/ metals in the sediments of Miri coast during POM season.

5.4 Distribution of total trace elements/metals in Monsoon Season

Iron concentrations in the sediments ranged from 1817.51 to 5789.45 µg/g with the highest concentration from the Kualabaram Estuary area and the lowest concentration from the Tanjong Lobang Beach. Manganese concentration was observed in the range of 20.64 to 47.07 µg/g with the maximum concentration from Esplanade Beach and the minimum concentration from Tanjong Lobang Beach. The distribution pattern of Cu and Zn was similar in the study area during the monsoon season. The concentration of Cu and Zn in the sediment samples varied between 135.34 – 326.92 µg/g and 75.28 – 159.59 µg/g respectively. The highest and lowest Cu and Zn concentration was noticed at the Lutong Beach and the Miri River Estuary area respectively. Lead concentration was in the range of 5.89 – 20.28 µg/g, maximum concentration is observed in the Kampong Baraya beach. Similar to Pb, Cd concentration was also higher in the Kampong Baraya beach and the concentration varied between 0.1 and 1.46 µg/g. The concentration of Cr in the sediment samples ranged from 30.03 to 58.80 µg/g. The higher and lower concentrations were observed from the Kualabaram Estuary and the Kampong Baraya Beach respectively.

Cobalt concentration was in the range of 5.20-18.52 µg/g and the highest and the lowest concentration was recorded from the Piasau Beach and Lutong Beach, respectively. Nickel concentration varied from 13.67 to 27.84 µg/g with the maximum and minimum concentrations from the Esplanade and Bungai Beach respectively. As the results illustrate, the sediment samples collected near the riverine and small drainage channels (i.e. the Kualabaram Estuary area, Lutong River, Miri River Estuary area, and Esplanade Beach) showed a higher concentration of Cu, Zn, Fe, Mn, Cr and Ni. Subsequently, these elements were distributed to the adjacent regions by longshore and littoral ocean currents. Except for Pb, Cd, Ni and Mn the remaining elements/metals were enriched in the NE segment of the study area.

5.5 Distribution of total trace metals in the POM Season

Iron concentration in the POM season showed a wide range of 1874.40 – 8609.05 µg/g and the highest and lowest concentrations were recorded from the same locations as the monsoon season. Manganese concentration was in the range of 22.15 – 83.68 µg/g with the highest concentration from the Fish Landing Center and the lowest concentration from Lutong Beach. The Cr concentration in the sediments varied between 39.34 and 101.72 µg/g with the maximum and minimum values coming from similar locations as in the monsoon season. Manganese and Cr concentration in the sediment samples showed a similar trend in their distribution, particularly in the NE segment of the Miri coast. Copper and Zn showed a similar distribution pattern as reported in the monsoon season and their concentration varied between 109.98 – 617.76 µg/g and 81.97 – 258.95 µg/g respectively. The highest concentration of Cu and Zn was noticed at the Fish Landing center.

Except Co and Ni, the remaining elements/ metals were marginally enriched in the POM compared to the monsoon season. Indications are there is a seasonal variation that affects the accumulation of trace/heavy metals in the sediment samples. Lead concentration was in the range of 8.57 – 44.73 µg/g with the maximum concentration from the Kualabaram Estuary. Cadmium concentration was higher in the Kampong Baraya sediments with concentrations in the range of 0.30 – 2.02 µg/g. Cobalt concentration was recorded in the ranges of 2.89 – 10.51 µg/g, and the highest concentration was from Kampong Baraya Beach. Nickel concentration varied between 13.05 and 27.22 µg/g with the maximum concentration coming from the Fish Landing Center and the minimum concentration coming from Esplanade Beach. Apart from Cd and Co, all other elements/metals concentrations were recorded higher in the NE segment of the Miri coast.

5.6 Characteristics of elements/metals based on sampling locations

5.6.1 Bungai Beach (BB)

Bungai Beach is located in the SW segment of the Miri coast, 74 Km from the Baram River outlet and this beach is a popular recreational area situated near Bekenu town. Bungai Beach consists of various natural cliffs and lithology such as sandstone, siltstone, coal laminae and an undisturbed fossil rocky shore. Agricultural activities such as chili plantations and palm plantations were observed in and around the Bungai Beach area. Higher concentrations of Cu, Co, Pb and Zn were observed in the sediments during the POM season, this may be due to natural processes, such as leaching of these elements/metals from sedimentary rocks/concretions. Apart from natural influences, anthropogenic sources also added additional stress to increase Pb concentration at certain sampling locations of the study area.

5.6.2 Kampong Baraya Beach (KPB)

Kampong Baraya Beach is located in the SW segment of the Miri coast. Palm plantations were commonly observed along the shoreline of this area. Three small streams were evident at this beach, with one to two kilometers between them, discharging water with organic debris from plantation sites and kampong (village) near this region into the SCS. In addition, shale with pyrite concretions was commonly noticed along or near the beach area. The sediments from this beach showed a slightly higher concentration of Pb and Cd and this may be due to the influence of leaching of pyrite concretions and shale from the sediments' source area.

5.6.3 Esplanade Beach (ESP)

Esplanade Beach is another important location for recreational activities along this shoreline. This is also the largest beach in the area, extending 5 to 6 km along a straight shoreline. Two small streams discharge domestic/storm water from nearby households and construction activities were also observed near this area during the sample collection. Higher Ni & Co concentration was observed in this location for both seasons. An increase in Cu, Cr, Pb and Zn concentrations during the POM was observed, which may be due to the influence of anthropogenic sources such as small-scale industrial manufacturing and household waste discharges located near the beach area as well as various natural causes.

5.6.4 Tanjong Lobang Beach (TB)

Tanjong Lobang Beach is also another important recreational area along the Miri coast and is very busy during the weekends. Sandstone cliffs are commonly noticed along this beach which is shaped somewhat like a bay. One segment of the beach area has been completed eroded by wave action. The analyzed elemental/metal concentrations were low in this beach area for both seasons, compared to other beaches. Newly developed shopping lots and housing apartments were common along the beach.

5.6.5 Park Everly Beach (PVB)

Park Everly Beach is a U-shaped bay and wave action is minimal in this zone compared to other beaches. The sediment samples were collected only during the POM season since construction activities were going on and the beach was inaccessible during the monsoon season. Iron and Mn concentrations were significantly higher in this area, due to the long-shore and littoral currents, which carried and discharged elements from the Miri River outlet. The increase in the Mn concentration in sediments may have arisen from the electroplating industries, automobile workshops and use of varnishes and anticorrosive paints for ship repairs at the dry-docks (Nagarajan et al. 2013) which are common near the waterfront area. Due to the minimal wave action in this area, the elemental/metal migration process is restricted and enrichment of elements was noticed.

5.6.6 **Miri River Estuary (MRE)**

The Miri River estuary zone is the outlet of Miri River. Among the analyzed elements/metals; Fe, Mn, Cr, Ni, Cu and Zn concentrations were higher in the river mouth area and these showed a decreasing trend moving towards the NE segment away from the river mouth. Many heavy and small-scale industries are located on the banks of the Miri River and enrichment of elements was noticed in the outlet of Miri River (Nagarajan personal collection) and finally discharged into the SCS.

5.6.7 **Piasau Boat Club Beach (PBC)**

The Piasau Boat Club Beach area is popular for leisure and sport activities, particularly for Shell and Petronas employees working offshore. Activities, like sailing, diving, fishing and other water sports and games are popular along this beach. Copper concentration in the sediments was higher at this beach during the monsoon season, particularly near the small stream emptying into the SCS. An increase in the Pb concentration was also noticed in the POM season near the drainage mixing zone.

5.6.8 **Lutong Beach (LB)**

Lutong beach is situated in front of the old Lutong Airfield and is also a popular entertainment zone for the local community. This beach is a popular location for activities such as paragliding, para-motor flying, swimming and motorcyclists. A small branch of the Miri River flows through the Lutong markets and household areas, finally discharging into the Miri coast near Lutong Beach. Another small stream runs through the areas of Satu Batu and a palm plantation (and along the Lutong-Kualabaram highway road) and finally discharges into the SCS near Lutong beach. In addition, there is a small village with approximately 50 families living along the shoreline of the Lutong Beach area. Their domestic and sewage waste have also had an impact on the increase of metal concentration at this beach. Higher concentrations of Cu and Zn were observed during monsoon season, at Lutong Beach near the discharging sites of the small streams which had flowed through household areas and a crude oil storage terminal area. An increase in the Mn and Cr concentration in the Lutong Beach sediments was also observed in the POM season.

5.6.9 **Fish Landing Center (FLC)**

The Fish Landing Center, covers a 5 to 6 km coastal stretch. Approximately 70 to 80 individual shops selling fish have been observed in this region. Industries such as vehicle tire, ceramics manufacturing, fiber boat construction and repair, concrete curling manufacturing, a shrimp hatchery as well as miscellaneous small-holder estates were situated in this zone. Nutrient loads from agriculture land (i.e. palm plantations and other crops) and prawn hatcheries located near the Satu Batu area have been mixed into this coastal area during the high tidal period. Among the analyzed elements/metals; Cu, Ni, Zn, Fe, Mn, Pb and Cr showed the maximum concentration in this zone during the POM season. The man-made activities observed were the application of anti-corrosive/fouling paints and dyes on fishing vessel hulls and nets; which contain zinc oxide. Zinc pyrithione is used to prevent boats from rusting (Braithwaite et al. 2007) and are regularly applied to fishing boats. As this matrix dissolves slowly in the seawater, it starts to leach into the water immediately and settles over the surface sediments.

5.6.10 **Kualabaram Estuary/beach (KBE)**

The Kualabaram estuary zone is located at the outlet of the Baram River and falls in the NE segment of the Miri coast. Sediments of this region were enriched with a concentration of natural elements such as Fe, Mn and Cr for both seasons. The Kualabaram River is the 2nd largest river in Sarawak and empties into the SCS near Kampong Kualabaram. The river was highly turbid due to high levels of suspended matter. The Baram River delivers, on average, 1445 m^3/s (4.55×10^{10} L/yr) of water and 12×10^{12} g/yr of sediment. Many public and private sector industries are situated on the banks of Baram River. Dry-docking facilities, ship building industries, timber processing plants, and construction companies, as well as Miri Port Authority activities including ferry and speed boat services are all located on the banks of the Baram River. A large quantity of freshwater flows into and oceanic currents disperse the organic matter wastes between the outlet of the Baram River and the Miri River area. Salinity along the Miri coast is mainly controlled by the Baram River, and the effect of a decrease in the salinity level was observed up to 20kms away from the Baram river mouth area. Agricultural (vegetation) and fishing activities were also noticed near the Baram River mouth zone. A large amount of organic and wood deposits were commonly observed during sample collection.

5.7 Modified BCR Sequential Extraction

For sediment quality assessment studies, measuring the total element/metal concentration alone is not sufficient to justify contamination status because heavy metals present in the sediments are in different chemical forms (Cottenie et al. 1980). So, in order to analyze the mobility and toxicity of bioavailable trace elements/metals, the sequential extraction procedure (SEP) is the best approach. This method provides more accurate information regarding the association and strength of the elements/metals with sediment and is successfully applied worldwide (Tessier et al. 1979; Ure et al. 1993; Morillo et al. 2004; Nemati et al. 2011; Chakraborty et al. 2014; Wali et al. 2015). The trace/heavy metals attached to the surface of sediments or minerals will be leached during certain changes in environmental conditions such as acidification, changes in the pH and oxidation/reduction potential conditions or, the trace/heavy metals will increase in the organic ligand concentration of an environment and enters into the aquatic environment and become readily available to aquatic organisms (Förstner 1985). The concentration of trace/heavy metals in the sediment reflects both the lithology and nature of the sediments (Govindasamy and Azariah 1999; Gopinath et al. 2010).

The average concentration of trace elements/metals in each of fractions of beach sediments collected during the monsoon and POM seasons are presented in Table 5.3 and Table 5.4 respectively. Among the nine elements analyzed (Cu, Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn); Cu, Cd, Pb and Zn are mainly associated with non-residual fractions (acid extractable/exchangeable fraction, reducible fraction and oxidizable fraction) during both seasons, and the remaining elements (Co, Cr, Fe, Mn and Ni) are associated with the residual fraction. The difference between the percentages of all analyzed fractions and trace element/metal concentrations extracted in each fraction is presented in Figure 5.6 (monsoon season) and Figure 5.7 (POM season).

Table 5.3 The average concentration of trace elements/metals in different fractions of beach sediments along the Miri coast (monsoon season)

	Cu μg/g					Pb μg/g					Cd μg/g				
Sample ID	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**
BB	161.79	23.65	3.73	5.53	194.69	3.46	1.85	0.58	2.95	8.84	0.04	0.03	0.29	0.35	0.71
KPB	188.01	14.65	2.55	6.38	211.59	2.38	1.72	0.45	5.50	10.05	0.07	0.08	0.36	0.30	0.81
ESP	220.73	19.81	3.31	5.80	249.65	1.47	2.16	0.74	3.22	7.59	0.05	0.02	0.19	0.26	0.52
TB	199.06	28.00	3.45	4.35	234.86	1.86	1.54	0.43	3.20	7.03	0.00	0.00	0.13	0.25	0.38
MRE	127.37	18.36	3.03	13.33	162.08	2.58	3.28	1.08	2.93	9.86	0.00	0.00	0.09	0.18	0.26
PBC	161.20	18.52	3.40	6.55	189.67	1.24	2.12	1.28	2.80	7.44	0.00	0.00	0.10	0.05	0.15
LB	244.77	22.29	3.92	5.43	276.42	1.48	2.63	1.08	3.53	8.72	0.03	0.01	0.28	0.00	0.32
KBE	193.26	20.72	3.00	6.75	223.73	0.88	2.22	0.33	4.25	7.68	0.02	0.02	0.30	0.05	0.39
Sample ID	**Co μg/g**					**Ni μg/g**					**Zn μg/g**				
BB	2.06	1.92	2.86	6.63	13.47	1.45	0.85	3.86	10.23	16.39	96.10	7.55	4.43	8.43	116.50
KPB	2.08	1.73	3.08	4.95	11.84	2.40	2.21	5.01	9.58	19.20	106.80	6.32	4.15	6.60	123.87
ESP	1.64	1.13	2.18	7.54	12.49	3.20	2.56	5.38	14.00	25.14	121.84	6.58	3.60	10.86	142.88
TB	2.62	2.34	3.58	6.25	14.79	0.22	0.00	1.15	13.90	15.27	111.40	10.78	4.65	8.45	135.28
MRE	0.73	0.76	1.19	5.73	8.40	0.43	0.48	2.44	15.70	19.05	69.50	7.00	3.43	11.40	91.33
PBC	3.34	3.38	4.70	5.35	16.77	0.14	0.00	1.68	13.60	15.42	89.00	5.68	3.15	9.35	107.18
LB	0.37	0.00	0.48	5.40	6.26	0.99	0.29	2.72	14.80	18.80	131.07	7.36	4.28	9.87	152.58
KBE	0.66	0.08	0.98	4.40	6.12	1.24	0.62	2.95	15.50	20.31	115.00	8.20	4.08	12.00	139.28
Sample ID	**Fe μg/g**					**Mn μg/g**					**Cr μg/g**				
BB	168.25	657.60	97.95	2905.00	3828.80	11.03	4.75	4.06	19.13	38.97	3.23	4.27	14.36	19.53	41.39
KPB	318.20	748.60	88.25	2370.00	3525.05	11.92	7.00	3.69	15.03	37.63	1.44	2.74	9.31	19.58	33.07
ESP	357.68	660.48	72.54	2394.00	3484.70	18.26	4.62	2.56	14.22	39.67	0.85	1.93	10.18	26.66	39.62
TB	188.92	293.00	31.93	1345.00	1858.85	5.64	1.96	1.70	11.65	20.95	2.40	4.08	12.43	27.10	46.01
MRE	230.30	577.10	55.94	2815.00	3678.34	8.29	2.94	1.64	20.25	33.12	0.00	0.50	9.69	30.83	41.01
PBC	197.78	490.60	51.45	2420.00	3159.83	10.58	2.40	1.10	15.20	29.28	2.96	2.82	12.43	30.25	48.46
LB	377.60	572.27	82.87	3126.67	4159.40	12.07	2.63	1.15	15.70	31.54	2.08	2.08	11.78	33.50	49.44
KBE	464.60	661.20	81.90	4350.00	5557.70	7.34	2.82	1.18	26.15	37.49	1.06	1.80	11.75	40.60	55.21

Table 5.4 The average concentration of trace elements/metals in different fractions of beach sediments along the Miri coast (POM season)

	Cu µg/g					Pb µg/g					Cd µg/g				
Sample ID	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**	**FR 01**	**FR 02**	**FR 03**	**FR 04**	**Total**
BB	474.00	51.91	7.55	6.10	539.56	15.27	3.88	0.95	3.25	23.35	0.25	0.26	0.51	0.28	1.30
KPB	297.60	35.41	6.25	4.63	343.89	14.38	4.90	1.21	3.18	23.67	0.27	0.26	0.56	0.78	1.87
ESP	247.21	23.52	8.13	6.16	285.02	12.67	6.26	0.85	4.10	23.89	0.20	0.20	0.44	0.34	1.18
TB	193.14	22.52	16.45	5.55	237.66	12.34	4.60	1.10	3.25	21.29	0.22	0.20	0.45	0.30	1.17
PVB	110.80	22.40	1.55	9.30	144.05	5.28	4.44	0.85	3.6	14.17	0.08	0.04	0.3	0.1	0.52
MRE	143.29	17.24	4.69	5.25	170.47	6.90	5.37	1.18	3.28	16.72	0.17	0.15	0.44	0.30	1.06
PBC	169.48	34.74	6.52	5.50	216.24	17.08	5.50	0.43	3.95	26.96	0.22	0.20	0.50	0.30	1.22
LB	215.89	20.20	7.12	4.77	247.98	5.87	3.60	0.30	2.90	12.67	0.25	0.25	0.53	0.27	1.31
FLC	456.53	34.76	6.67	6.50	504.46	9.65	5.53	1.07	4.07	20.32	0.09	0.07	0.30	0.17	0.63
KBE	223.09	25.08	4.93	6.60	259.71	9.96	6.05	0.35	4.70	21.06	0.12	0.09	0.35	0.13	0.70
Sample ID	**Co µg/g**					**Ni µg/g**					**Zn µg/g**				
BB	0.94	0.87	1.50	6.13	9.44	1.04	0.48	2.31	13.70	17.53	192.00	17.14	5.13	9.08	223.34
KPB	0.44	0.33	1.14	3.78	5.68	1.32	0.66	2.81	12.10	16.89	132.90	13.53	3.83	6.80	157.06
ESP	0.83	0.58	1.10	4.86	7.38	1.15	0.68	2.75	11.12	15.70	129.60	8.60	4.67	9.94	152.81
TB	0.46	0.24	1.15	3.80	5.65	0.72	0.26	2.60	11.45	15.03	120.20	7.56	3.73	10.95	142.44
PVB	0.96	1.32	0.55	5.70	8.53	1.24	1.4	2.95	14	19.59	66.4	10.68	2.8	11.6	91.48
MRE	0.36	0.33	0.93	2.38	3.99	1.29	1.19	3.29	13.03	18.79	86.90	7.25	5.04	12.38	111.56
PBC	0.64	0.44	1.43	2.55	5.06	1.06	0.58	3.48	12.90	18.02	95.80	13.58	4.28	11.20	124.86
LB	0.36	0.40	1.13	3.00	4.89	1.57	1.20	3.72	14.27	20.76	128.80	7.84	5.08	10.40	152.12
FLC	0.71	0.35	0.62	4.80	6.47	1.13	0.41	2.53	17.83	21.91	198.67	12.72	4.35	11.97	227.70
KBE	1.28	1.09	1.07	5.23	8.67	1.48	1.15	2.87	16.17	21.66	116.80	9.53	7.73	13.13	147.20
Sample ID	**Fe µg/g**					**Mn µg/g**					**Cr µg/g**				
BB	463.90	581.10	36.30	3967.50	5048.80	12.31	5.26	3.76	22.98	44.31	0.78	1.28	7.60	41.93	51.59
KPB	386.50	551.80	36.25	3525.00	4499.55	14.92	5.94	4.19	18.75	43.80	1.05	1.48	7.54	34.53	44.59
ESP	404.88	419.36	42.50	2686.00	3552.74	17.83	3.66	3.00	15.30	39.79	0.54	0.97	7.40	34.42	43.32
TB	255.80	221.80	26.20	1495.00	1998.80	8.28	2.02	2.60	14.35	27.25	0.66	1.66	7.80	36.10	46.22
PVB	390.00	1635.6	60.65	3690.00	5776.25	27.76	15.56	1.60	24.9	69.82	3.72	6.4	16.15	33.1	59.37
MRE	369.60	603.40	39.73	2850.00	3862.73	8.99	3.86	1.76	16.35	30.96	3.91	6.23	11.73	43.30	65.17
PBC	205.60	236.80	26.48	2075.00	2543.88	5.22	2.40	2.85	16.85	27.32	0.58	1.30	6.83	40.35	49.06
LB	279.60	411.87	30.82	3013.33	3735.62	5.99	4.39	2.02	30.27	42.66	0.47	4.01	7.72	55.50	67.70
FLC	286.09	620.67	58.90	4213.33	5178.99	6.17	2.63	1.60	41.53	51.93	1.52	2.53	10.85	58.23	73.14
KBE	546.40	972.93	73.55	4756.67	6349.55	7.51	4.95	2.25	33.03	47.74	1.31	3.13	10.90	57.70	73.04

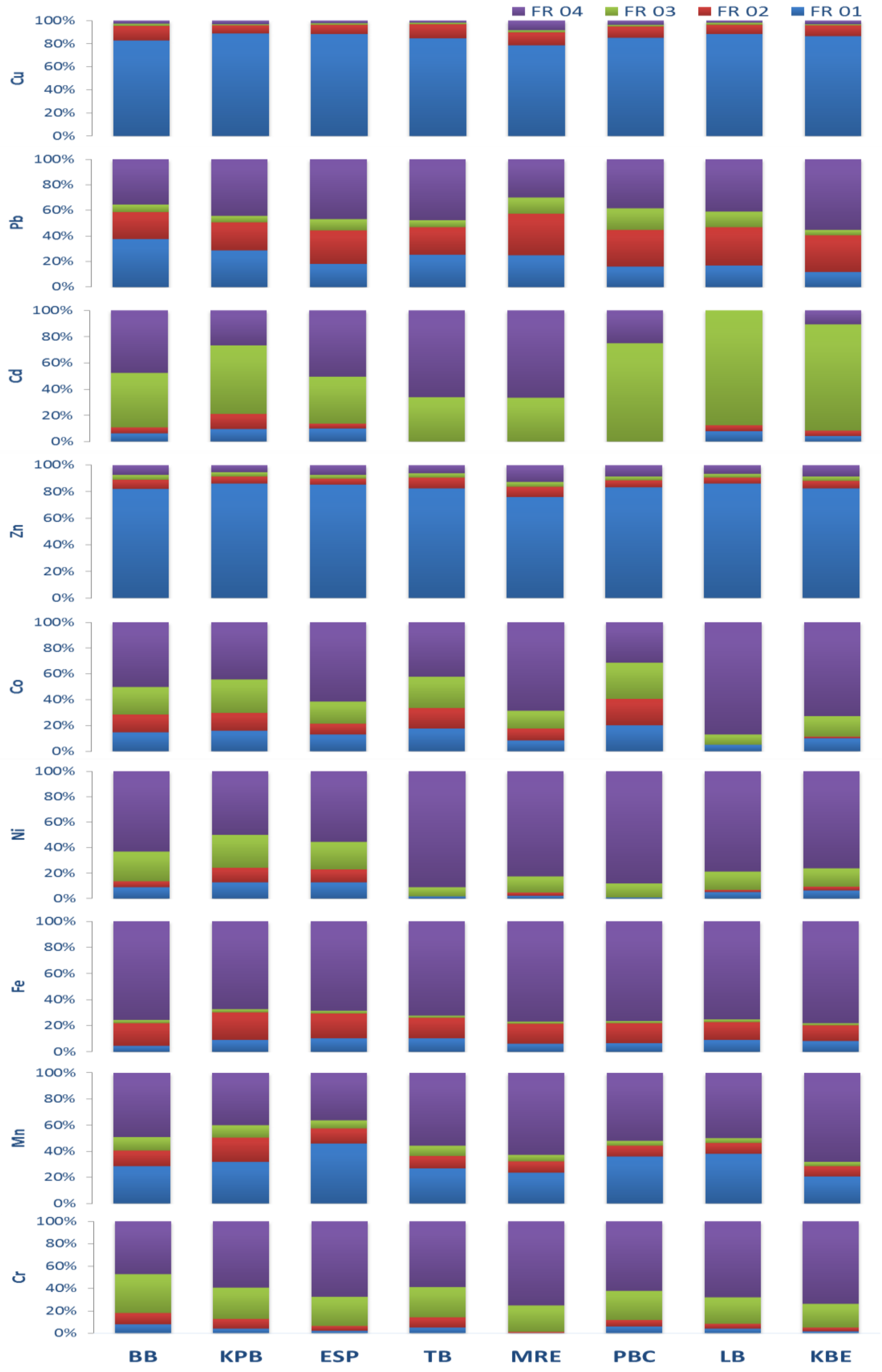

Figure 5.6 The average percentage of element in different fraction of beach sediments of Miri coast (monsoon season)

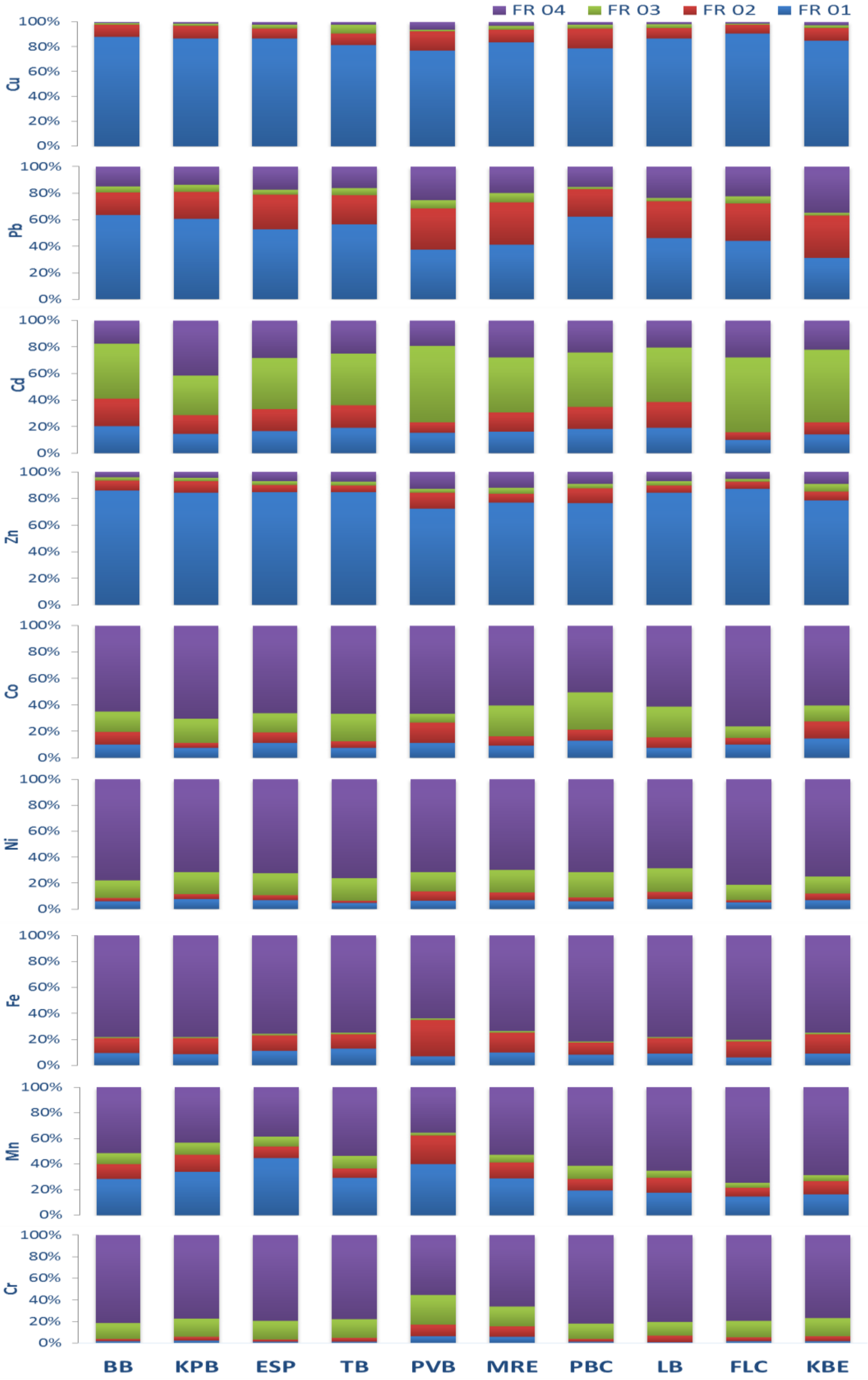

Figure 5.7 The average percentage of element different fraction of beach sediments of Miri coast (POM season)

5.7.1 Fraction 1 (acid extractable/exchangeable)

Fraction 1 represents the elements/metals present in an ionic form bound to carbonates and the exchangeable fraction (Rauret et al. 1999; Nemati et al. 2011). Copper and Zn content in sediments are mainly associated with this fraction at 85 % and 83% during the monsoon and 84 % and 82% during the POM respectively. Lead's association with this fraction varies between the seasons at 22% during the monsoon and 49.5% during the POM respectively. The highest concentration of Pb in this fraction (63.7%) was recorded from Bungai Beach. The high association of Cu, Zn and Pb in this fraction indicates their higher mobility and bio-availability for aquatic organisms. The mean proportions of Cd, Co, Ni, Fe, Mn and Cr in this fraction were 4.7%, 13.15%, 6.25%, 8%, 31.4% and 3.95% during the monsoon and 16.39%, 10.18%, 6.40%, 9.04%, 27.16% and 2.48% during the POM season indicating, their low mobility compared to Cu, Zn and Pb. The association of elements/metals in this fraction for both seasons can be summarized as: (decreasing trend), Cu > Zn > Pb > Mn > Co > Fe > Ni > Cd > Cr (during monsoon) and Cu > Zn > Pb > Mn > Cd > Co > Fe > Ni > Cr (during POM) respectively. The elements/metals associated with this fraction were considered to be the weakest bonded elements/metals in the sediments. These can be easily passed into the water column when there is a change in the pH condition of the environment and thus become readily bioavailable to marine organisms (Pardo et al. 1990). The high concentration of elements/metals in this fraction (i.e. Cu, Zn and Pb), indicate their greater mobility and thus greater toxicity which pose a higher risk to their environment.

5.7.2 Fraction 2 (easily reducible fraction)

This fraction explains the elements/metals attached to the amorphous Fe and Mn oxides and hydroxides (when the sediments change from oxic to anoxic state) by the presence of microorganisms in that environment (Morillo et al. 2004). The association of elements/metals in this fraction for both seasons can be summarized as: Pb > Fe > Mn > Co > Cu > Cr > Zn > Ni > Cd (during monsoon) and Pb > Cd > Fe > Mn > Cu > Co > Zn > Cr > Ni (during POM), respectively. Among the metals, Pb concentration was mainly associated with this fraction at 27% during the monsoon and 26% in the POM season, respectively. The higher Pb concentration (32%) was recorded from the Miri River estuary area for both seasons. An increase in the Pb concentration of this fraction was observed at three river outlets for both seasons (i.e. the Miri River, the Lutong River and the Baram River).

5.7.3 **Fraction 3 (oxidizable fraction)**

This fraction explains the elements/metals bound to the organic matter and sulphides in the sediments. The association of elements in this fraction for both seasons can be summarized as: Cd > Cr > Co > Ni > Fe > Pb > Mn > Zn > Cu (during monsoon) and Cd > Cr > Co > Ni > Mn > Pb > Zn > Cu > Fe (during POM). Cadmium concentration in this fraction was higher in many samples and was recorded at 55% during the monsoon and 44% during the POM season. In addition to Cd; Co (19.27% during monsoon & 17.06 during POM), Ni (16.36% during monsoon & 15.89% during POM) and Cr (26.26% during monsoon & 16.92% during POM) were also significantly associated in this phase. Cu (1.55% during monsoon) and Fe (1.04% during POM) were partially associated with this fraction. Elements/metals leached from this fraction are mainly bound to various forms of organic matter and sulphur compounds by complexation and peptization properties; it attaches to natural organic matter through the process of bioaccumulation in certain living organisms in different ways (Nemati et al. 2011).

5.7.4 **Fraction 4 (residual)**

The elements/metals found in this fraction are primarily associated with minerals, lattices and silicate materials. They are unlikely to be released from the sediments during other extractions. The association of elements/metals in this fraction for both seasons can be summarized as follows: Fe > Ni > Cr > Co > Mn > Pb > Cd > Zn > Cu in the monsoon season and Fe > Cr > Ni > Co> Mn > Cd> Pb > Zn > Cu in the POM season respectively. In the present study, a major proportion of Co (57.28% during monsoon & 64.46% during POM), Ni (73.17% during monsoon & 73.61% during POM), Fe (73.83% during monsoon & 75.98% during POM), Mn (51.71% during monsoon & 54.60% during POM) and Cr (63.95% during monsoon & 75.75% during POM) were mainly associated with this phase for both seasons.

5.8 Element/metal Distribution

5.8.1 Copper and Zinc

Copper exists in various chemical forms in the environment such as free Cu ions or complexed with organic ligands or suspended particles and settles in the surface layers of sediments by precipitating or being adsorbed into the organic matter (Mance et al. 1984). If, Cu and Zn exceed the recommended limits it causes harmful effects to the aquatic organisms through the bioaccumulation process. Among the elements/metals studied, Cu and Zn have the highest mobility since their concentrations were more in the fraction 1 (the most liable) in all the sampling locations of the study area. The average Cu and Zn association with this fraction reached > 80% of the total concentration for both seasons. The higher proportion of Cu and Zn was obtained at Lutong Beach during the monsoon season and at the Fish Landing center during the POM season. The lower proportions of Cu and Zn were noticed near the Miri River Estuary during the monsoon season. Ten percent of Cu is associated with reducible fraction for both seasons and was less associated with the oxidizable (1.5% during monsoon and 2.6% during POM) and residual phase (3.5% during monsoon and 2.3% during POM). A minor amount of Zn was associated with reducible (6.5% during monsoon and 7% during POM), oxidizable (3% for both seasons) and residual (9% during monsoon and 7.2% during POM) fractions for both seasons.

The highest proportion of Cu and Zn in the exchangeable fraction (F1) indicates these metals are readily available to the environment if there is a small change in the water ionic strength. Elements extracted in this fraction could be regarded as a pollution indicator (Forstner 1979). Cu and Zn are mainly associated with natural sources (i.e. shales). In addition, these elements are also derived from anthropogenic sources such as anti-fouling/corrosive paints used in fishing boats, nets, dyes, ship dry-docking facilities, timber processing, wood preservatives, steel processing as well as leaching from dry cell batteries (Hanson et al. 1993) (Cuong and Obbard 2006) (Zulkifli et al. 2010). These industrial activities were commonly noticed in the NE segment of the study area, whereas in the SW segment, no major industries were located but Cu and Zn may leach from the shale and pyrite concretions in the SW segment. The geology of the SW segment consists mainly of sedimentary rocks such as sandstone, shale, siltstone with clay and coal laminae and mino limestone. In addition, pyrite concretions are common in Tukau and Sibuti formations.

5.8.2 Lead

Pb (II) and lead-hydroxy complexes are the most stable forms of lead. Lead phosphates, lead carbonates and lead hydroxides are the insoluble compounds of Pb, which are formed when the pH is more than 6 (Raskin and Ensley 2000). During the increased concentration of sulfide, under the reducing condition, the most stable solid form of lead sulfide (PbS) is formed. The distribution of Pb among the four fractions varies significantly between the beaches for both seasons. Overall, during the monsoon season, ~ 42% of the total Pb was associated with residual fraction, 26% in the reducible, 22% in the exchangeable fraction and the rest, 8% in the oxidizable fraction. Whilst during the POM season, 50% of the total Pb was associated with the exchangeable fraction, 26% in the reducible, 20% in the residual and the rest 4% in the oxidizable fraction respectively. There was a two-fold increase of the Pb concentration in the exchangeable fraction during the POM which has greater mobility.

Higher proportions of Pb in the exchangeable fraction was noticed from Bungai Beach at 37.59% and 63.69% for the monsoon and POM seasons, respectively. 26% of Pb in reducible phase in both seasons indicates Fe and Mn hydrous oxides are important scavengers of Pb along this coast. Similar results have been reported from the SW coast of Spain (Morillo et al. 2004) and from Great Britain (Dawson and Macklin 1998). The overall association of Pb in the oxidizable fraction is small (8.96% during monsoon and 4.31% during POM) for both seasons and the results observed was similar to the findings of Morillo et al. (2004) from the SW coast of Spain.

Pb enters the aquatic environment through anthropogenic sources such as vehicle emissions, petroleum products, burning of fossil fuels, storage batteries, use of Pb in circuit boards in computers and electronic equipment, industrial effluents as well as from atmospheric deposition (Ritson et al. 1999; Hansmann and Köppel 2000). Overall, the Pb association was mostly with non-residual fraction (F1-F3) at 60% during monsoon season and 80% during the POM season. Pb concentration levels have increased significantly during the POM season and enriched all the sampling locations of the Miri coast compared to the monsoon season. The increased level of Pb in a particular location (i.e. the Fish Landing center) during the POM season can be linked with the use of petrol in boats used for fishing, and this area is also used as a berthing facility for sea-going boats and boat services. It is well supported by the enrichment of Pb in the sediment samples collected nearby the fish landing centers during both seasons.

5.8.3 **Cadmium**

Among the metals studied, the greater proportion of Cd was in the oxidizable fraction for both seasons. Generally, an average of 55% during the monsoon and 44% during the POM season was associated with this fraction, matching with organic and sulphur compounds. The overall association of Cd in the monsoon season was 4%, 4% and 37% in the exchangeable, reducible and residual fractions, respectively while this association was subject to seasonal variation as 16%, 14% and 25% in exchangeable, reducible and residual fractions, respectively were observed during the POM. Overall, ~ 64% of Cd in the monsoon season and ~75% of Cd in the POM season was associated with a non-residual fraction (F1+F2+F3), indicating a high chance of Cd mobility in this coastal area. However in the SW segment of the study area, (i.e. Esplanade beach (51%), Tanjong Beach (66%) and Miri River Estuary (66%) the Cd was mainly associated with the residual fraction. Thus, the Cd mobility in the SW segment beaches was low.

Cd association in the oxidizable fraction increased in the NE segment of the Miri coast from Piasau Beach to the Kualabaram estuary. During the monsoon season, there was a sharp increase in the mobility of Cd at Lutong Beach compared to the residual fraction. Similar results were observed by Morillo et al. (2009) in the sediment samples collected near the Tinto and Odiel river mouths on the southwest coast of Spain. At the Baram River mouth region, only 10% of total Cd was associated with residual fraction and the remaining Cd was associated with non-residual fractions during the monsoon season. The distribution of Cd in each fraction differed significantly between the beaches and seasons. Overall, there was a fourfold increase in the percentage of Cd in the exchangeable fraction during the POM season compared to the monsoon season.

5.8.4 Cobalt and Nickel

Nickel occurs at very low levels in the environment and it is required in trace amounts for phytoplankton to maintain health (Dupont et al. 2010). Nickel enters the environment through man-made activities such as metal plating industries, mining, electroplating, battery manufacturing, processing machinery and the combustion of fossil fuels (Khodadoust et al. 2004). Nickel is naturally associated with detrital minerals in different rock types. Nickel from all these activities enters the aquatic environment through surface runoff of wastes and incineration (WHO 1991). It exists in coastal systems as soluble salts, absorbed on clay particles or together with organic materials.

Cobalt and Ni are distributed in all four fractions during both seasons. Cobalt is mainly associated with the residual fraction, which accounted for 58% in the monsoon and 64% in the POM season while 73% of Ni was associated with residual fraction for both seasons. Of the remaining Co; 42% in the monsoon and 36% in the POM and 27% of Ni in both seasons were associated with the non-residual fractions (F1+F2+F3). Among the non-residual fractions, a majority of these metals were associated with the oxidizable fraction followed by an exchangeable and reducible fraction. Cobalt was significantly associated with the non-residual fraction (> 55%) during the monsoon season in Kampong Baraya, Tanjong Lobang and Piasau Beaches indicating a higher chance of mobility of this metal.

The major proportions of Co (87%) and Ni (91%) were associated with the residual fraction during the monsoon season in Lutong and Tanjong Beach sediments respectively. However, Ni in the Kampong Baraya samples (50%) was associated with non-residual fractions. The presence of Ni in the reducible fraction (4%) and exchangeable fraction (6%) is negligible for both seasons. An association of Ni and Co with residual fractions was reported from Barcelona (Lopez-Sanchez et al. 1996); the Mediterranean Sea (Martin et al. 1998); the Persian Gulf (Karbassi 1998); Spain (Morillo et al. 2004) and were comparable with the present study. Co and Ni, associated with the residual fraction in the study area indicates the mobility and leaching effects of these metals are very low and should not cause harmful effects to the Miri coastal environment.

5.8.5 Iron and Manganese

The major proportion of Fe is associated within the residual fraction, as was recorded; 74% in the monsoon and 76% in the POM season. A negligible amount of Fe was associated in the reducible form at (16% in the monsoon and 14% in the POM) as well as an exchangeable fraction at (8% in the monsoon and 9% in the POM). The presence of Fe in the oxidizable fraction is very low for both seasons (< 2%). The maximum presence at 28% of Fe was bounded to a reducible fraction in the sediments of Park Everly Beach during the POM season. Fe easily leaches from the parental rocks such as sedimentary and meta-sedimentary rocks from the hinterlands and then enters into the coastal areas where it reacts with water and sediments and can be fixed alternatively, depending on environmental conditions of an aquatic system. Iron may be released and become mobile if the sediment column changes from an oxic to an/oxic condition. Higher proportions of Fe (78%) in the residual fraction was noticed in the Kualabaram river estuary area during the monsoon season and at Piasau Beach area (81%) during the POM season. The higher accumulation of Fe in the residual fraction was due to the natural origin of this metal through weathering of rocks from the source regions.

Various forms of Mn are present in aquatic environments such as Mn (II), Mn (III) oxyhydroxide and Mn (IV) oxides (Post 1999). Among these three forms Mn (III) and (IV) oxides exist as insoluble forms in the oxygenated marine environment, whereas Mn (II) is present in soluble or dissolved conditions. When Mn (II) enters an oxidized zone it precipitates again as Mn (III) and (IV) and settles aquatic environments are fluvial, atmospheric inputs, domestic & industrial wastes from the point and non-point sources and benthic fluxes from sediments (Adriano 2013).

Unlike Fe, the distribution of Mn among the four fractions varied significantly along the coast. Overall, Mn was associated with the residual fraction (52% in the monsoon and 55% in the POM season) with a significant amount of Mn in the exchangeable fraction (31% in the monsoon and 27% in the POM), which is comparable to the work by Morillo et al. (2004) in the marine sediments of Spain, where 25% of Mn had been extracted in exchangeable fraction and 57% in residual fraction, respectively.

In addition to the exchangeable fraction, Mn was also extracted from the reducible fraction (10% in the monsoon and 11% in the POM seasons) and oxidizable fraction (6% for both seasons). A high proportion of Mn (45%) was associated with the exchangeable fraction at Esplanade Beach for both seasons, indicating a higher chance of mobility in these beach sediments. An increase in the Mn concentration in the residual fraction was noticed in the NE segment of the study area for both seasons, reflecting low mobility. When compared to the POM season, a significant association of Mn (48%) with the non-residual fractions (F1+F2+F3) was noticed during the monsoon season, indicating their higher mobility. Aa association of Mn with residual fraction has been often reported elsewhere (i.e. Spain, Usero et al. 1998; Penang Malaysia, (Ngiam and Lim 2001) and East China Sea, Yuan et al. 2004) which is comparable with the present study findings.

5.8.6 Chromium

Different forms of Cr are available in the aquatic environment, as Cr (III) and Cr (VI) and these forms biologically important. Cr (III) is useful for the metabolic process of lipid, protein and glucose, whereas Cr (VI) is comparatively more toxic and can be found in contaminated soils (Eisler 1986) (Levy and Venitt 1986). The major source of Cr in the aquatic environment is mainly attached to organic matter and detrital minerals. In addition to natural sources, domestic and industrial wastes (electroplating, tanning) and domestic wastes (dumping of solid wastes from the households) (Smith et al. 1995) are also responsible.

Chromium is mainly associated with the residual fraction in all the samples for both seasons (64% in the monsoon and 76% during the POM), except from Bungai Beach during the monsoon season. About 36% of Cr in the monsoon season and 24% in the POM season were associated with the non-residual fraction in which 26% in the monsoon and 17% in the POM was associated with the oxidizable fraction alone. The presence of a large proportion of Cr in the residual fraction was also observed and reported by other researchers: (i.e. Martin et al. (1998) in the north-western Mediterranean Sea; Yuan et al. (2004) in China and Morillo et al. (2004) in Spain) which are comparable with the present study. A higher proportion of Cr in the residual fraction was noticed in the Miri River estuary area (75% in the monsoon season) and at Piasau Boat Club Beach (82% in the

POM season). A maximum, 53% of Cr was associated with a non-residual fraction in Bungai Beach during the monsoon season in which 35% was associated with the oxidizable fraction. In this study, a major part of Cr was associated with residual fraction indicating their presence in detrital minerals and clay. Thus, Cr has a low mobility and was unlikely to be released to the environment.

5.9 Discussion

5.9.1 Statistical Analysis: Factor Analysis

Factor analytical results were obtained through SPSS software using PCA extraction and varimax rotation. This has been reflected in the factor analysis as follows: 1) Six factors had Eigen values greater than 1, which were considered for extraction. The main purpose of factor analysis is to reduce the data set into meaningful factors that can be easily interpretable. However, when the number of factors increases, the factor model becomes unable to meet this requirement; 2) The grouping of variables based on factor loadings did not provide meaningful results. This contention was largely based on earlier findings regarding the geochemical association of elements and their behavior in the environment; 3) The factor model could explain only a small percentage of total variance in the data (around 70%). When the variance explained in the factor model is less, the factor model becomes unsuitable to describe the data. These types of incompatible results are possible if the assumptions of normality and constant variance are violated. In order to solve this problem, the *Shapiro-Wilk* test was employed to remove non-normal data from the statistical analysis.

The factor model also fails if the major governing processes responsible for observed variations in the elemental concentrations are different for any of the beaches and segments of the coast. Such a possibility exists due to the prevailing hydrological conditions here. In the coastal areas the dominant processes are 1) mixing of river water (i.e. Baram River, Miri River and Sibuti River) with seawater which introduces gradients in various water column parameters viz., salinity, pH and composition of major ions; 2) sediment input from the river; 3) prevailing hydrological regime within the mixing zone[2]

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[2] Which is largely influenced by river water input.

as well as in the seawater[3]; 4) changes in the water column energy that exerts control over sediment texture and composition. Since all these factors are influenced by waves and currents, the prevailing hydrological regime in the study area was considered the most important factor used for dividing the coastal area into functional segments. Thereafter, the sediment characteristics and their influencing factors could be easily found. Each segment may have dominance of different mechanisms which determine the sediment characteristics. With this understanding, the grain size of the sediment may be considered for demarcation of the coastal areas as this is closely related to water column energy, its flow direction, and mixing pattern. The grain size variation of the collected sediments is listed in Table 5.5.

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[3] Which is normally controlled by wind direction and currents.

Table 5.5 Grain Size variation in the sediments of the Miri coast during Monsoon and POM Seasons

Sample ID	Coarse	Fine	Silt	Sample ID	Coarse	Fine	Silt
BB 01	0.00	85.88	14.12	BB 01	5.86	87.65	6.50
BB02	0.06	96.29	3.65	BB02	0.00	81.27	18.73
BB 03	0.21	96.44	3.35	BB 03	2.90	94.67	2.43
BB 04	0.04	84.61	15.35	BB 04	0.16	94.09	5.75
KPB 01	0.00	83.22	16.78	KPB 01	1.54	79.97	18.49
KPB 02	0.00	77.39	22.61	KPB 02	0.13	86.83	13.04
KPB 03	0.00	97.12	2.88	KPB 03	0.11	78.71	21.18
HWB 01	0.00	77.58	22.42	HWB 01	0.03	88.05	11.92
ESP 01	0.00	46.90	53.10	ESP 01	0.13	61.32	38.55
ESP 02	0.08	46.81	53.11	ESP 02	0.05	59.74	40.21
ESP 03	0.02	33.58	66.40	ESP 03	0.24	50.96	48.80
ESP 04	0.06	53.18	46.76	ESP 04	0.10	68.50	31.40
ESP 05	0.00	45.98	54.02	ESP 05	0.00	74.59	25.41
TB 01	0.02	73.09	26.89	TB 01	0.00	81.93	18.07
TB 02	0.00	79.46	20.54	TB 02	0.14	88.47	11.39
MRE 01	0.00	22.89	77.11	PVB 01	0.68	83.07	16.25
MRE 02	0.02	49.26	50.72	MRE 01	0.00	45.42	54.58
MRE 03	0.00	57.92	42.08	MRE 02	0.00	68.23	31.77
MRE 04	0.04	66.05	33.91	MRE 03	0.00	60.37	39.63
PBC 01	0.02	56.93	43.05	MRE 04	0.08	63.51	36.41
PBC 02	0.06	55.36	44.58	PBC 01	0.00	79.33	20.67
LB 01	0.01	42.94	57.05	PBC 02	0.00	77.96	22.04
LB 02	0.00	49.36	50.64	LB 01	0.00	82.65	17.35
LB 03	0.02	58.63	41.35	LB 02	0.00	72.69	27.31
FLC 03	0.00	30.78	69.22	LB 03	0.11	76.21	23.68
KBE 01	0.00	39.02	60.98	FLC 01	0.25	83.90	15.85
				FLC 02	0.00	60.37	39.63
				FLC 03	0.00	64.50	35.50
				KBE 01	0.00	67.60	32.40
				KBE 02	0.11	54.66	45.23
				KBE 03	0.10	20.68	79.22

The inference from this data is the coarse fraction is negligible and therefore, should not be considered. The fine sand and silt fractions show a wider variation and can be used as a tool to demarcate the prevailing hydrological regime of the coast. When the percentage of fine sand and silt was plotted (Figure 5.8), it was observed there was a gradual decrease in fine sand and a complementary increase in silt content moving towards the NE direction. This clearly indicated the supply of sediments coming from the river and its dispersion towards the SW direction along the coast. Thus, the entire study area of the coast was divided into two segments – one with the sampling stations 1-9 (Bungai Beach, Kampong Baraya and Esplanade Beach), and the other with sampling stations 10-28 (Esplanade, Tanjong, Miri River Estuary, Piasau, Lutong, Fish Landing Center and Kualabaram Estuary area) for the monsoon season.

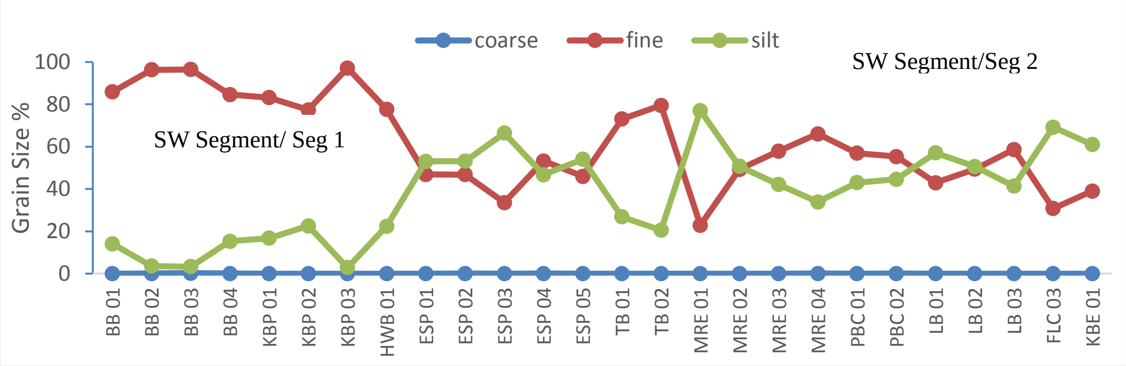

Figure 5.8 Grain Size variation of beach sediments in the Monsoon Season

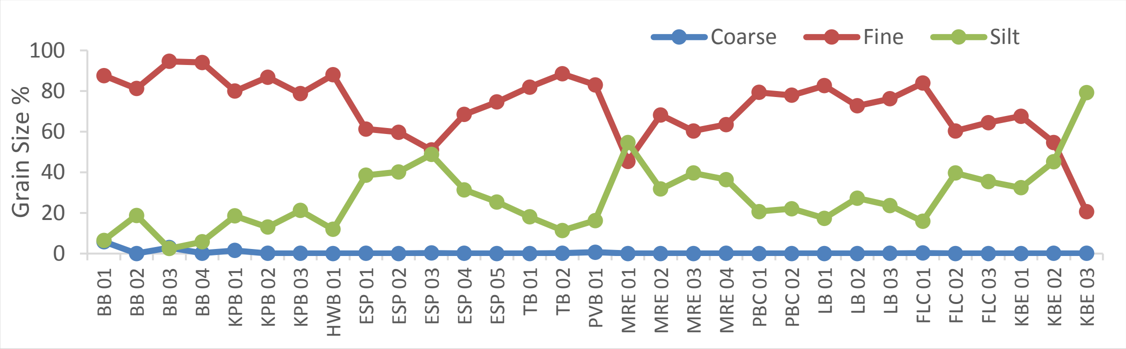

Figure 5.9 Grain size variation of beach sediments in the POM season

Based on the profile of fine sand and silt distribution (Figure 5.9), the same criteria were used for demarcating the coastal area into two segments during the POM season. As can be clearly seen, the divisions during the monsoon and post monsoon seasons were not equivalent – indicating different prevailing hydrological regimes during these two different seasons. This was quite understandable as the river input during the rainy months can influence the flow and mixing patterns and alter the characteristics of turbulence. Thus, for each season, there were two factor models to describe the major geochemical processes occurring within each segment. Such a factor model resulted in a small number of factors with Eigen values greater than 1 (which was the criteria used for factor extraction following Davis, 2002), and helped explain why there was a high percentage of variance in the data. This factor model also provided more meaningful results by grouping the variables according to their geochemical nature.

Another addition to the factor model was some of the water column characteristics which are thought to influence sediment, were also adopted into this factor model. This is quite logical since there is a continuous exchange of energy and matter between the water column and the sediments, and any changes occurring to one of them is likely to affect the physico-chemical characteristics of the other. By modifying the factor model, the interpretability becomes more efficient in terms of determining the interaction between the sediment characteristics and the water column parameters. Further, total elemental concentrations were considered for the factor model, as meaningful factor results could not be obtained using various fractions of the elements/metals in different compartments of the sediment.

In order to avoid the problems arising due to the use of different units for different parameters (like µg/g, percentage, *etc.*), the data had to be standardized. This was done by the SPSS package itself to carry out the PCA extraction using a correlation matrix. Thus, PCA extraction was performed using the correlation matrix for the total metal concentration in the sediment samples collected during the monsoon and POM seasons (The other option was to use a covariance matrix, for which the data had to be standardized before PCA extraction). The extracted factors were varimax rotated so orthogonal factors could be obtained (Davis 2002). When orthogonal factors are obtained, the extracted factors can be directly related to independent geochemical processes occurring in the study area.

5.9.1.1 *Factor analytical results for the monsoon season sediments: Segment-1 (Samples: 1 to 9)*

Five factors were found to be dominant during the monsoon season and the factor model explained about 91.5% of the variance in the data (Table 5.6). In this factor model, all variables had good communality except the water column SO_4^{2-} (0.777), sedimentary $CaCO_3$ (0.811), Ni (0.817) and Co (0.825), implying this factor model could explain only 60%, 65%, 67% and 68% of variance of these parameters, respectively (Table 5.6). The low communality values indicated influences from other factors which were not considered in this factor model. However, albeit being on the lower side, the variance in the concentrations of these metals in the sediments could be largely explained. In each and every study only after the collection of samples and the processing of the results, was there any understanding of the inherent structure within the data, and any gaps would have to be filled in the future work. Nevertheless, there was an attempt to understand the factors leading to the low communality values for these parameters.

For $SO_4^{2-,}$ the low communality values could be attributed to its contribution both from marine and riverine sources. Sea water was comparatively enriched with sulphate compared to the river water. At the same time, the basin area of the rivers draining into the Miri coast consist of shale formations which might release sulphate, upon oxidation of pyrite and other sulphide minerals (Nagarajan et al. 2015). The mixing up of riverine and marine water will introduce perturbation in their distribution in the water column. In addition, the biological processes of sulphate reduction and sulphide oxidation, as influenced by water and sediment column redox potential will introduce further perturbation along with temperature. It may not be practicable to either observe or consider all such variables.

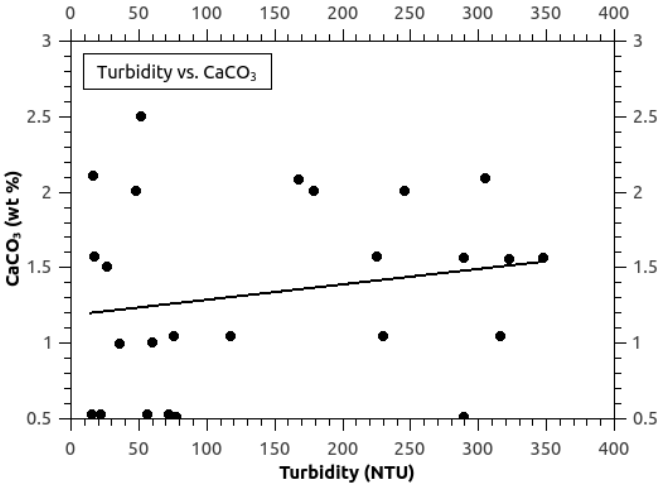

Figure 5.10 Absence of significant correlation between $CaCO_3$ vs Turbidity

Considering the low communality value for $CaCO_3$, in earlier studies $CaCO_3$ exists as particulate matter within the suspended solids of seawater (Boughriet et al. 1992; Guay and Bishop 2002). These suspended particles may become deposited when the water column energy is less; similarly, they may be resuspended under increased energy environment. However, water column turbidity does not exhibit significant correlation with calcium carbonate (Figure 5.10); illustrating the fact the dynamics of the calcium carbonate in the coastal sediments of Miri was highly complex. The low communality for $CaCO_3$ in this factor model may be related to productivity in the water column and may be ascertained if we consider the fact the coastal zone contributes about 20% of global marine production albeit occupying only 10% of the global marine surface (Wollast 1998), and also significantly contributing to the biological precipitation of calcium carbonate in shallow shelves (Milliman 1993).

In the case of Ni and Co, the low communality could be attributed to the ionic interactions of major ions of the seawater which influence the partitioning of these metals between the sediment and the water column, the details of which are discussed later. Such ionic interactions can introduce complexity in the variability of metal concentrations in the sediments. For example, the partition coefficient of Ni in the exchangeable fraction of the sediment (i.e. adsorbed and carbonate-bound) exhibit significant correlation with Ca^{2+} (-0.391; $P < 0.05$), and turbidity (-0.527; $P < 0.05$) implying ionic interactions and exchange of elements/metals between the water column and the sediments. Although significant ($P<0.05$), the correlation coefficients were less, implying weak interactions.

The factor model reveals among the observed five factors, the first factor accounts for 22.9% of variance in the data, and is characterized by positive loadings of Cu (0.928), Zn (0.924), silt (0.642) (Table 5.6). Copper and Zn exist as strong metal-organic complexes in fresh water (Baeyens et al. 1997; Kozelka and Bruland 1998; Bruland et al. 2000; Ndung'u et al. 2003), and flocculates to various degrees upon mixing with seawater (Sholkovitz 1978; Karbassi et al. 2008; Karbassi et al. 2014). Such a flocculation process will result in their accumulation in the sediments. The positive loading of Cu and Zn with silt fraction indicates these metals are mainly associated with finer fraction of the sediments. There is also evidence of formation of extremely fine particles during the formation of metal sulphides (Lewis 2010), and this may be one of the reasons for the observed loading of Cu and Zn with silt fraction.

In the estuarine region and the sea, Cu tends to form Cu-carbonate and Cu-bicarbonate species (Byrne and Miller 1985) while, Zn and Co mostly remains in free or hydrolyzed form (Flegal et al. 1991; Ćosović et al. 1982). The ionic species Cu (II), Zn (II) and Co (II) also form complexes with chloride ions in the seawater (Turner et al. 1981).

Since these element/metal species are positively charged, they may tend to adhere to negatively charged fine particles and organic matter in the water column (Hunter and Liss 1982), and become deposited along with them. In order to confirm this postulation, the zeta potential of the suspended particles in the seawater samples was measured using Malvern Zetasizer ZS, and they were found to have a negative charge. Further, it was revealed the suspended particles in the collected seawater samples contain colloids in size ranging from 1 to 1280 nm.

Table 5.6 Rotated Component Matrix[a] segments (1-9 locations)

	Component					
Elements	**1**	**2**	**3**	**4**	**5**	**Communalities**
Cu	**.928**	-.036	-.032	-.082	.305	.964
Pb	.205	.148	.687	-.032	.616	.917
Cd	.191	-.128	**.940**	.148	.155	.983
Co	**-.841**	.139	-.163	.112	.243	.825
Ni	.052	-.505	-.697	.207	.174	.817
Zn	**.924**	.034	.044	-.061	.296	.947
Fe	-.357	.147	-.150	**.809**	-.374	.966
Mn	.029	.200	.014	**.912**	.335	.985
Cr	-.143	**.961**	.127	-.045	.052	.965
silt	.642	-.126	**-.715**	.183	-.079	.979
$CaCO_3$	-.017	.529	-.061	**-.723**	-.063	.811
pH	.114	.015	.084	.109	**.954**	.943
Sulphate	.346	.608	.153	-.365	.362	.777
HCO_3^-	-.118	**.882**	-.034	.379	-.023	.938
Eigen Value	3.922	3.356	2.355	2.011	1.174	
% of Variance	22.93	16.61	17.55	17.30	14.16	
Cumulative %	22.93	42.54	60.09	77.39	91.55	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 6 iterations.

Cobalt was found to be particle reactive and Kharkar et al. (1968) have experimentally demonstrated around 90% of Co is adsorbed by montmorillonite and illite under conditions resembling that found in streams, and 40-70% of it is desorbed under seawater conditions. Irrespective of being mainly composed of recycled sediments, the Baram River basin is a source of clay minerals (i.e. illite, kaolinite and chlorite) (Liu et al. 2012; Nagarajan et al. 2014). Thus, it is expected Co might have been adsorbed onto these clay particles and transported to sea. The observed negative loading of Co (-0.841) and the positive loading of silt (0.642) on the first factor implies desorption of Co from clay minerals once they are delivered to the seawater (Turner and Milward 2002).

The Neogene sedimentary succession in the west Baram delta consists of an organic rich layer, and has been grouped into Lambir formation (Middle to Late Miocene), Miri formation (Middle to Late Miocene), and Tukau formation (Late Miocene to Early Pliocene) (Hutchison 2005; Togunwa et al. 2015). Organic rich layers associated with these formations have the potential to accumulate the chalcophile elements Cu. Zinc and Co due to the formation of pyrite during sulphate reduction. Evidence of pyrite has been reported in the catchment areas of the study area, (Nagarajan et al. 2014; 2015). Thus, the source for Cu, Zn and Co was identified to be natural. These metals are dissolved during pyrite oxidation and transported through the river to the coastal areas. Shale is another component from which these elements/metals may be derived due to moderate to intensive chemical weathering in a region. The Cu, Zn and Co released during sulphide oxidation may be transported both in dissolved and particulate form, and in both phases, these elements/metals may also exist as metal-humic complexes (Tessier et al. 1980; Takata et al. 2012).

As per the foregoing discussion, the presence of Cu, Zn, and Co in the sediments of the SW segment of the study area was due to leaching from the hinterland. Since these metals exhibit association with silt, the prevailing *hydrological regime* (*i.e.*, the flow velocity of currents, action by waves and tides) can influence the distribution of these sediments, and therefore the levels of Cu, Zn and Co. The higher percentage of variance explained for Cu (86.1%), Zn (85.3%) and to a lesser extent for silt (41.2%) by factor-1 is further evidence for the influence of grain size on the distribution of these metals in the sediments. However, not all riverine dissolved Cu, Zn and Co can be deposited to the sediments, as they exist in the seawater as metal-organic complexes (Batley and Gardner 1978; Balls 1989; Laslett 1995; Kozelka and Bruland 1998). This is most applicable in the case of Co, where it tends to remain in the water column as cobalt-organic complexes in the seawater (Ellwood and van den Berg, 2001; Saito and Moffett, 2001) after desorption from the riverine sediments.

Factor-2 explains 19.6% variance in the data, and has a high positive loading of Cr (0.961), and water column HCO_3^- (0.882) while, SO_4^{2-} (0.608), $CaCO_3$ (0.529) and Ni

(-0.505) have moderate loadings. Chromium has a distinct character as it is mobile under an oxic environment, and becomes immobile under a reducing environment. Therefore, association of Cr with the water column parameters (i.e. HCO_3^- and SO_4^{2-}) implies sulphide oxidation in the sediments. During sulphide oxidation, Cr within the anoxic sediments could become oxidized and then diffuses towards a water-sediment interface and finally released into the water column (Murray et al. 1983; Gaillard et al. 1986; Douglas et al. 1986). This Cr mobilization process can be best understood from its longitudinal profile, where its concentration in the sediments decreased as it moved towards the SW (Figure 5.11) where sulphide oxidation was found to be a dominant process.

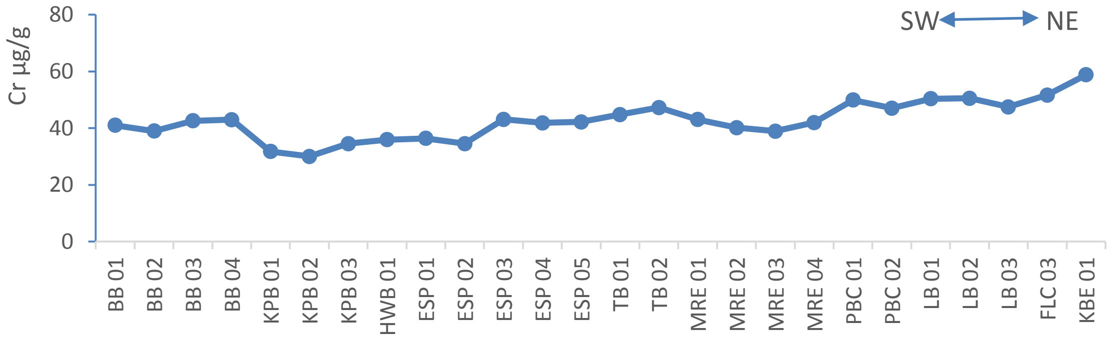

Figure 5.11 Longitudinal profile of total Cr moving from south to north side of the sampling locations

Pyrite oxidation is catalyzed by the availability of dissolved oxygen and Fe (III) in the circumneutral pH (Moses and Herman 1991). The observed water column pH in the SW segment fell to the circumneutral range of (pH = 7.2 to 7.5) and the water column was well- oxygenated (DO=3.4 to 5.1 mg/L), which is conducive for pyrite oxidation to take place. The release of sedimentary Cr and Fe was exemplified by a negative correlation (-0.909; $P < 0.001$) between exchangeable Cr and Fe. This observation can be interpreted as due to the release of remobilized Cr to the water column, while Fe tends to form a coating on $CaCO_3$ in the sediments as ferric hydroxide (Whitney 1975; Cravotta III and Trahan 1996)[4]. There is one more piece of evidence in favor of this theory; the significant positive correlation (0.651; $P< 0.05$) between oxidizable fractions of Fe and Cr. This can

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[4] This is the most obvious reason for the observed loading of CaCO3 on factor-1.

be further substantiated by the observed positive correlation of $CaCO_3$ with the oxidizable fraction of Cu (0.484; $P < 0.1$), reducible fraction of Pb (0.515; $P < 0.1$) and oxidizable fraction of Zn (0.541). Though Cu, Pb and Zn are in different fractions, their association with “thought to be” iron oxide coating on $CaCO_3$ is due to their enhanced interaction with iron oxide surface that result from the formation of iron-organic complexes, which serve to complex the trace metals (Tipping and Cooke 1982; Davis 1982; Laxen 1985; Young and Harvey 1992; Gu et al. 1995). This interpretation may be questioned on the observation Cu, Pb and Zn have not loaded on factor-2; instead, their factor loadings are on other factors. Subscribing to the fact the factor model was based on the variance in the data, it was understood the compositional variability introduced by $CaCO_3$ adsorption of Cu, Pb and Zn should be less than the variability arising from the processes described under the factors where these metals exhibit high loading. Finally, it should be stated the observed negative correlation (-0.527; $P < 0.1$) between $CaCO_3$ and the reducible fraction of Fe illustrated the loss of remobilized Fe towards forming the coating on $CaCO_3$ and tends to diminish the quantity of iron that may otherwise become absorbed into the reducible fraction. Also, from the foregoing discussion, it was concluded the first step extraction in the BCR procedure, which is meant to dissolve adsorbed and carbonate-bound fractions, also dissolved the iron oxide coating on the $CaCO_3$. Thus, care should be exercised when interpreting the data obtained from sequential extraction.

Finally, it should be emphasized pyrite oxidation results in the generation of SO_4^{2-} ions and the resulting acidity increases the HCO_3^- concentration in the water column. This is true for river water as well as for seawater. From the observation SO_4^{2-} and HCO_3^- only exhibits high loading on factor-2, it can be conclude these ions were mostly contributed from the seawater rather than being supplied by the river. Such a sulphide oxidation occurring in the coastal area of Miri would also release sedimentary Ni to the water column as inferred from its negative loading on factor-2 (Naylor et al. 2004). These observations lead to the belief sulphide oxidation in the river basin influences the concentration of Cu, Zn and Co in the Miri coastal environment, while the same process occurring within the coastal sediments is responsible for the observed distribution of Cr, Ni, SO_4^{2-} and HCO_3^-.

Factor-3 accounts for 17.5% variance in the data and was positively loaded with Pb (0.687), Cd (0.940) and negatively loaded with Ni (-0.697) and silt (-0.715). The metals Pb and Cd are particle reactive (Tang et al. 2002; García-Rico et al. 2011) and may be affected by biological processes occurring in the water column (James et al. 1993; Tappin et al. 1995; Cotté-Krief et al. 2002). The negative correlation (0.-639; P<0.1) between the water column PO_4 and the oxidizable fraction of Pb in the sediments did not point to such a biological control on its concentration in the sediments (since, increased PO_4 concentration should result in increased productivity and enhance particulate removal of Pb). Moreover, Cd does not exhibit any correlation with PO_4. However, a close look at the data shows water column PO_4 levels were less significantly associated with the levels of the residual fraction of Co (0.431; P<0.15), Fe (0.454; P<0.15) and the reducible fraction of Mn (0.415; P<0.15) in the sediments and the values of correlation coefficients were not high. This possibly implied the leaching of phosphate minerals from the sediments. At the same time, the negative loading of Ni (-0.697) and silt (-0.715) has to be explained.

From earlier work, it can be understood Ni associated with riverine sediment is found to exhibit little or no tendency to desorb upon contact with seawater (Turner et al. 1998: Martin et al. 2004). Further, river water also supplies fine particles to the coastal environment and later becomes flocculated in the seawater (Wolanski and Gibbs 1995). Thus, clearly the variability in the content of Ni and silt, that was accountable for factor-3, was of detrital origin. The association of Ni and silt with the factor-3 was interpreted as a riverine supply of Ni with silt but the source for Pb and Cd was not of riverine origin as both Ni and silt are oppositely loaded with Pb and Cd. The inference now is atmospheric fall out from forest fires, which is quite common in Borneo and SE Asia, may be the source for these metals in the coastal sediments as well as in emergent trees of the tropical forests (Wooster et al. 2012). This is further confirmed by the observed strong negative correlation between Pb and Ni in their exchangeable fractions (-0.811; P<0.05), and Pb and Ni in their reducible fractions (-0.640; P<0.05). Similarly, there is a significant negative correlation of Cd in the exchangeable fraction (-0.793; P<0.05) with Pb in the exchangeable fraction. If Pb, Cd and Ni have a similar source, it was difficult to observe such a negative correlation among their mobile phases. However, the residual fraction of Pb and Cd had a significant positive correlation (0.820; P<0.05) but these two metals did not exhibit such a relationship with residual Ni, again indicating different sources for their residual fractions too.

Factor-4 was responsible for 17.3% variance in the data and is loaded with Fe (0.809) and Mn (0.912) and negatively loaded with $CaCO_3$ (-0.723). Such a relationship simply means the flocculation of dissolved Fe and Mn as their respective hydrous oxides and further precipitation to the sediments (Sholkovitz, 1976, 1978; Boyle et al. 1977; Karbassi et al. 2013) . Such a process is not expected to occur in a location far from the Baram river mouth. However, input from small channels, such as the Miri River and Sibuti River in the SW part of the study area might have a significant supply of dissolved Fe and Mn. Further, the salinity values along the coastal region were only transitional during this season which then introduced a salinity gradient in the water column and promoted flocculation to occur along the coast. The reductive dissolution of Fe and Mn hydrous oxides may have dissolved $CaCO_3$ and then was responsible for the observed negative correlation of $CaCO_3$. Factor-5 explained 14.1% variance in the data and was positively loaded with Pb (0.616) and pH (0.954). This can be ascribed as due to the effect of the water column pH on the adsorption of Pb to the sediments (Impellitteri et al. 2002; Wang et al. 2009).

5.9.1.2 *Factor analytical results for monsoon sediments: Segment-2 (10 to 26 locations)*

Five factors accounted for 91.3% variance in the data (Table 5.7). The communality values for all the variables were also high (Table 5.7). Factor-1 accounted for 28% variance in the data and was positively loaded with Fe (0.935), Mn (0.824), silt (0.939) and negatively loaded with fine sand (-0.893), organic carbon (-0.557), water column HCO_3^- (-0.698) and Co (-0.466) respectively (Table 5.7). The loadings for organic carbon, bicarbonate and Co was only moderate. The positive loading of Fe, Mn and silt along with the negative loading of fine sand, organic carbon, water column HCO_3^- and Co on a single factor reflected the effect of mixing up of riverine water with the seawater. During this season the river water input was greater, which would have delivered a greater amount of sediments to the coastal region. Upon entering the sea, riverine Fe and Mn adsorbed onto the silt fraction could be deposited near the river mouth whereas, fine sand and organic debris would be deposited in the far-off distance. The negative loading of fine sand, organic carbon, water column bicarbonate and Co implied wherever seawater influence is great, fine sand (the silt fraction is seemingly washed out by waves and currents), organic carbon and Co will also be greater.

This also implies the bicarbonate concentration is more in places where seawater influence is significant. Thus, riverine Fe, Mn, Co, organic carbon, fine sand and silt are differentiated in the sediment and water column. This factor is interpreted to be "*water column energy*". Such a kind of metal removal from the water column wasobserved in large and middle size estuaries in China (Zhang and Liu 2002). From these observations, it is evident Fe and Mn distribution in the NE segment (stations 10-26) was dominated by water column energy (accounting for 28% of variance), while in the SW segment (stations 1-9) they were controlled by flocculation (accounting for 17.3% variance). This observation further validated the division of the entire coast into two segments based on the prevailing hydrological regime of the area.

Factor-2 accounted for 19.5% variance in the data, and was positively loaded with Cu (0.878), Zn (0.931) and to a lesser extent by Pb (0.681). Organic carbon (-0.671) and Co (-0.395) exhibit moderate negative loading. Considering several processes: i) flocculation cannot be invoked as neither salinity nor pH is loaded on this factor; ii) grain size effect cannot be involved as neither silt nor fine sand load on this factor; iii) complexation with organics can be invoked but, the negative loading of organic carbon on this factor should be explained. Therefore, water column chemistry may play a role in metal distribution and, thus the correlation coefficient of partition coefficient (K_d = [element/metal concentration in the sediment / element/metal concentration in the water column]) with water column parameters was calculated (Table 5.8). There was a positive correlation between Cu and Zn (0.925; $P<0.05$), Cu and SO_4^{2-} (0.517; $P<0.05$), Cu and NO_3^- (0.534; $P<0.05$); Zn exhibited significant correlation with Mg (0.416; $P<0.05$), SO_4^{2-} (0.410; $P<0.1$) and NO_3^- (0.534; $P<0.1$).

From these observations it is clear that *organic complexation as affected by ionic interactions and competitive binding* were responsible for the observed variations in the concentrations of Cu, Zn, Pb and Co in the sediments (Zirino and Yamamoto 1972; Tipping 1981; Davis 1984; Millward and Liu 2003; Hatje et al. 2003; Ciffroy et al. 2003;

Garnier et al. 2006). The overall net effect of these interactions for the case of Cu, Zn and Pb seemed to be a simultaneous decrease in humic acid binding with increased adsorption onto clay particles under increasing ionic strength conditions (Liu and Gonzalez, 1999) whereas, in the case of Co, it did not seem to be greatly affected, possibly due to the existence of strong Co-organic complexes in the riverine sediments as demonstrated for Pb by Hizal and Apak (2006) or, due to its strong binding with iron oxides (Backes et al. 1995).

Table 5.7 Rotated Component Matrix[a] segment-2 (10-26 locations)

	Component					
Elements	**1**	**2**	**3**	**4**	**5**	**Communalities**
Cu	.034	**.878**	.075	.050	.202	.821
Pb	.248	.681	.036	.225	-.542	.872
Cd	-.015	.353	**.912**	-.033	.038	.959
Co	-.466	-.395	.368	.656	-.023	.939
Ni	.581	.114	.680	.065	-.106	.828
Zn	.133	**.931**	.134	.236	.127	.974
Fe	**.935**	.228	-.119	-.179	-.025	.972
Mn	**.824**	.008	.512	-.004	-.162	.967
Cr	-.139	.301	**-.905**	.133	-.039	.948
Fine	**-.893**	-.115	-.117	-.298	-.087	.920
Silt	**.939**	.084	.122	.230	.056	.960
Organic Carbon	-.557	-.671	.189	.135	-.157	.838
pH	.260	.110	-.057	**.906**	.128	.919
Salinity	.049	.350	-.021	**.871**	.014	.884
Sulphate	.123	.394	.069	.192	**.816**	.877
HCO_3^-	-.698	-.125	-.221	.599	-.225	.962
Turbidity	.068	.098	**.709**	.589	.139	.884
Eigen Value	6.10	3.41	3.04	1.86	1.09	
% of Variance	28.08	19.55	18.67	18.09	6.94	
Cumulative %	28.08	47.62	66.29	84.38	91.32	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 8 iterations.

Table 5.8 Correlation coefficient of partition coefficient (K_d) in the sediment of segment 2 (samples 10-26) significance level 0.05

	Cu	Zn	Pb	Co	Ni	Cd	Mn	Fe	pH	TUR	SAL	Eh	DO	PO_4	SO_4	NO_3N	NH_3N	CO_3	HCO_3	Ca	Mg	Cl	K	B	Fine	Silt
Cu	1.000																									
Zn	**.925**	1.000																								
Pb	-.421	-.370	1.000																							
Co	.292	.094	-.262	1.000																						
Ni	**.491**	**.492**	.043	-.057	1.000																					
Cd	**.464**	.324	-.172	.107	**.556**	1.000																				
Mn	-.163	-.117	.396	-.099	**.434**	-.020	1.000																			
Fe	-.176	-.022	.325	-.551	.292	-.336	**.554**	1.000																		
pH	.133	-.063	.307	**.510**	-.052	.086	.068	-.477	1.000																	
TUR	.175	.257	-.292	-.193	.277	.221	.025	**.467**	-.720	1.000																
SAL	.181	.077	.105	**.458**	-.083	.055	.084	-.619	**.850**	-.807	1.000															
Eh	-.236	-.123	-.395	-.024	-.178	-.251	-.152	.253	-.596	**.500**	-.613	1.000														
DO	-.049	-.171	.028	.387	.017	.150	.186	-.558	**.564**	-.650	**.774**	-.437	1.000													
PO_4	.136	.207	-.210	-.132	.019	-.166	-.308	**.438**	-.580	**.645**	-.744	**.430**	-.678	1.000												
SO_4	**.517**	.410	-.156	**.420**	.130	.247	-.086	-.543	**.701**	-.559	**.816**	-.585	**.549**	-.359	1.000											
NO_3N	**.534**	.341	-.388	**.759**	-.077	.327	-.277	-.601	.369	-.070	.404	-.111	.227	-.093	**.479**	1.000										
NH_3N	-.091	-.026	-.175	-.389	.195	.051	-.004	**.592**	-.819	**.857**	-.957	**.533**	-.769	**.652**	-.776	-.303	1.000									
CO_3	-.239	-.286	.382	.138	-.118	.007	.153	-.440	**.558**	-.693	**.711**	-.402	**.608**	-.772	**.416**	.064	-.680	1.000								
HCO_3	.356	.284	-.153	**.637**	-.139	.014	-.086	-.661	**.719**	-.602	**.887**	-.415	**.669**	-.479	**.780**	**.577**	-.868	.390	1.000							
Ca	.056	-.041	.149	.358	-.129	.027	.126	-.585	**.821**	-.863	**.984**	-.595	**.805**	-.799	**.756**	.310	-.956	**.747**	.826	1.000						
Mg	.326	**.416**	-.178	-.062	.232	-.003	-.120	**.470**	-.581	**.863**	-.729	**.437**	-.736	**.815**	-.423	-.003	**.726**	-.684	-.480	-.833	1.000					
Cl	.142	.038	.112	**.431**	-.090	.047	.112	-.606	**.848**	-.817	**.996**	-.601	**.777**	-.768	**.799**	.384	-.951	**.722**	**.864**	**.988**	-.751	1.000				
K	.144	.092	.168	.349	.026	.132	.151	-.551	**.788**	-.744	**.959**	-.624	**.751**	-.784	**.801**	.303	-.908	**.739**	**.807**	**.950**	-.728	**.952**	1.000			
B	.105	.025	-.119	.294	-.159	.167	-.269	-.710	**.622**	-.576	**.732**	-.351	**.558**	-.624	**.534**	.255	-.685	**.500**	**.714**	**.727**	-.643	**.710**	**.713**	1.000		
Fine	.007	-.011	-.331	.342	-.546	.117	-.608	-.853	.167	-.349	**.421**	-.066	.366	-.280	.338	**.531**	-.455	.294	**.531**	**.416**	-.381	.409	.389	**.511**	1.000	
Silt	-.007	.011	.331	-.343	**.545**	-.118	**.607**	**.854**	-.167	.349	-.422	.066	-.367	.281	-.338	-.532	**.455**	-.294	-.531	-.417	.381	-.410	-.390	-.512	1.000	1.000

The dominance of river derived sediments along the NE segment of the study area may, then, explain the distribution pattern of Co in the sediments. In order to examine this postulate, the Co content of the sediments based on its partition coefficient (Table 5.9), was examined and was found to be positively correlated with a pH of (0.337; $P<0.05$) and salinity of (0.331; $P<0.05$). Though the correlation coefficient was less, the high significance ($P<0.05$) implied both pH and salinity may increase Co adsorption to the sediments or, may retard it's desorption from the sediments, once it is delivered to the sea from the river. Of these two processes, "*retardation of desorption*" seems to better explain the situation as the NE segment of the study area is near the Baram River outlet, thereby rendering a much higher riverine influence on the characteristics of the water and sediment column in the nearby areas.

Though Co mainly exists in seawater as a free ion (Wen et al. 2011), a contrasting behaviour is implicated here that can possibly be explained by a differentiation of mobility of the elements/metals upon mixing with the seawater as observed for the elements/metals leached from acid sulphate soils in the Vörå River system of Finland (Nordmyr et al. 2008). Moreover, the dominance of riverine organic matter and iron oxides in the NE segment of the study area was expected to influence the Co chemistry in the sediments. A strong association of Co with iron oxides (Backes et al. 1995) may be mediated through surface complexation of organics with the binding sites on iron oxides (Stumm and Sulzberger 1992; Weng et al. 2006; Takata et al. 2010). This kind of metal adsorption may explain the negative loading of Co with the sedimentary organic matter on factor-2.

It has been demonstrated by Balistrieri and Murray (1982) major ion chemistry may affect the adsorption of trace elements/metals from seawater. Balls (1989) has shown in the coastal water, the partition coefficient (K_d), defined as the ratio of metal concentration in the particulates to that in solution, decreases in the order Pb, Hg > Cu, Zn, Ni > Cd, and this sequence applies within the given area though, the values of partition coefficient may vary from place to place. In this series, Pb tends to be in the particulate phase and Cd tends to be in the solution phase. Thus, the observed correlation between Cu and Zn (0.925; $P<0.05$) could be ascribed to their adsorption or, complexation with particulate matter. Whereas, the positive correlation between Cu and SO_4^{2-} (0.517; $P<0.1$), Cu and NO_3^- (0.534; $P<0.05$), Zn and Mg^{2+} (0.416; $P<0.05$) is due to weak ionic interactions (since the correlation coefficient is less). The release of Cu, Zn, Pb and Co due to sulphide oxidation in the river basin, and their transport and deposition in the coastal sediment, was the main source for these metals.

Factor-3 accounted for 18.6% variance in the data and was positively loaded with Cd (0.912) and turbidity (0.709) and negatively loaded with Cr (-0.905). Moderate positive loadings were observed for Ni (0.680) and Mn (0.512). Significant positive correlation was observed between the partition coefficients of Cd and Fe (0.858; $P<0.05$), and, Cd and the water column PO_4^- (0.927), both in the exchangeable fraction. A similar relationship existed between the partition coefficients of Cd and Ca^{2+} (0.781; $P<0.05$) in the reducible fraction (Table 5.10). At the same time, Cd in the oxidizable fraction exhibited significant negative correlation with turbidity (-0.632; $P<0.05$). Negative correlation was also observed between Cd and Zn (-0.622; $P<0.05$) in the exchangeable fraction. The $CaCO_3$ content of the sediment was positively correlated with oxidizable fraction of Cd.

From these observations, it can be inferred the variability of Cd in the sediment was mainly associated with its interaction with Fe in the carbonate phase (the first step of the BCR method extracts metals both in the exchangeable and carbonate bound phase), and PO_4^-, Ca^{2+} in the water column. The relationship between Cd and turbidity mainly arose from its oxidizable fraction in the sediments. In order to explain the variance on factor-3, all these mechanisms should be linked together and explained. Such a possible mechanism is the formation of ferric hydroxide layers on silicate and carbonate fragments (Whitney 1975), over which Mn oxides can become coated (Hem 1977), and trace metals could be adsorbed on to these surfaces. Under such a situation, ionic interactions, competitive binding, and organic complexation may control the adsorption-desorption processes. The following processes are thought to occur: i) higher primary productivity due to availability of PO_4^-; ii) removal of Cd by phytoplankton during primary productivity (Kuwabara et al. 1989; Bown et al. 2011); iii) productivity enhanced $CaCO_3$ saturation[5] in the water column and precipitation to the sediments (Milliman et al. 2012);

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[5] In many parts of the ocean, $CaCO_3$ was found to be supersaturated; however, its precipitation is prevented due to non-specific inorganic/organic reaction kinetic control (Chave 1965; Chave and Suess 1967). During photosynthesis, dissolved CO_2 is taken up, and there is an increase in pH. As a result of pH increase, the saturation level of $CaCO_3$ further goes up, resulting in the precipitation of $CaCO_3$. For a

iv) formation of Fe-oxide coating on these precipitated $CaCO_3$ fragments (Whitney, 1975); v) adsorption of Mn^{2+} and PO_4^- on iron oxides (Hem, 1964); This assumption is further supported by the observed positive correlation of partition coefficients between the reducible fraction of Fe and Mn (0.672; $P<0.05$), and the reducible Mn and the water column PO_4^- (0.543; $P<0.05$); (Table 5.9).

The high loading of Cd and turbidity on factor-3 should then be interpreted as "*resuspension of the sediments*" that is expected to provide more nutrient to the water column and thereby enhance phytoplankton productivity. This resuspension is quite possible due to the currents set by the riverine water along the coast (Nagarajan et al. 2015a). Under such a scenario, the organics brought by the river water deplete oxygen levels in the water column, and render Cr in the sediments immobile[6]. This explains its negative loading on (-0.905) factor-3. The moderate positive loading of Ni and Mn was due their remobilization from the sediments along with Cd.

Factor-4 explained around 18% of variance in the data and was positively loaded with pH (0.906) and salinity (0.871). Moderate positive loading was observed for Co (0.656), HCO_3- (0.599), and turbidity (0.589). This essentially implied the desorption of Co as a salinity increases. Under such an environment, Co mainly exists as free ion (Wen et al. 2011; Raymont 2014). The loading of bicarbonate and turbidity can be explained as due to riverine input. Looking at the partition coefficient, the reducible fraction of Co had a significant correlation with the water column Ca^{2+} (0.781; $P<0.05$). From this, the loading of Co, pH, salinity and HCO_3^- on factor-4 can be understood as the dissolution of calcium carbonate [$CaCO_3 + H^+ + HCO_3^- \Rightarrow Ca^{2+} + 2\ HCO_3^-$; Milliman et al. 2012] due to low pH river water, the rapid flow of which creates turbulence in the seawater column, resuspends the sediments, remobilizes Co from the sediments and dissolves $CaCO_3$. During this process, the Ca^{2+} and HCO_3^- concentration in the water column increases.

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detailed discussion and related developments on this topic please refer Larson et al. (1942); Chave and Suess (1967); Jackson and Bischoff (1971); Chierici and Fransson (2009); Milliman et al. (2012); Drake et al. (2015).

[6] Under reducing condition Cr is immobile

Table 5.9 Correlation between partition coefficient (K_d) with both water parameters and reducible fraction significance level 0.05

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Eh	PO_4	SO_4	NH_3N	CO_3	HCO_3	Mg	Ca	Cl	k	pH	DO	TUR	SAL
Cu	1.000																					
Pb	-.058	1.000																				
Cd	-.419	-.371	1.000																			
Co	-.028	-.220	.120	1.000																		
Ni	-.179	-.114	.564	.131	1.000																	
Zn	**.719**	-.069	-.364	-.104	-.363	1.000																
Fe	-.273	.218	.327	-.161	.369	-.193	1.000															
Mn	-.043	-.105	.215	.138	.401	-.006	**.672**	1.000														
Eh	-.264	-.481	.221	.072	-.014	.045	.086	.055	1.000													
PO_4	-.126	-.245	.140	.180	.169	-.032	.266	**.543**	.273	1.000												
SO_4	.240	-.072	-.036	.173	.035	.153	-.064	.189	-.337	-.177	1.000											
NH_3N	-.154	-.210	-.034	.043	-.049	-.004	.410	.589	.276	.516	.034	1.000										
CO_3	-.213	.168	.070	.290	.120	-.055	-.107	.163	-.156	-.028	.279	-.186	1.000									
HCO_3	**.571**	.067	-.562	.254	-.252	.297	-.443	-.035	-.468	-.229	.496	-.206	.258	1.000								
Mg	**.361**	.281	-.543	.189	-.219	.190	-.334	.081	-.536	-.181	.467	-.196	.534	.882	1.000							
Ca	**-.353**	-.388	**.781**	-.007	.427	-.220	.355	.049	.421	.173	-.209	-.003	-.229	-.700	-.844	1.000						
Cl	.249	.077	-.163	.287	.047	.073	-.199	.215	-.506	-.108	.573	-.285	.652	.782	.856	-.461	1.000					
k	.165	.129	-.153	.101	-.042	.120	-.073	.216	-.344	-.087	.752	.130	.478	.592	.652	-.409	.708	1.000				
pH	.122	.290	-.033	**.337**	.043	-.101	-.178	-.106	-.498	-.362	.421	-.571	.493	.559	.610	-.264	.731	.448	1.000			
DO	.095	-.056	-.333	.260	-.017	.074	-.052	.458	-.226	.137	.300	.170	.390	.565	.629	-.514	.583	.274	.160	1.000		
TUR	-.123	-.432	.342	-.011	.204	-.021	.452	.521	.451	.465	-.039	.846	-.357	-.426	-.547	.424	-.484	-.063	-.650	-.090	1.000	
SAL	.285	.114	-.228	**.331**	.019	.103	-.256	.168	-.522	-.138	.595	-.290	.653	.833	.899	-.528	.985	.719	.756	.579	-.507	1.000

Table 5.10 Correlation between partition coefficient (K_d) with both water parameters and exchangeable fraction significance level 0.05

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Eh	PO_4	SO_4	NH_3N	CO_3	HCO_3	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.000																					
Pb	-.146	1.000																				
Cd	-.145	1.000	1.000																			
Co	-.145	1.000	1.000	1.000																		
Ni	-.143	1.000	1.000	1.000	1.000																	
Zn	**.777**	**-.622**	-.622	**-.622**	**-.621**	1.000																
Fe	.083	**.858**	**.858**	**.857**	**.859**	**-.347**	1.000															
Mn	.212	-.281	-.281	-.282	-.280	**.350**	-.197	1.000														
Eh	-.249	.125	.125	.126	.125	-.194	.185	-.310	1.000													
PO_4	-.150	**.927**	**.927**	**.927**	**.927**	**-.570**	**.858**	**-.378**	.273	1.000												
SO_4	.191	-.146	-.147	-.145	-.146	**.347**	-.294	**.503**	**-.337**	-.177	1.000											
NH_3N	**-.379**	**.483**	**.483**	**.482**	**.483**	**-.384**	**.374**	.032	.276	**.516**	.034	1.000										
CO_3	-.279	.112	.111	.112	.111	-.287	-.148	.058	-.156	-.028	.279	-.186	1.000									
HCO_3	.261	.041	.040	.042	.040	.181	-.175	.305	**-.468**	-.229	**.496**	-.206	.258	1.000								
Mg	.059	.126	.126	.126	.125	-.042	-.152	.325	**-.536**	-.181	**.467**	-.196	**.534**	**.882**	1.000							
Ca	.032	-.135	-.135	-.134	-.134	.107	.084	-.201	**.421**	.173	-.209	-.003	-.229	**-.700**	**-.844**	1.000						
Cl	.097	.101	.100	.102	.100	-.007	-.181	**.365**	**-.506**	-.108	**.573**	-.285	**.652**	**.782**	**.856**	**-.461**	1.000					
K	-.011	.071	.070	.070	.070	.125	-.167	**.487**	**-.344**	-.087	**.752**	.130	**.478**	**.592**	**.652**	**-.409**	**.708**	1.000				
pH	.187	-.218	-.218	-.216	-.218	.141	**-.365**	.319	**-.498**	**-.362**	**.421**	**-.571**	**.493**	**.559**	**.610**	-.264	**.731**	**.448**	1.000			
DO	-.195	.315	.314	.315	.314	**-.385**	.028	.166	-.226	.137	.300	.170	**.390**	**.565**	**.629**	**-.514**	**.583**	.274	.160	1.000		
TUR	-.180	.312	.312	.312	.313	-.146	**.379**	.033	**.451**	**.465**	-.039	**.846**	**-.357**	**-.426**	**-.547**	**.424**	**-.484**	-.063	**-.650**	-.090	1.000	
SAL	.126	.091	.091	.093	.091	.027	-.185	**.352**	**-.522**	-.138	**.595**	-.290	**.653**	**.833**	**.899**	**-.528**	**.985**	**.719**	**.756**	**.579**	**-.507**	1.000

Factor-5 accounted for 6.9% variance and was loaded only with water column SO_4^{2-} (0.816). Pb showed moderate negative loading (-0.542). This was due to the effect of SO_4^{2-} on Pb adsorption to the sediments. Balistrieri and Murray (1982) demonstrated the adsorption of SO_4^{2-} alters the electrostatic conditions on the surface of goethite (α-FeOOH) and increases adsorption of trace metals, including Pb, in the seawater. Ferrihydrite and goethite are naturally occurring iron hydroxide minerals, which are highly reactive and capable of exerting control over the concentrations of nutrients and trace elements in the natural environment (Van Der Zee et al. 2003; Marchand and Rancourt 2009; Bosch et al. 2010; Chesne and Kim 2014). Thus, ionic interaction, especially with SO_4^{2-} was mainly responsible for the observed variation of Pb concentration in the sediments.

5.9.1.3 ***Factor analytical results for post-monsoon sediments: Segment-1 (1 to 11 locations)***

The factor model accounted for 84.5% variance in the data with four factors explaining around 29.6%, 21.7%, 17.6% and 15.4% variability, respectively (Table 5.11). The communality values for all of the variables were also high except for Zn (Table 5.11). Factor-1 was loaded with Cu (0.851), Fe (0.827), $CaCO_3$ (0.783) and silt (0.881) (Table 5.11). The percent contribution of each variables in the factor-1 was 20.3%, 19.2%, 17.2%, 21.8%, respectively. The first factor explained 72.5% of total variance in Cu, 68.4% of total variance in Fe, 61.3% of total variance in $CaCO_3$, and 77.6% of total variance in silt. The loading of Cu, Fe and $CaCO_3$ together with silt was due to the formation of an iron hydrous oxide coating on calcium carbonate and its adsorption of Cu (Whitney, 1975; Cravota III, 1993). An elaborate discussion about this mechanism was already described under factor-2 for the SW segment samples collected during the monsoon period. Their association with silt fraction revealed the fine nature of $CaCO_3$.

Factor-2 was loaded with Pb (0.777), pH (0.766), SO_4^{2-} (0.860). On factor-2, Pb contributes about 23.1% of variance whereas, pH and SO_4^{2-} contributed about 22.5% and 28.3% variability. The total variance of Pb, pH and SO_4^{2-} explained by factor-2 were 60.4%, 58.7% and 74%, respectively. Briefly, the association of Pb, pH and SO_4^{2-} on factor-2 can be explained as due to the effect of pH on galena oxidation (Steger and Desjardins 1980); (Heidel and Tichomirowa 2011); (Hampton et al. 2011) or, its formation

(Smieja-Król et al. 2015). The available data is inadequate to point out any one of these processes.

Table 5.11 Rotated Component Matrix^a segment-1 (SW segment; 1-11 locations)

	Component				
Elements	**1**	**2**	**3**	**4**	**Communalities**
Cu	**.851**	-.070	.461	.078	.949
Pb	.401	**.777**	.020	-.127	.781
Ni	.111	-.157	-.024	**.872**	.797
Zn	-.379	-.530	.008	.480	.656
Fe	**.827**	.064	.431	.214	.919
Mn	.232	-.004	**.897**	.027	.859
Cr	.185	.553	**.762**	.129	.938
$CaCO_3$	**.783**	-.223	.507	.011	.919
Silt	**.881**	.048	-.090	.227	.838
pH	-.435	**.766**	-.043	-.224	.828
Sulphate	-.250	**.860**	.179	.134	.852
HCO_3-	.329	.094	.179	**.814**	.812
Eigen Value	4.681	2.860	1.522	1.086	
% of Variance	29.68	21.77	17.63	15.48	
Cumulative %	29.68	51.45	69.08	84.57	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 9 iterations.

Factor-3 was loaded with Mn (0.897) and Cr (0.762); moderate loadings were observed for Cu (0.461) and $CaCO_3$ (0.783). This can be explained as due to the formation of $MnCO_3$ during organic matter oxidation[7] resulting in the conversion of Mn-oxides in the sediment into $MnCO_3$. This is implied by the fact $MnCO_3$ has a very large stability field if a high concentration of dissolved Mn is present (Hem 1977). As the Baram River supplies large amounts of silt and humus material which are buried along the coast, intense organic matter oxidation mediated through Mn-oxide reduction, was possible and it may have significantly contributed to the high level of dissolved Mn in the sediments. This is the plausible mechanism for the formation of $MnCO_3$. The association of Cr with Mn indicates the adsorption of reduced Cr (i.e., Cr (III)) by Mn-oxides and its oxidation to Cr (VI) (Namieśnik and Rabajczyk 2012). Similarly, the adsorption of Cu, though, to a lesser extent, by Mn-oxides was responsible for its observed loading. On factor-4, Ni (0.872)

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[7] The analytial procedure employed for the estimation of $CaCO_3$ does not distinguish between $CaCO_3$ and $MnCO_3$. Thus, the association of Mn with $CaCO_3$ is considered to be due to the formation of $MnCO_3$.

and HCO_3- (0.814) were loaded and is interpreted as the desorption of Ni upon contact with the seawater (Edmond et al. 1985; Windom et al. 1991; Shiller and Boyle 1991).

5.9.1.4 *Factor analytical results for post-monsoon sediments: Segment-2 (Samples: 12 to 31)*

Three factors accounted for 74.2% variance in the data (Table 5.12). The first, second and third factors explained about 27.6%, 24.5% and 21.9% of the total variance, respectively. In this factor model, all variables have good communality except Pb, Mn and HCO_3^- (Table 5.12). The first factor (Table 5.12) was loaded with Ni (0.879), Fe (0.842) and silt (0.739) and can be explained as riverine input of Ni was adsorbed onto an iron oxide coating on clay minerals (Xu and Axe, 2005). About 77.2% of variance in Ni, 70.9% variance of Fe, and 54.6% of variance in silt was explained by factor-1. The second factor was loaded with Cu (0.983) and Zn (0.973). These trace metals belong to the group of "*chalcophile elements*" and their association on factor-2 indicated leaching out during sulphide oxidation in the river basin and delivery to the sea. Factor-3 was loaded with Co (0.808), Mn (0.645) and HCO_3^- (-0.691) and implied desorption of riverine particulate Co and Mn upon mixing with the seawater (Ackroyd et al. 1986; Takata et al. 2010).

Table 5.12 Rotated Component Matrix^a segment-2 (NE segment; 12-31 locations)

	Component			
Elements	**1**	**2**	**3**	**Communalities**
Cu	.077	**.983**	.053	.975
Pb	-.437	.476	.353	.542
Co	.095	.216	**.808**	.709
Ni	**.879**	.080	-.057	.782
Zn	.108	**.973**	-.014	.958
Fe	**.842**	-.040	.482	.943
Mn	.491	-.051	.645	.660
Silt	**.739**	.108	.252	.621
HCO_3-	-.069	.032	-.691	.483
Eigen Value	3.176	2.191	1.307	
% of Variance	27.69	24.55	21.93	
Cumulative %	27.69	52.23	74.16	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 5 iterations.

5.10 Sediment quality assessment

Several factors and calculation methods are described in the literature to calculate the enrichment of elements/metals and to evaluate the natural and anthropogenic origin of elements/metals in beach sediments (Muller 1969; Hakanson 1980; Szefer et al. 1995; Chen and Kandasamy 2008; Sun et al. 2010; Rajmohan et al. 2014). Several studies engaged these factors to distinguish the source of contamination (Ansari et al. 2000; Feng et al. 2004; Jayaprakash et al. 2012; Nagarajan et al. 2013). Among these contamination factor and geo-accumulation index were used in this study.

5.10.1 Contamination Factor (CF)

CF is defined as the ratio between the element/metal concentration of the sediment at a given site and the background value of the metal (McLennan 2001). It is a suitable tool for monitoring the contamination over a period of time as suggested by Pekey et al. (2004).

$$C_f = \frac{C_{metal}}{B_{metal}}$$

Where C_f is the contamination factor, C_{metal} is the concentration of measured metal and B_{metal} is the background value of the metal. The contamination factor is classified into four groups by Pekey et al. (2004), as low (CF<1), moderate ($1 \leq CF \leq 3$), considerable ($3 \leq CF \leq 6$) and very high (CF>6).

CF has been calculated for all the elements/metals analyzed in sediments for both seasons in order to estimate the enrichment of trace metals along the Miri coast. In this study, each elements/metals were enriched at different levels for both seasons, with respect to the sampling locations. The range and average value of CF for the analyzed elements/metals are presented in Table 5.13 & Table 5.14 and Figure 5.12 & Figure 5.13 for both seasons. Spatial distribution of CF in the monsoon and post-monsoon season are shown in Figure 5.14 to Figure 5.17. The average CF values vary from 0.04 to 8.69 for the monsoon season and 0.07 to 12.55 for the POM season. CF of elements/metals in the beach sediments of Miri coast can be ranked in the decreasing order as Cu>Zn>Co>Pb>Cr>Ni>Fe>Mn for monsoon season and Cu>Zn>Pb>Cr>Ni>Co>Fe>Mn during the POM season. According to Pekey et al. (2004), the sediment samples in the monsoon season were contaminated in the range of low contamination to very high contamination for both seasons. Thus, with respect to the background values, the beach sediments from the Miri coast are highly contaminated by Cu (CF=8.69) in the monsoon and (CF=12.55) POM season. Lutong Beach in the monsoon season and the Fish Landing Center in the POM season, showed a higher contamination factor for Cu. In addition to Cu, the beach sediments of the Miri coast were moderately contaminated by Zn and Pb at particular locations. The CF values for remaining trace metals such as Cr, Co, Fe, Mn and Ni were less than 1 for both seasons and considered less contaminated.

Table 5.13. CF values for beach sediments during the Monsoon season

Descriptive Statistics					
Elements	**N**	**Mini**	**Maxi**	**Mean**	**Std. Dev**
Cu	26	5.41	13.08	8.69	1.71
Cr	26	0.36	0.71	0.51	0.08
Co	26	0.31	1.09	0.66	0.24
Fe	26	0.05	0.17	0.10	0.03
Mn	26	0.03	0.06	0.04	0.01
Ni	26	0.31	0.63	0.44	0.08
Pb	26	0.31	1.19	0.51	0.18
Zn	26	0.48	2.25	1.71	0.41

Table 5.14 CF values for beach sediments during the POM season

Descriptive Statistics					
Elements	**N**	**Mini**	**Maxi**	**Mean**	**Std. Dev**
Cu	31	4.40	24.71	12.55	6.01
Cr	31	0.47	1.23	0.68	0.20
Co	31	0.17	0.62	0.39	0.13
Fe	31	0.05	0.25	0.12	0.04
Mn	31	0.04	0.14	0.07	0.02
Ni	31	0.30	0.62	0.42	0.07
Pb	31	0.50	2.63	1.23	0.47
Zn	31	0.15	3.65	2.24	0.70

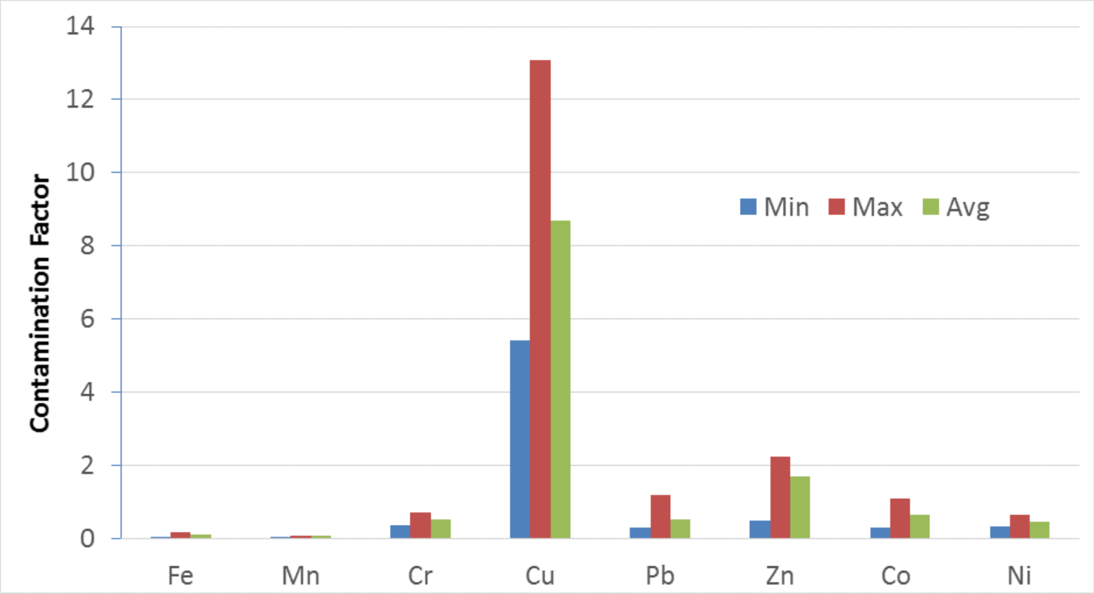


Figure 5.12 Level of CF values for beach sediments during the monsoon seasons

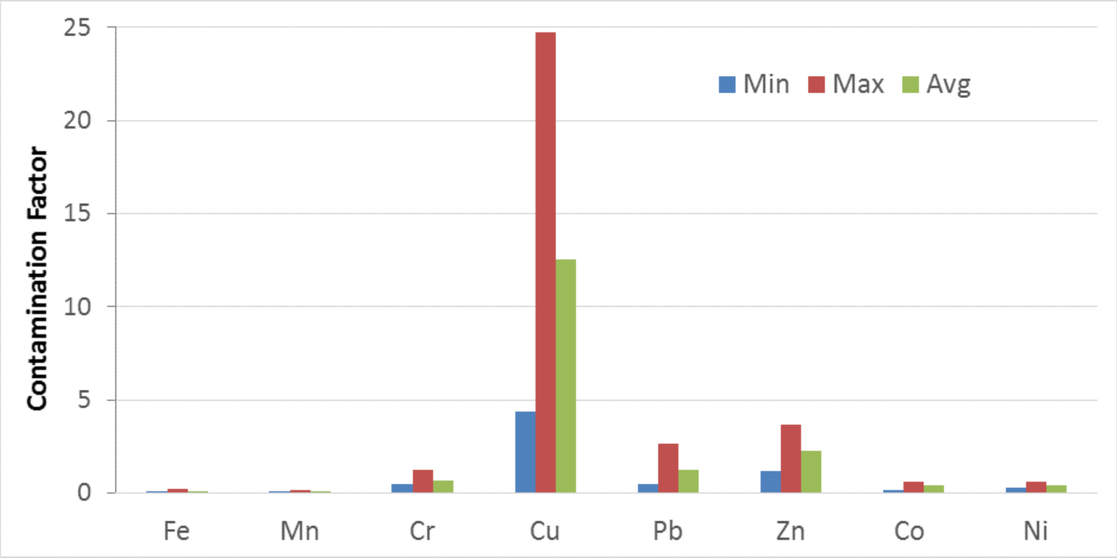


Figure 5.13 Level of CF values for beach sediments during the POM seasons

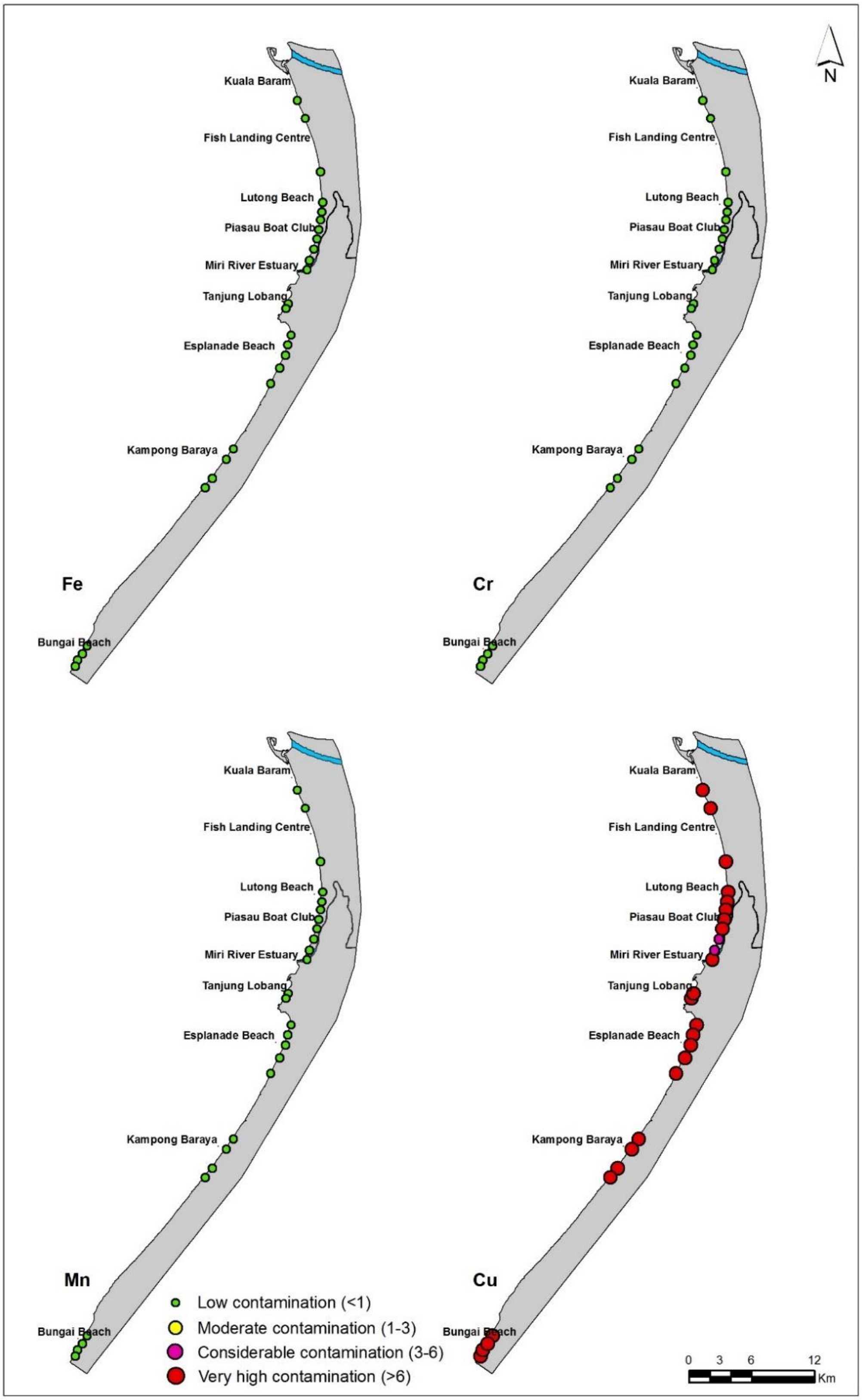


Figure 5.14 Spatial representation of CF values for Fe, Cr, Mn and Cu in the monsoon season

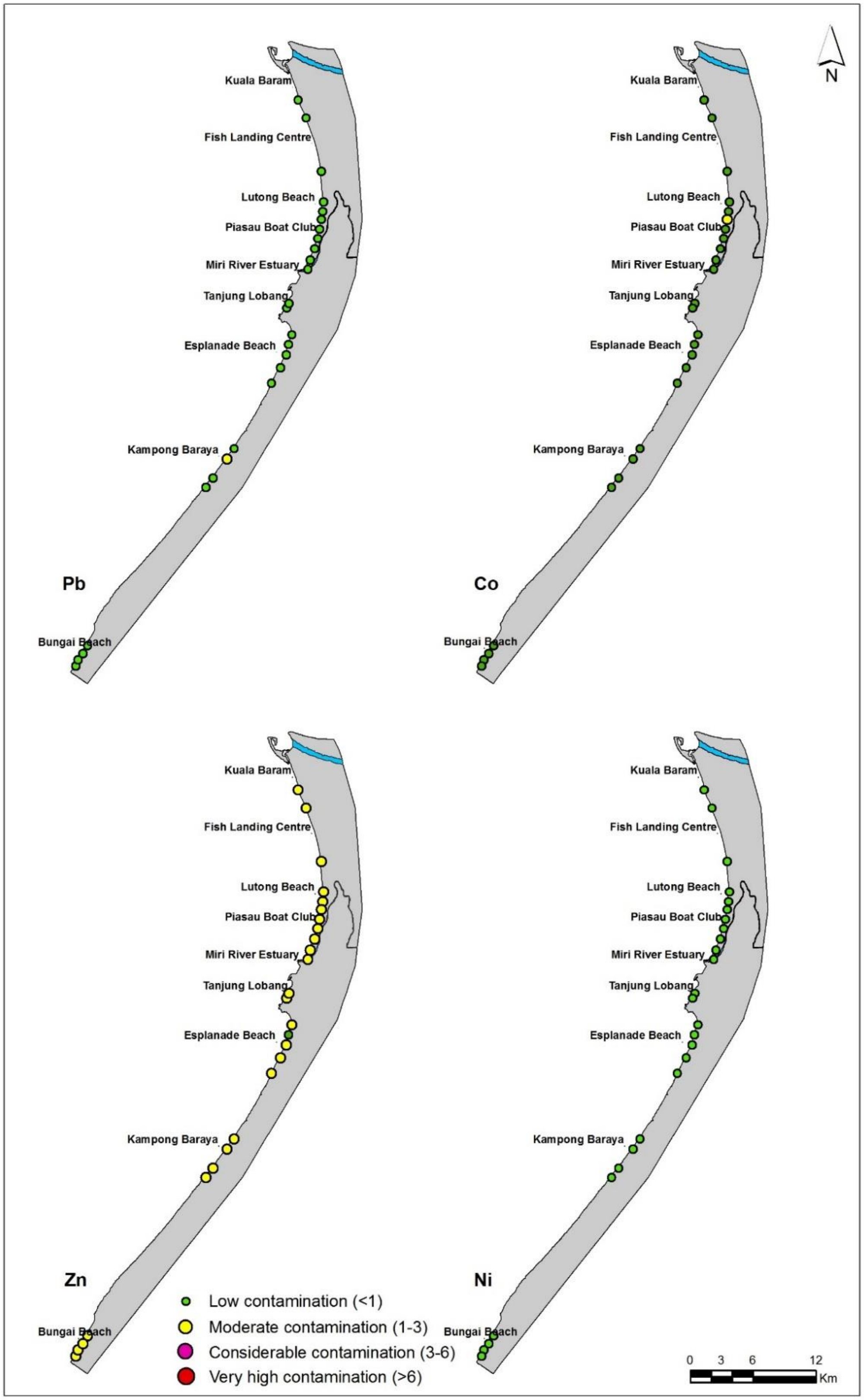


Figure 5.15 Spatial representation of CF values for Pb, Co, Zn and Ni in the monsoon season

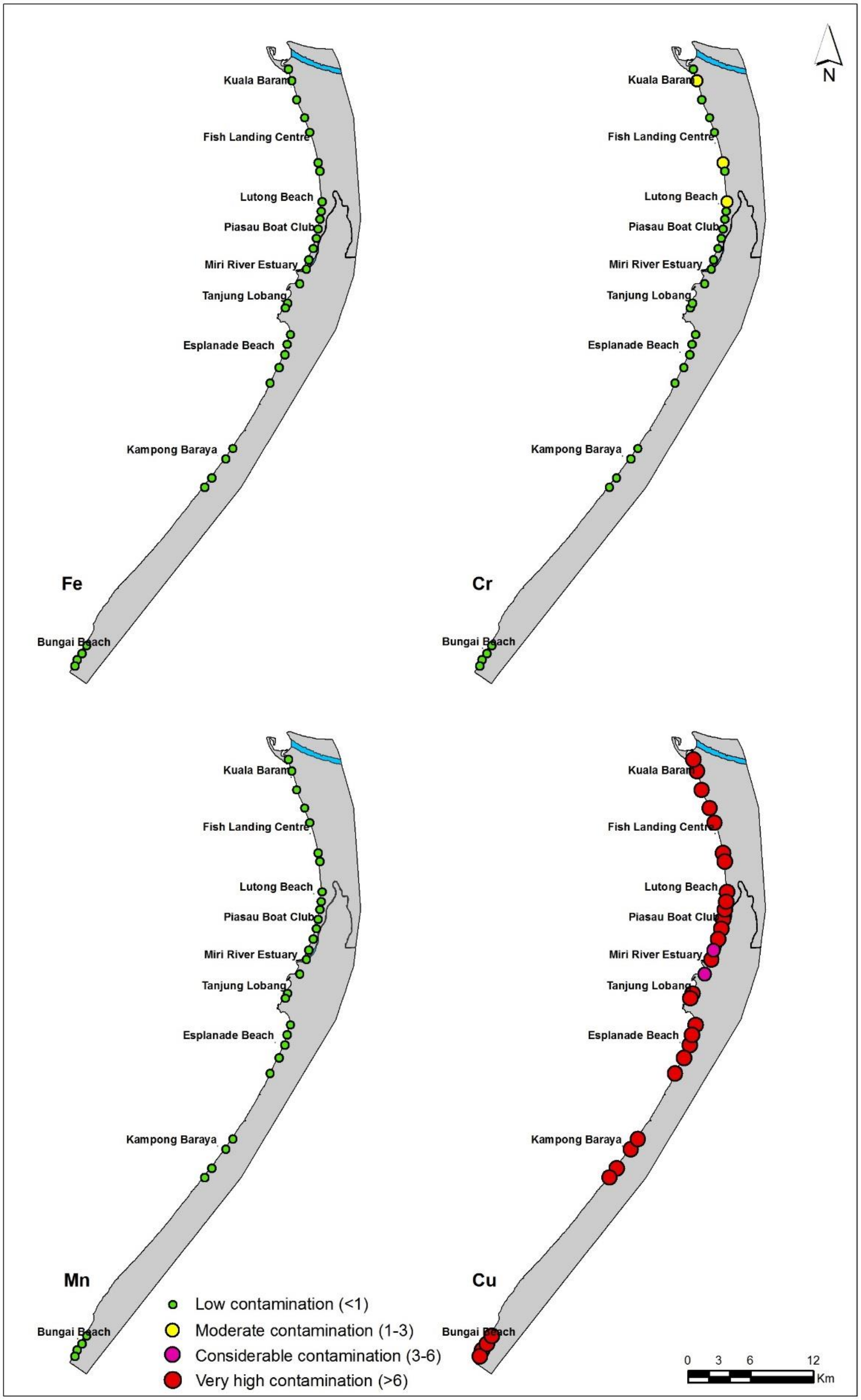


Figure 5.16 Spatial representation of CF values for Fe, Cr, Mn and Cu in the POM season

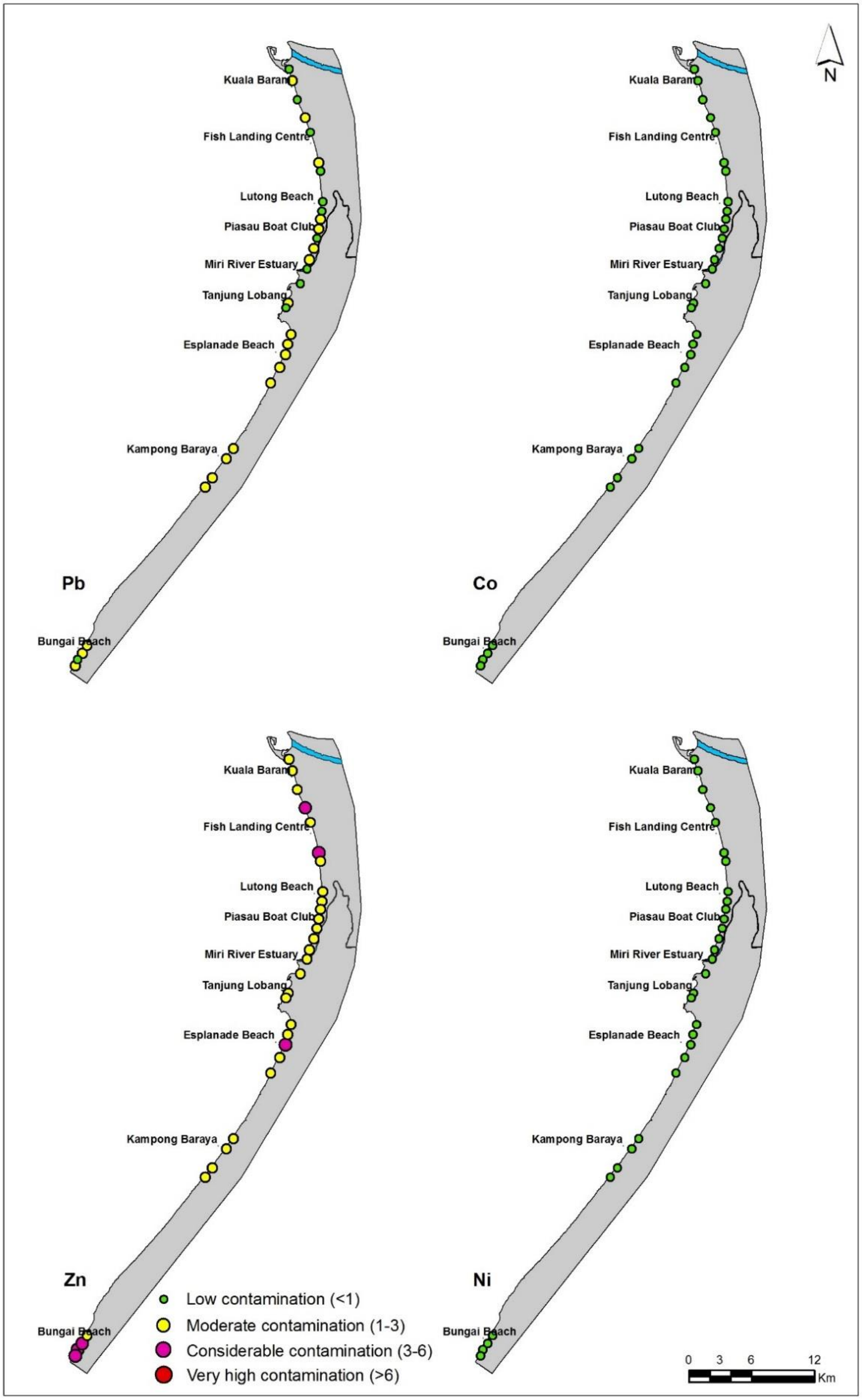


Figure 5.17 Spatial representation of CF values for Pb, Co, Zn and Ni in the POM season

5.10.2 Geo-accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}), is a quantitative measure of the trace/heavy metal contamination in aquatic sediments. It was originally defined by Muller (1979), and used to characterize the level of pollution in each sampling sites by using the mathematical formula

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right)$$

Where, C_n is the measured concentration of the element; B_n is the geochemical background value of the same element in the Upper Continental Crust (McLennan, 2001), since there were no background values for Malaysian sediments. The 1.5 is a factor introduced to include possible variations of background values due to lithogenic effects (Salomons and Forstner 1984). According to Muller (1979), the pollution level is categorized into seven classes (0-6) (see Table 5.15) namely:

Table 5.15 Ranges of Geo-accumulation Index

Class	I_{geo}	Pollution Status
1	<0	Uncontaminated
2	0-1	Uncontaminated to moderately contaminated
3	1-2	Moderately contaminated
4	2-3	Moderately contaminated to strongly contaminated
5	3-4	Strongly contaminated
6	4-5	Strongly to extremely contaminated
7	5-6	Extremely contaminated

The calculated Igeo values for the beach sediments are shown clearly for the monsoon in Figure 5.18 and POM season in Figure 5.19. Table 5.16 and Table 5.17 depict the range and average Igeo values in the monsoon and POM seasons. Spatial distribution of Igeo values for the monsoon and POM seasons are presented in Figure 5.20 to Figure 5.23. In the present study, the geo-accumulation Index (I_{geo}) signifies sediments of the Miri coast remain uncontaminated by Fe, Mn, Cr, Pb, Zn, Co and Ni for both seasons, as most of the I_{geo} values were less than 0. In this study, all the Igeo values for elements/metals fell under Igeo classes 1-4 (Table 5.15). In contrast, Cu in both (1.85 to

3.12 monsoon and 1.55 to 4.04 POM) seasons and Zn in (-0.38 to 1.28) the POM season showed a positive Igeo index. Overall nearly 78.85% in the monsoon season and 73.39% in the POM season of total analyzed elements/metals such as (Fe, Mn, Cr, Pb, Co and Ni) had the I_{geo} values of ≤ 0 for both seasons. Zn alone at nearly 8.65% in the monsoon and 11.69% in the POM season showed the I_{geo} value as 0-1, and was considered uncontaminated to moderately contaminated. The remaining 12.50% of Cu in the monsoon and 14.92% in the POM season fell in the Igeo level 2-4 indicating moderately to strongly contaminated by this element. Also, the average Igeo value of Cu, (Igeo class 6 = 5-6) 0.48% during the monsoon and 4.84% during the POM season indicated strongly to extremely contaminated.

Table 5.16 Descriptive statistics of Igeo values for the Monsoon season

Elements	Minimum	Maximum	Mean	Std
Fe	-4.85	-3.18	-3.89	0.39
Mn	-5.45	-4.26	-4.72	0.30
Cr	-2.05	-1.08	-1.56	0.23
Cu	1.85	3.12	2.51	0.29
Pb	-2.29	-0.33	-1.63	0.42
Zn	-1.64	0.58	-0.13	0.46
Co	-2.29	-0.46	-1.28	0.55
Ni	-2.27	-1.25	-1.79	0.25

Table 5.17 Descriptive statistics of Igeo values for the POM season

Elements	Minimum	Maximum	Mean	Std
Fe	-4.81	-2.61	-3.71	0.51
Mn	-5.34	-3.43	-4.52	0.47
Cr	-1.66	-0.29	-1.19	0.36
Cu	1.55	4.04	2.91	0.67
Pb	-1.57	0.81	-0.39	0.56
Zn	-0.38	1.28	0.52	0.44
Co	-3.14	-1.28	-2.04	0.52
Ni	-2.34	-1.28	-1.86	0.24

Figure 5.18 Geo-accumulation index (I_{geo}) value of analyzed metals during the monsoon season.

Figure 5.19 Geo-accumulation index (I_{geo}) value of analyzed metals in the POM season.

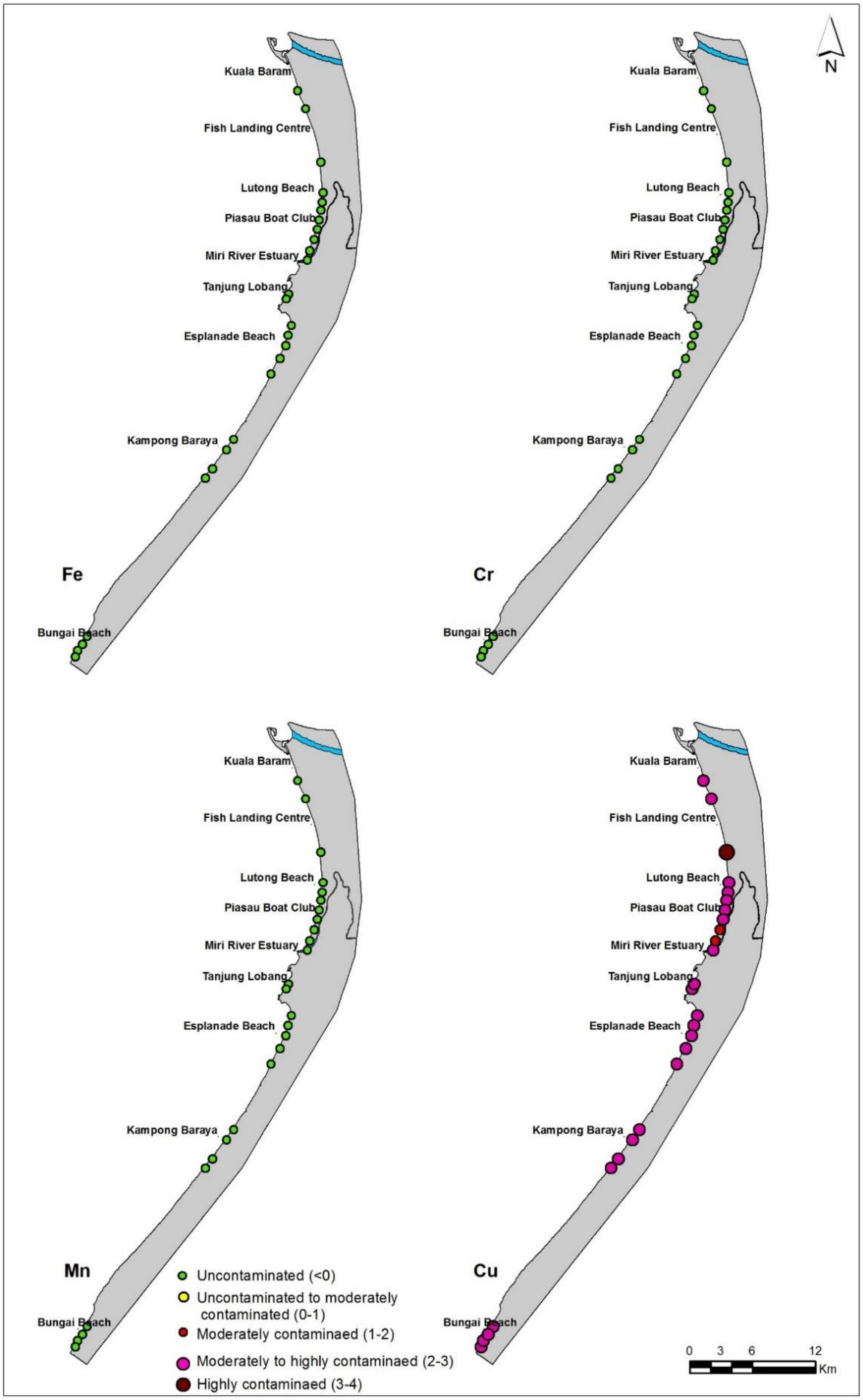


Figure 5.20 Spatial representation of Igeo values for Fe, Cr, Mn and Cu in the monsoon season

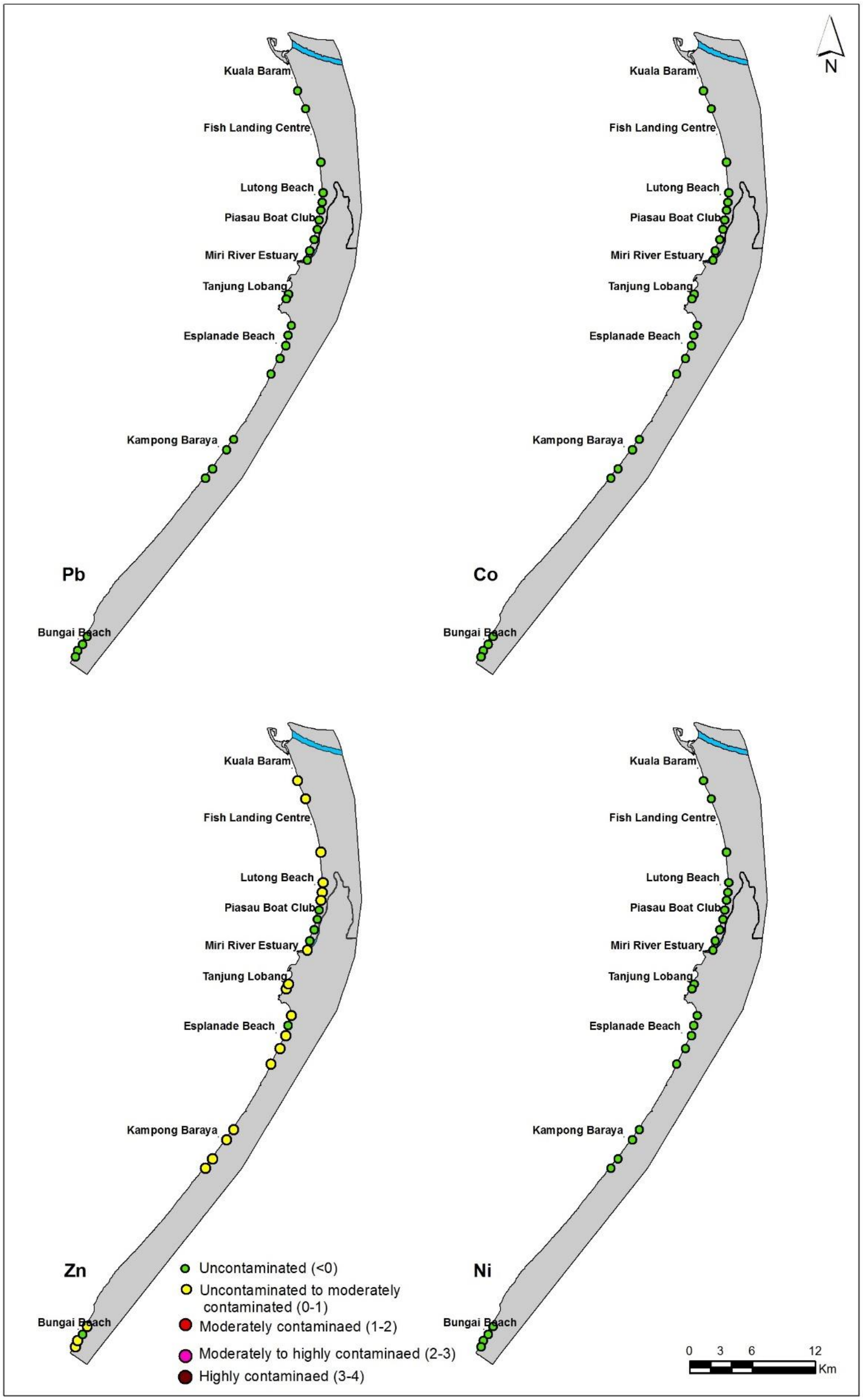


Figure 5.21 Spatial representation of Igeo values for Pb, Co, Zn and Ni in the monsoon season

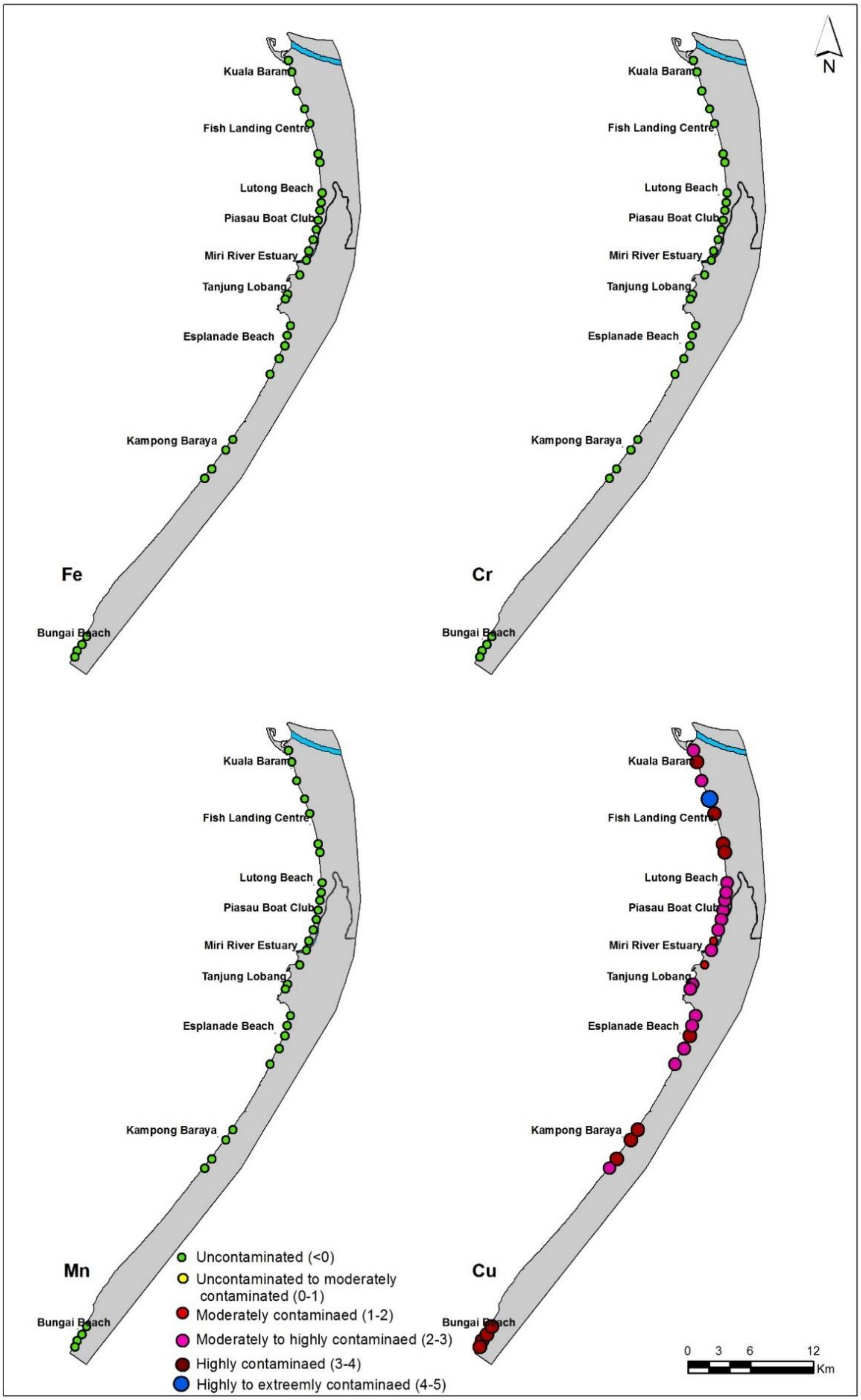


Figure 5.22 Spatial representation of Igeo values for Fe, Cr, Mn and Cu in the POM season

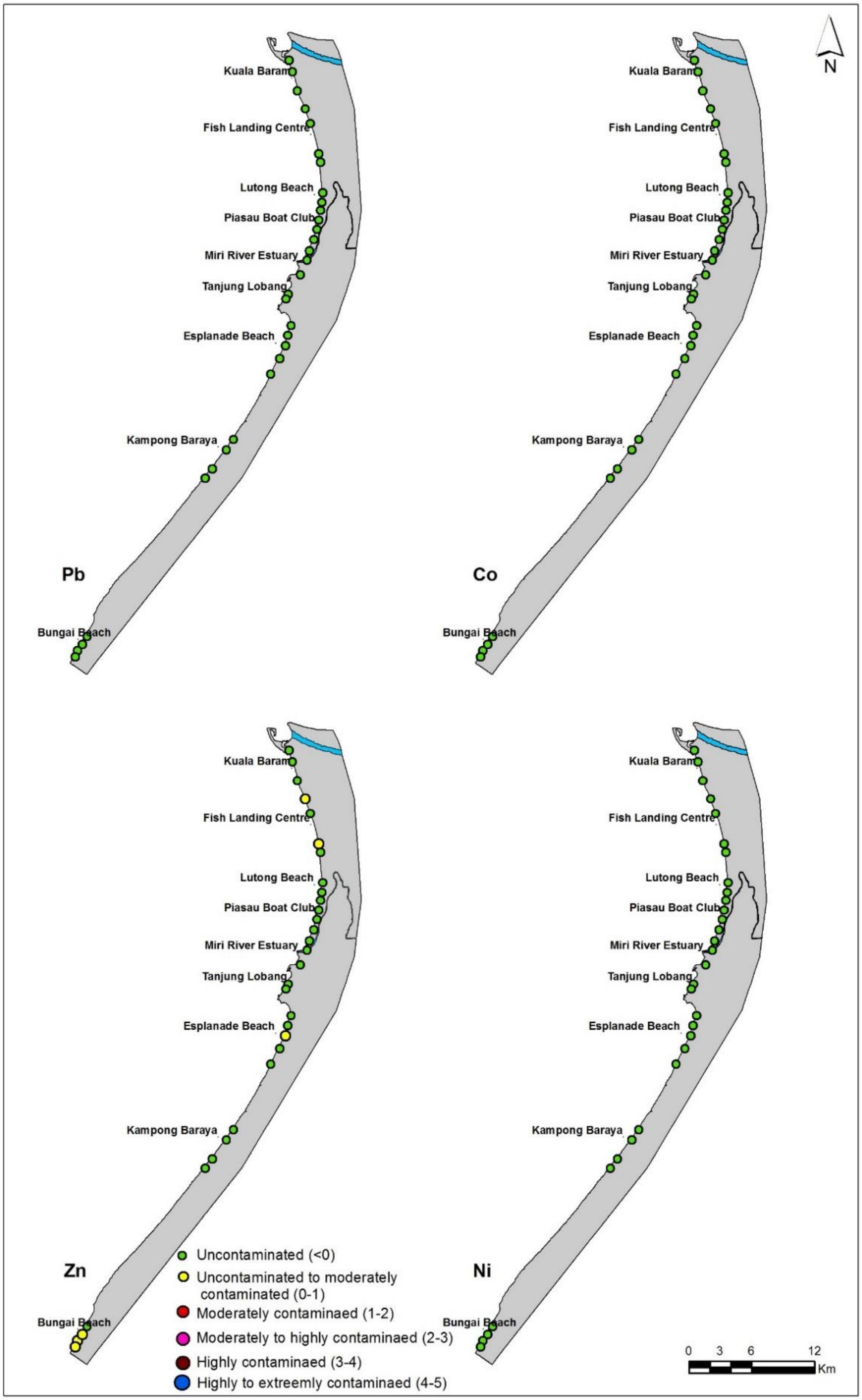


Figure 5.23 Spatial representation of Igeo values for Pb, Co, Zn and Ni in the POM season

5.11 Ecotoxicological effects of total trace metals

Most heavy metals are toxic, and cause acute and chronic toxicity to living organisms even at low concentrations. Various sediment quality guidelines (SQGs) have been established to deal with environmental concerns and two of them, effects range low (ERL) and effects range median (ERM) were selected to measure the degree of contamination of specific metals connected with biological effects (Long et al. 1995) in the beach sediments of the Miri coast. The level of ecotoxicological effects for the elements/metals along the Miri coast for both seasons are presented in Table 5.18.

Trace/heavy metal concentrations of less than ERL are considered to have little or no adverse effects on sediment-dwelling fauna. In contrast, metals exceeding ERM values can cause adverse health effects to aquatic organisms. Among the analyzed elements, only Cu exceeded the SQGs values, whereas all the remaining metals; Cd, Cr, Ni, and Zn, were less than ERL or between ERL and ERM values (Figure 5.24). Lead and Cr concentrations were less than ERL values in all samples during the monsoon season. Most of the samples recorded concentrations below the ERL value Cd (96%), Ni (77%) and Zn (88%). For the monsoon season, samples were recorded between ERL and ERM values (92% (Cu), 4% (Cd), 23% (Ni) and 13% (Zn)). In the case of Cu, 8% of samples exceeded the ERM value and may cause adverse biological effects.

During the POM a similar trend was maintained as in the monsoon, however 55% of the samples showed Cu concentrations between ERL and ERM values and 45% of the samples were enriched with Cu (i.e. > ERM values) indicating possible adverse biological effects. The average concentrations of elements/metals in the individual beaches of Miri coast were compared with other SQGs such as the Threshold Effect Low (TEL), Lowest Effect Level (LEL) and Severe Effects Level (SEL) values (Table 5.19). Among all the analyzed elements/ metals, Cu concentration in all beach samples exceeded the maximum permissible value of SEL (110 µg/g), while all other elements were under the acceptable limits of SQGs values for both seasons.

Table 5.18 Guideline values and biological effects of heavy metals (after Long et al. 1995)

Elements	**Guideline values (mg/kg)**		**Adverse effects in Monsoon season (%)**			**Adverse effects in POM season (%)**		
	ERL	**ERM**	**<ERL**	**ERL-ERM**	**>ERM**	**<ERL**	**ERL-ERM**	**>ERM**
Cu	34	270	0	92.31	7.69	0	54.84	45.16
Pb	46.7	218	100	0	0	100.00	0	0
Cd	1.2	9.6	96.15	3.85	0	54.84	45.16	0
Ni	20.9	51.6	76.92	23.08	0	83.87	16.13	0
Zn	150	410	88.46	13.04	0	58.06	41.94	0
Cr	81	370	100	0	0	90.32	9.68	0

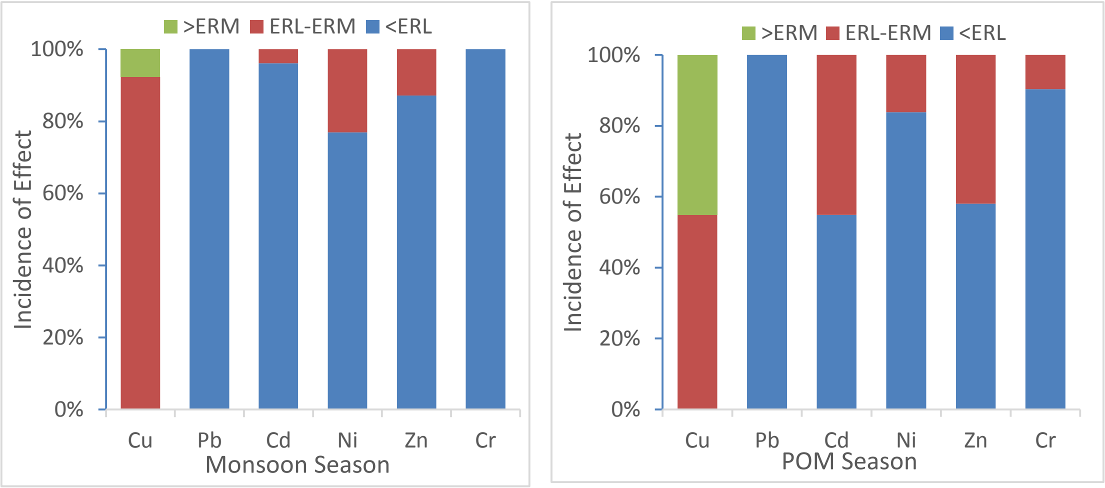


Figure 5.24 Biological effects of selected trace metals on living organisms based on the guideline value (Long et al. 1995)

Table 5.19 Comparison of total elements concentration in different beaches of the Miri coast with the eco-toxicological values used to determine marine sediment quality

Elements	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr
Monsoon season									
BB	194.69	8.84	0.71	13.47	16.39	116.50	3828.80	38.97	41.39
KPB	211.59	10.05	0.81	11.84	19.20	123.87	3525.05	37.63	33.07
ESP	249.65	8.25	0.52	12.49	25.14	142.88	3484.70	39.67	39.62
TB	234.86	7.03	0.38	14.79	15.27	135.28	1858.85	20.95	46.01
MRE	162.08	9.86	0.26	8.40	19.05	91.33	3678.34	33.12	41.01
PBC	189.67	7.44	0.15	16.77	15.42	107.18	3159.83	29.28	48.46
LB	276.42	8.72	0.32	6.26	18.80	152.58	4159.40	31.54	49.44
KBE	223.73	7.68	0.39	6.12	20.31	139.28	5557.70	37.49	55.21
POM season									
BB	539.56	23.35	1.30	9.44	17.53	223.34	5048.80	44.31	51.59
KPB	343.89	23.67	1.87	5.68	16.89	157.06	4499.55	43.80	44.59
ESP	285.02	23.89	1.18	7.38	15.70	152.81	3552.74	39.79	43.32
TB	237.66	21.29	1.17	5.65	15.03	142.44	1998.80	27.25	46.22
PVB	144.05	14.17	0.52	8.53	19.59	91.48	5776.25	69.82	59.37
MRE	170.47	16.72	1.06	3.99	18.79	111.56	3862.73	30.96	65.17
PBC	216.24	26.96	1.22	5.06	18.02	124.86	2543.88	27.32	49.06
LB	247.98	12.67	1.31	4.89	20.76	152.12	3735.62	42.66	67.70
FLC	504.46	20.32	0.63	6.47	21.91	227.70	5178.99	51.93	73.14
KBE	259.71	21.06	0.70	8.67	21.66	147.20	6349.55	47.74	73.04
SQGs values									
TEL	35.7	35	0.6	-	18	123	-	-	37.3
LEL	16	31	0.6	-	16	120	20,000	460	26
SEL	110	250	10	-	75	820	40,000	1110	110

All values are expressed in (µg g^{-1}), TEL - Threshold Effect Low (MacDonald et al. 2000), LEL – Lowest Effect Level (Persaud et al. 1993) and SEL – Severe Effect Level (Persaud et al, 1993).

5.12 Risk Assessment Code (RAC)

The risk assessment code is defined as the metals associated with carbonates/ exchangeable fractions in the sequential extraction process (% F1 of BCR). The RAC was determined for the analyzed nine elements/metals in the present study and the values were interpreted in agreement with the RAC classifications (Table 5.20) described by (Perin et al. 1985). Elements/metals might attach to a different fraction of sediments, and their bioavailability and risk association to the marine environment depends upon their binding strength. Metals present in the fraction 1 (% F1) are weakly bounded to the sediments, hence they pose a greater risk to aquatic systems and organisms (Jain 2004).

Table 5.20 Criteria of Risk Assessment Code (Perin et al. 1985)

Fraction 1 Percentage (%)	Risk Level
< 1%	No risk
1 to 10%	Low risk
11 to 30%	Medium risk
31 to 50%	High risk
50% >	Very high risk

In general, a low or no risk was indicated by Cd, Ni, Fe, and Cr (except some beaches) during the monsoon (Table 5.21) and Ni, Fe, Cr during the POM seasons (Table 5.22) which were confirmed by their RAC values. A medium risk was associated with Pb, Co during the monsoon season and Cd, Co and Mn during the POM season. A high to very high risk was associated with Mn, Cu and Zn in the monsoon and Cu, Zn, Pb and Mn during the POM season. Though Cu had a high risk in the beach sediments, these elements are naturally derived from the hinterland of the study area. Lead risk can be controlled by more effective regulation of source pollutants and by controlling wild fires in the Borneo tropical and peat forests.

Table 5.21 Comparison of RAC values for all the beaches in the Monsoon seasons and elements

Elements	**Cu**	**Pb**	**Cd**	**Co**	**Ni**	**Zn**	**Fe**	**Mn**	**Cr**
Bungai Beach	V	H	L	M	L	V	L	M	L
Kampong Baraya	V	M	L	M	M	V	L	H	L
Esplanade Beach	V	M	L	M	M	V	M	H	L
Tanjong Beach	V	M	N	M	L	V	M	M	L
Miri River Estuary	V	M	N	L	L	V	L	M	N
Piasau Boat Club	V	M	N	M	L	V	L	H	L
Lutong Beach	V	M	L	L	L	V	L	H	L
Fish Landing Center	V	M	L	L	L	V	L	H	L
Kualabaram Estuary	V	M	L	M	L	V	L	M	L

N – No risk; L – Low risk; M – Medium risk; H – High risk; V – very high risk

Table 5.22 Comparison of RAC values for all the beaches in the POM seasons and elements

Elements	**Cu**	**Pb**	**Cd**	**Co**	**Ni**	**Zn**	**Fe**	**Mn**	**Cr**
Bungai Beach	V	V	M	M	L	V	L	M	L
Kampong Baraya	V	V	M	L	L	V	L	H	L
Esplanade Beach	V	V	M	M	L	V	M	H	L
Tanjong Beach	V	V	M	L	L	V	M	M	L
Park Everly Beach	V	H	M	M	L	V	L	H	L
Miri River Estuary	V	H	M	L	L	V	L	M	L
Piasau Boat Club	V	V	M	M	L	V	L	M	L
Lutong Beach	V	H	M	L	L	V	L	M	L
Fish Landing Center	V	H	M	M	L	V	L	M	L
Kualabaram Estuary	V	H	M	M	L	V	L	M	L

N – No risk; L – Low risk; M – Medium risk; H – High risk; V – very high risk

5.13 Comparison with background values and reported values for similar environments

For the comparison, the average total concentration of surface sediments reported from other coastal areas the Miri River sediments, and the background values of sedimentary rocks and concretions from the geological formations exposed along the coastal region of Miri and the Upper Continental Crust (UCC McLennan, 2001) were used and summarized in Table 5.23. The concentrations of Cu, Cd and Zn in both seasons and Pb in the POM season were comparatively higher than UCC values, whereas Ni, Cr, Co, Fe and Mn concentrations in the surface sediments for both seasons were lower than the UCC values (Table 5.23).

The average concentrations of Cd, Co, Cr, Ni, Pb and Zn for both seasons were significantly lower than those reported in the coastal sediments of Masan Bay, Korea (Hyun et al. 2007) and Izmit Bay, Turkey (Pekey, 2006) but the observed Cu concentration in the present study for both seasons is several times higher. The observed average concentration of Cu in the present study was higher than those Cu values reported for sedimentary rocks from the coastal region, such as Sibuti formations (65.30 µg/g; Nagarajan et al, 2015), Tukau formations (43.0 µg/g; Nagarajan et al, 2014a), Lambir formations (77 µg/g; Nagarajan et al, 2015), Bintulu coast (7-13 µg/g; Ismail et al. 1993), and Port Klang, Malaysia (17.43 µg/g; Sany et al. 2013); but lower than the Southwest coast of Spain (41-336 µg/g; Morillo et al. (2004) and the Ennore coast, India (506.2 µg/g;

Jayaprakash et al. 2007). The average Cu concentration was eight times higher in the monsoon season and 12 times higher in the POM season compared to the UCC values (25 µg/g) reported by McLennan (2001). Thus, the Cu values were recorded lower than the sedimentary rocks of NW Borneo, while Cu content was higher in shales and mudstones. However the Cu values were comparable with the Miri River sediments.

Table 5.23 The summary of element/metal (μg g^{-1}) contents in sediments from the Miri coast and related values reported from the other coastal surface sediments and UCC values.

Location	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr	Reference
Monsoon Range (n=26)	135.34 - 326.92	5.89 – 20.28	0.1 – 1.46	5.2 – 18.52	13.67 – 27.84	75.28 – 159.59	1817.54 – 5789.45	20.64 – 47.06	30.03 – 58.80	Present study
POM range (n=31)	109.98 – 617.76	8.57 – 44.73	0.3 – 2.02	2.89 – 10.51	13.05 – 27.22	81.97 – 258.95	1874.4 – 8609.05	22.15 – 83.68	39.34 – 101.72	Present study
Monsoon Average (n=26)	217.21	8.72	0.48	11.21	19.33	125.48	3660.89 (0.52%)	34.90	42.60	Present study
POM Average (n=31)	313.84	20.88	1.16	6.56	18.39	159.32	4260.07 (0.60%)	41.33	56.57	Present study
Bintulu, Malaysia	7-13	11 -36	-	-	-	39 - 91	-	-		Ismail (1993)
UCC	25	20	0.098	10	20	71	4.49%	600	35	McLennan (2001)
South west coast, Spain	41-336	20-197	0.19-2.50	-	10-61	141-649	1.6-3.5%	-	-	Morillo et al. (2004)
Izmit Bay, Turkey	67.6	102	4.9	-	-	930	-	-	74.3	Pekey (2006)
Masan Bay, Korea	43.4	44	1.24	11.53	28.8	206.3	-	-	67.1	Hyun et al. (2007)
Coast off Southwestern Taiwan	32	44	0.56	-	35	158	3.57%	369	73	Chen and Kandasamy (2008)
Dumai coast, Indonesia	6.08	32.34	0.88	-	11.48	53.87	3.01%	-	-	Amin et al. (2009)
Daya Bay, China	20.8	45.7	0.049	12.7	31.2	113	-	837	-	Gao et al. (2010)
Coastal Bohai Bay, China	38.5	34.7	0.22	-	40.7	131.1	-	-	101.4	Gao and Chen (2012)
Port Klang, Malaysia	17.43	59.45	0.83	-	11.44	51.05	-	-	46.4	Sany et al. (2013)
Shandong Peninsula, China (Yellow Sea)	20	28.4	-	-	31.2	74.7	-	-	57.8	Li et al. (2013a)
San Nicolas beach, Mexico (n=10)	-	-		3.9	2.6	29	1.68%	0.0021	15.1	Armstrong-Altrin et al. (2014)

Location	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr	Reference
San Carlos, Mexico (n=10)	25	8.5		2.5	7	19	1.11%	0.01	12	Armstrong-Altrin et al. (2014)
Tukau formation (n=15)	43.00	17.50	-	5.2	18.07	35.7	1.01%	0.009%	168	Nagarajan et al. (2014b)
Concretions from Tukau (n=30)	-	60.7	-	-	660		24.5%	717		Nagarajan et al. (2014b)
Chachalacas beach, Mexico(n=15)	16.5	7.86	-	14.3	27	53	4.0%	0.07	84	Armstrong-Altrin et al. (2015)
Yeracruz beach, Mexico (n=15)	52	14.8	-	26	31.2	90	2.6%	0.04	43.8	Armstrong-Altrin et al. (2015)
Sibuti formations (n=25)	65.30	47.61	-	13.40	65.35	117.35	4.40%	478	94.95	Nagarajan et al. (2015)
Lambir formation (n=30)	77	18.23	-	7.97	27.86	73.47	3.03%	0.030%	54.07	Nagarajan et al. (2015)
Miri River (n=27) Range	20 -270	6 - 20	-	1-12	20 -30	40 - 220	0.26 – 6.1%	0.002 – 0.054%	30 - 130	Project, Nagarajan personal collection
Average	82.59	11.57	-	6.04	26.43	102.38	3.14%	0.014%	84.58	

5.14 Summary

The modified BCR sequential extraction method has been applied successfully to analyze potential mobility of trace/heavy metals and its seasonal variations in the sediment samples collected from the different beaches of the Miri coast. The sediments are predominantly composed of fine sand (SW segment), and followed by silt (NE segment). The association of elements/metals in the exchangeable fraction (the most mobile and bioavailable) can be ranked as Cu > Zn > Mn > Pb > Co > Fe > Ni > Cd > Cr (during the monsoon) and Cu > Zn > Pb > Mn > Cd > Co > Fe > Ni > Cr (during the POM). Cu and Zn were dominant in the exchangeable fraction for both seasons. Pb and Cd were also dominant in the non-residual fraction (F1+F2+F3) for both seasons and elements may be exchanged from the water column due to changes in pH and/or oxidation/reduction conditions of the coastal environment. Cd was the only element showing a high proportion in the oxidizable fraction for both seasons, highlighting the important role played by organic matter. Mn showed intermediate mobility and was mainly associated with residual fraction. Iron, Co, Ni and Cr were mainly associated with the residual fraction for both seasons and not involved in the remobilization process under normal environmental conditions.

Finally, among the studied metals Fe, Mn, Co, Cr and Ni were influenced by natural sources, such as weathering of the parental rocks, from clastic sediments and from periodic deposition of river sediments from the Baram River, Miri River and Sibuti River which all discharge into the SCS along the Miri coast. Copper, Cd, Pb and Zn were derived from both natural sources as well as man-made activities in the study area. These elements have a higher chance to leach from sedimentary rocks such as sandstone, shale, siltstone with clay seams, coal laminae, pyrite concretions and then enrich their concentration in the adjacent coastal regions in the SW segment of the study area. Apart from natural influence, anthropogenic sources such atmospheric depositions, agricultural wastes, and direct discharge of domestic and industrial effluents through small drainage streams and channels increase the concentration of these metals in the marine environment. Sulphide oxidation within the river basin was the main source for Cu, Zn, Co, Ni which were leached out, transported, and delivered to the SCS by the Baram River. In addition to this, iron hydroxide coatings were thought to occur on $CaCO_3$. This facilitates the formation of manganese hydroxide coating onto iron oxides, and adsorbs Cu, Pb and Zn. Copper and Zn exhibited typical chalcophile characteristics and moved together in the environment – the main source of them being sulphide oxidation occurring within the river basin. Desorption of Co and Mn was also evident from the statistical observations. Pb and Cd was also found coming from atmospheric fallout particularly during the wildfire/haze episodes in the Borneo/Miri region.

Based on the pollution indexes such as the geo-accumulation index and the contamination factor, the beach sediments were contaminated with Cu, followed by Zn and both may pose some biological threats to the aquatic organism in the near future, which was confirmed by the RAC values. In this study, Cu exceeded the ERM values, in 7% of the samples in the monsoon and 45% of the samples in the POM and hence, may cause biological adverse effects. The accumulation of trace elements in aquatic organisms and their associated risk assessment factors were discussed in the following chapter 6.

Finally, the concentration of analyzed trace elements/metals were comparable with the UCC values, except for Cu and Zn in all locations for both seasons and Pb in certain sampling locations in the POM season. All the remaining elements/metals were below the UCC values.

Chapter 6 **Accumulation of trace elements/metals in marine organisms**

This chapter clarifies the effects of trace/heavy metals present in commercially available aquatic organisms such as fish, shrimp, crabs and bivalves.

6.1 **Introduction**

In recent years, worldwide fish consumption has increased several fold due to their nutritional and therapeutic benefits. Culture and capture fisheries support one of the major food sources for the survival of the human population (FAO 1999b; Pauly et al. 2002). These aquatic organisms are affected by the dissolved toxic metals concentrated in sediments and water. The toxic metals come from untreated wastewater, industrial, agricultural, municipal, domestic, mining activities and enter into the coastal environment through rivers and small streams.

Studies of elements/metal accumulation in aquatic organisms have been made due to outbreaks of mercury and cadmium poisoning in humans during the late 1950's and early 1960's in Minamata Bay, Japan. The release of methylmercury in particular, into the bay water from industrial wastewater by a chemical company resulted in serious health problems including loss of consciousness, neurotoxic effects and congenital abnormalities (Grandjean et al. 2010). These symptoms followed after the consumption of fish and shellfish contaminated with methylmercury. There is a lack of information about the history and present status of pollution along the Miri coast. Therefore, it is important to determine the level of heavy metals/trace elements in commercially important marine species in order to estimate the possible risk from human consumption. This study will be the first baseline data since there is no previous published data for risk analysis of seafood consumption available for this study area where it is clearly stated from the literature (Yap et al. 2002a; Shazili et al. 2006; Hossen et al. 2015). Most of the previous studies were focused on Peninsular Malaysia rather than Sarawak, East Malaysia. Thus, in order to avoid the possibility of human consumption of contaminated seafood and its associated environmental risks, the Miri coastal area was analyzed. The scientific data obtained and conclusions made were based on statistical analyses. The risk factor calculations were based on the United States Environmental Protection Agency (USEPA 2000) guidelines.

6.2 Fish – A Bioindicator

Fish are consumed worldwide by humans due to their superior nutritional content of protein, vitamins, essential minerals and omega 3 fatty acids (Verbeke et al. 2007; Castro-González and Méndez-Armenta 2008; Hajeb et al. 2009). Fish accumulate heavy metals/trace elements through direct absorption from water in minor amounts and greater amounts through trophic transfer from prey (Handy 1996; Zhang and Wang 2006). Humans are then exposed through the food chain. Elements such as Cu, Fe, Co and Zn are essential for fish growth and metabolic activities (WHO 1996), however, heavy metals such as Cd, As, Hg and Pb are non-essential and even toxic at low levels of concentration to humans an all biotic life (Rejomon et al. 2010; El-Moselhy et al. 2014). Due to long-term exposure in the aquatic environment, fish and sessile organisms (non-movable) accumulates heavy metals in different parts of their body tissues and thus may be used as a sensitive bioindicator to study pollution and the ecological status of a particular environment (Krishnakumar et al. 1994; Jenkins 2004; Zhao et al. 2012; Abdel-Baki et al. 2013). In addition, crustaceans are also frequently used as bioindicators for various aquatic ecosystems since they are distributed in a wide variety of habitats, including marine, freshwater and terrestrial environments (Rinderhagen et al. 2000).

6.3 Controlling factors and Bioaccumulation

Accumulation of heavy metals/trace elements in marine organisms is controlled by exogenous and endogenous factors. Exogenous factors include environmental conditions such as temperature, metal bioavailability and the alkalinity of aquatic surroundings. Endogenous factors include age, size, species, and the physiological state and feeding habits of the organism (Moiseenko and Kudryavtseva 2001). Much research has been concentrated on shellfish as their sessile condition is more than appropriate for the identification of toxic heavy metals from local waters.

The accumulation of elements/metals in different tissues within an organism depends on the mode of exposure (Nair et al. 2006). Normally muscle, gills, liver and gonads are frequently used for the analysis of element/metal accumulation. Among these organs, muscle is considered as the most appropriate as it is the most abundant and the most consumed part of fish.

6.4 Heavy/trace metals' effect on living organisms

Chromium is a naturally occurring element and is essential for humans. It plays an important role in the metabolism of glucose, carbohydrates, lipids and protein (Mertz 1969; Biswas et al. 2012). Long-term exposures of moderate to high levels of Cr may cause damage to the respiratory tract, lungs and kidney by inhalation or oral exposure (Edward et al. 1985). Manganese is a natural element present in surface water and biota, and is an essential nutrient for micro-organisms, plants, animals and humans. It is required in minor quantities for bio-chemical processes in the human body, including the processing of cholesterol, carbohydrates, proteins and metabolism as well as in bone formation. Manganese is present in enzymes, such as oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases (Goldhaber 2003). Over exposure of Mn in humans can cause nerve damage, forgetfulness, lung embolism, bronchitis, mitochondrial abnormalities and infertility (ATSDR 2012).

Cobalt is an essential element required by marine algae for their growth and is an integral component of Vitamin B 12, a necessary nutrient for humans. Cobalt is toxic to humans in high concentrations and may cause harmful effects in aquatic organisms as well as humans as it leads to the damage of lungs, including asthma, pneumonia, hair loss, vomiting, bleeding and even death (ATSDR 2004). Cobalt enters the environment from natural sources and from the burning of coal and oil. It is used in many corrosion resistant alloys, dying agents for paints and inks and as a catalyst for the petroleum and chemical industries (Zodape 2014). Nickel is a very abundant element in the environment and often combines with oxygen (oxides) or sulfur (sulfides). A low quantity of Ni is required by the human body to produce red blood cells. Surplus amounts in the human body can become poisonous and is a particularly deadly toxic metal (Sunderman and Oskarsson 1991). Generally, in aquatic environments, Ni concentrations are low. The source of Ni may arise from industrial wastes where Ni compounds have been used for nickel plating, to color ceramics, in batteries, metal coins and as a catalyst that increases the rate of some chemical reactions (Singh 2005).

Copper is an essential element for the normal growth and metabolic processes of all living organisms. It is required for several enzymatic reactions in humans and is necessary for the synthesis of hemoglobin (Sivaperumal et al. 2007). Copper may cause health problems if the intake is excessive. Zinc is a common element in the earth's crust and an essential trace nutrient element, like Cu, in biological systems. A small amount of Zn is necessary for biological organisms and human health (Louis and John 1975). It is involved in nucleic acid synthesis and occurs in many enzymatic activities. Zinc is also used in the treatment of diabetes, down syndrome, alzheimer's disease and peptic ulcers (Nelms and Sucher 2015). It is an essential element in the human diet, but excessive amounts of Zn is harmful and may result in chronic toxicity, diarrhea, nausea, pancreas damage and anemia (Hambidge et al. 1986). Rubidium is an alkali metal and is an ultra-trace element essential to humans and other organisms (Campbell et al. 2005).

Cadmium is a highly toxic heavy metal and merits special attention due to its destructive potential to aquatic biota and humans. It is present throughout the environment and accumulates in the liver and kidney of mammals. Cadmium may cause kidney dysfunction, salvation and skeletal damage through magnification in the food chain (Barber and Sharma 1998). Lead is a toxic metal and one of the most serious environmental pollutants and is toxic to biota even when consumed in small quantities (Crosby 1977). It is a non-essential trace metal and does not perform any function in biochemical processes. The main sources of Pb pollution in the environment include effluents and emissions from vehicles, paints, anti-rust agents and dust emissions from coal and gas-fired power stations (Adeyeye et al. 1996). Lead poisoning is a serious environmental problem which may cause damage to organs such as the liver, kidney, and heart and result in damage effects to the immune and central nervous system (Manahan 1992). Over exposure may also cause carcinogenic effects in humans (Adeyeye et al. 1996).

6.5 Analysis of Data

In this study, the most commonly consumed and commercially important fish and shellfish samples were obtained from the fish landing center located at the Satu Batu area near Kampong Kualabaram and then analyzed for the accumulation of trace elements/metals in their different organ tissues. Seven species of fish (*Carcharhinus leucas, Scomberomorus lineolatus, Sphyraena qenie, Setipinna tenuifilis, Psettodes* *erumei, Trichiurus lepturus* and *Otolithes ruber*), five species of shrimp (*Parapenaeopsis sculptilis, Litopenaeus vannamei, Penaeus merguiensis, Harpiosquilla harpax* and *Acetes indicus),* three species of crab (*Portunus sanguinolentus, Portunus pelagicus* and *Scylla serrata*) and one species of bivalve (*Polymesoda erosa*) were obtained and used to determine the uptake and bioaccumulation level of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Rb, Cd, and Pb) concentrations in their body organs. Copper, Pb, Cd, Mn and Zn were analyzed in four different organs (namely muscle, gill liver and gonad) of the fish except in the case of only the (gills of *Otolithes ruber*, the gonads of *Trichiurus lepturus* and the liver of *Trichiurus lepturus, Otolithes ruber* and *Setipinna tenuifilis)* and are shown in Figure 6.1. Cobalt, Ni, Rb and Cr were analyzed in three species (*Carcharhinus leucas, Scomberomorus lineolatus* and *Sphyraena qenie*) of fish organs and are represented in (Figure 6.2). The concentration of heavy metals in the tissues of the various aquatic organisms in this study are shown in the following figures; shrimps (Figure 6.3 and Figure 6.4), crabs (Figure 6.5 and Figure 6.6) and bivalve (Figure 6.7 and Figure 6.8). The concentration of trace metals in the studied aquatic organisms are reported in Table 6.1.

6.6 Results

6.6.1 Pelagic and Demersal Fishes

Fish are classified as either pelagic or demersal. Demersal species feed mostly on the sea floor, whereas pelagic species mainly feed in the water column. Among the collected fish species, *Scomberomorus lineolatus* and *Setipinna tenuifilis* belong to the pelagic habitat and the rest of the fish species (*Carcharhinus leucas, Sphyraena qenie, Psettodes erumei, Trichiurus lepturus* and *Otolithes ruber*) are demersal habitat occupants.

6.6.2 Length and Weight of the samples

Upon reaching the laboratory, the size (length in cm and weight in grams) of the fish and shellfish were calculated. The fish species name and feeding habits were referred from various taxonomy books and the *fishbase.org* website, which provides broad information about all known fish species. The average length, weight, scientific name, English/common name, habitat and feeding nature of the collected aquatic organisms were recorded and reported in Table 6.2. From each species, a minimum of 10 numbers/samples were obtained from the fish landing center and analyzed for metal content.

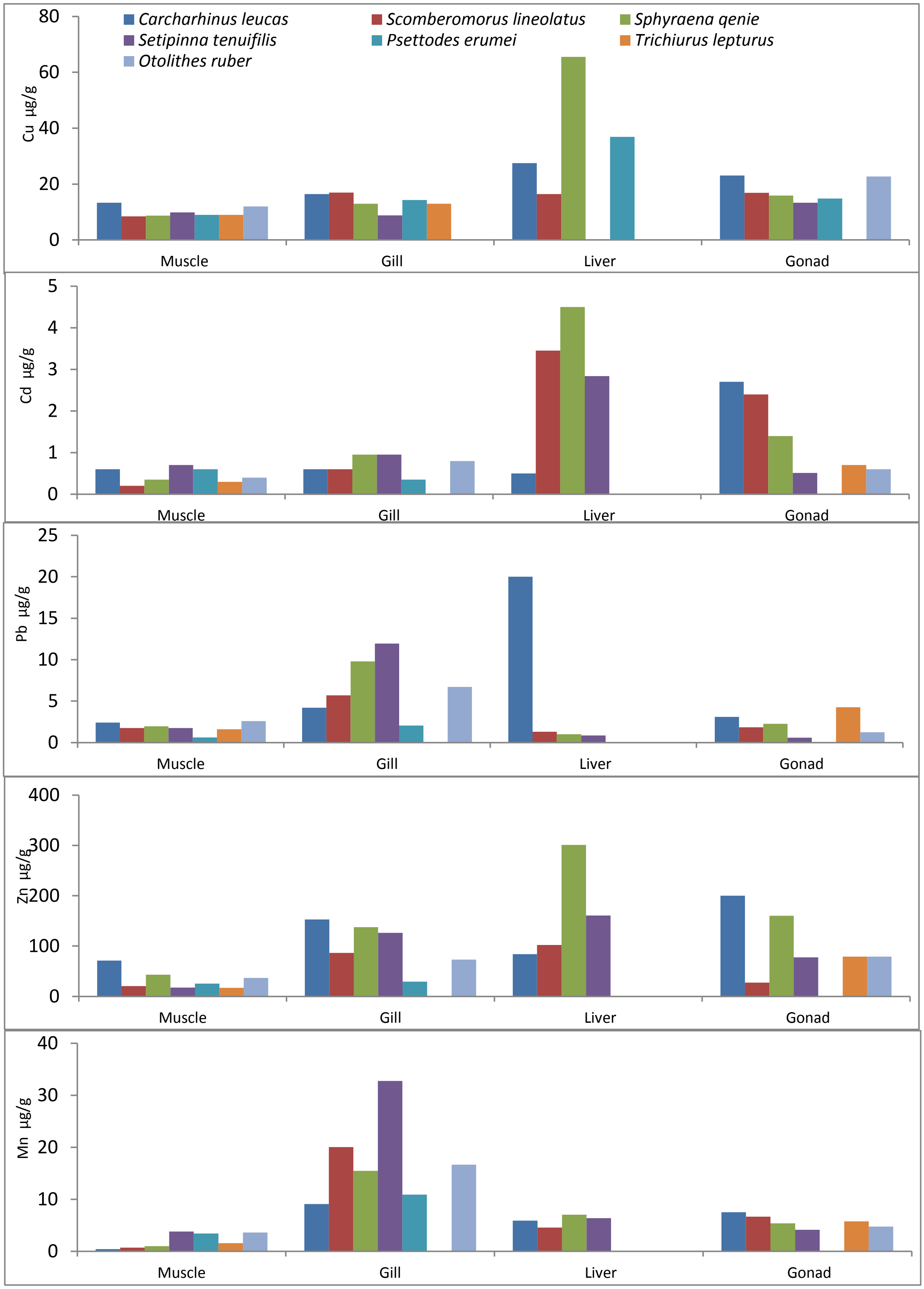


Figure 6.1 Concentration of Mn, Zn, Pb, Cd and Cu in seven different species of fish and their organs

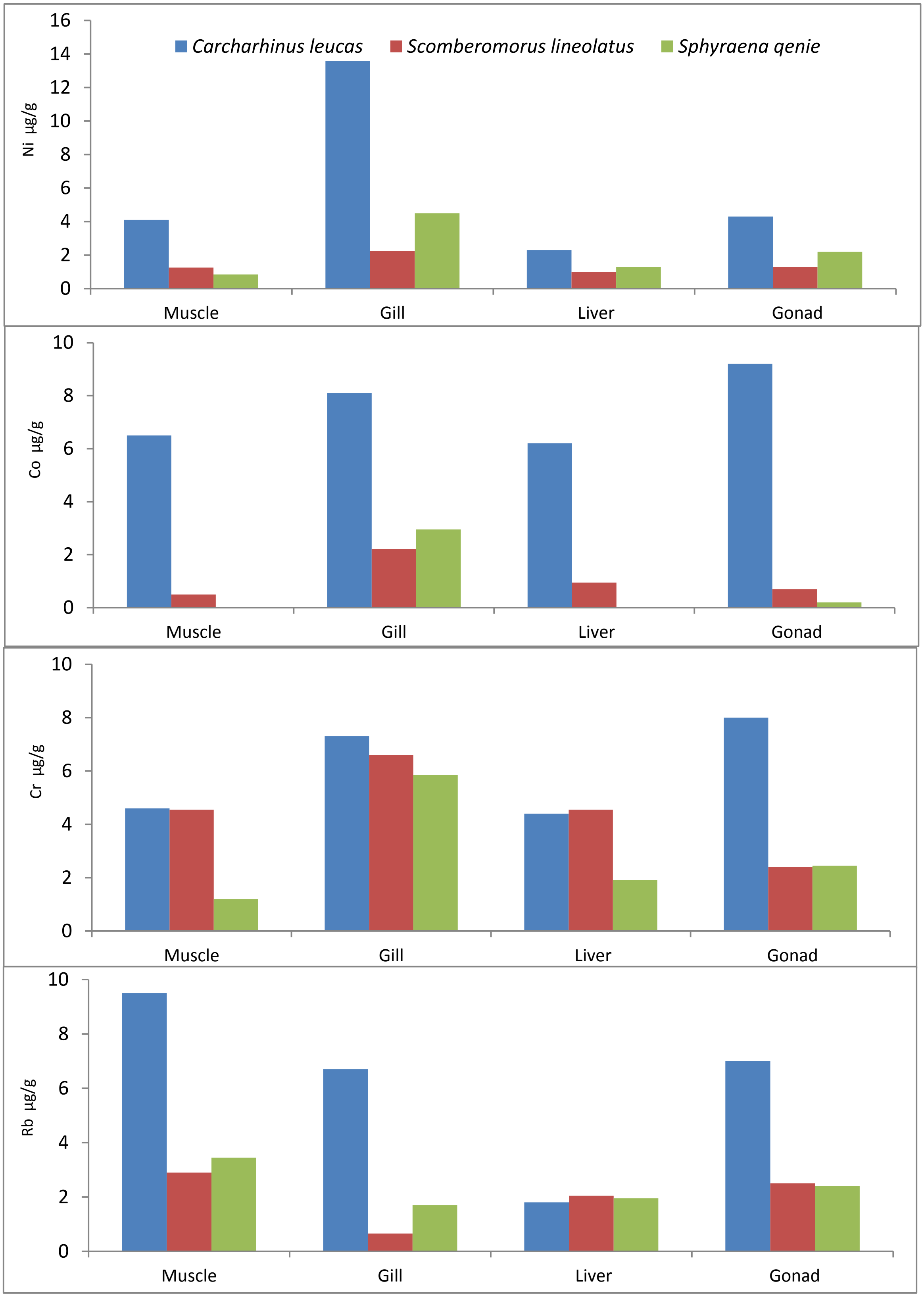


Figure 6.2 Concentration of Rb, Cr, Co and Ni in three different species of fish and their organs

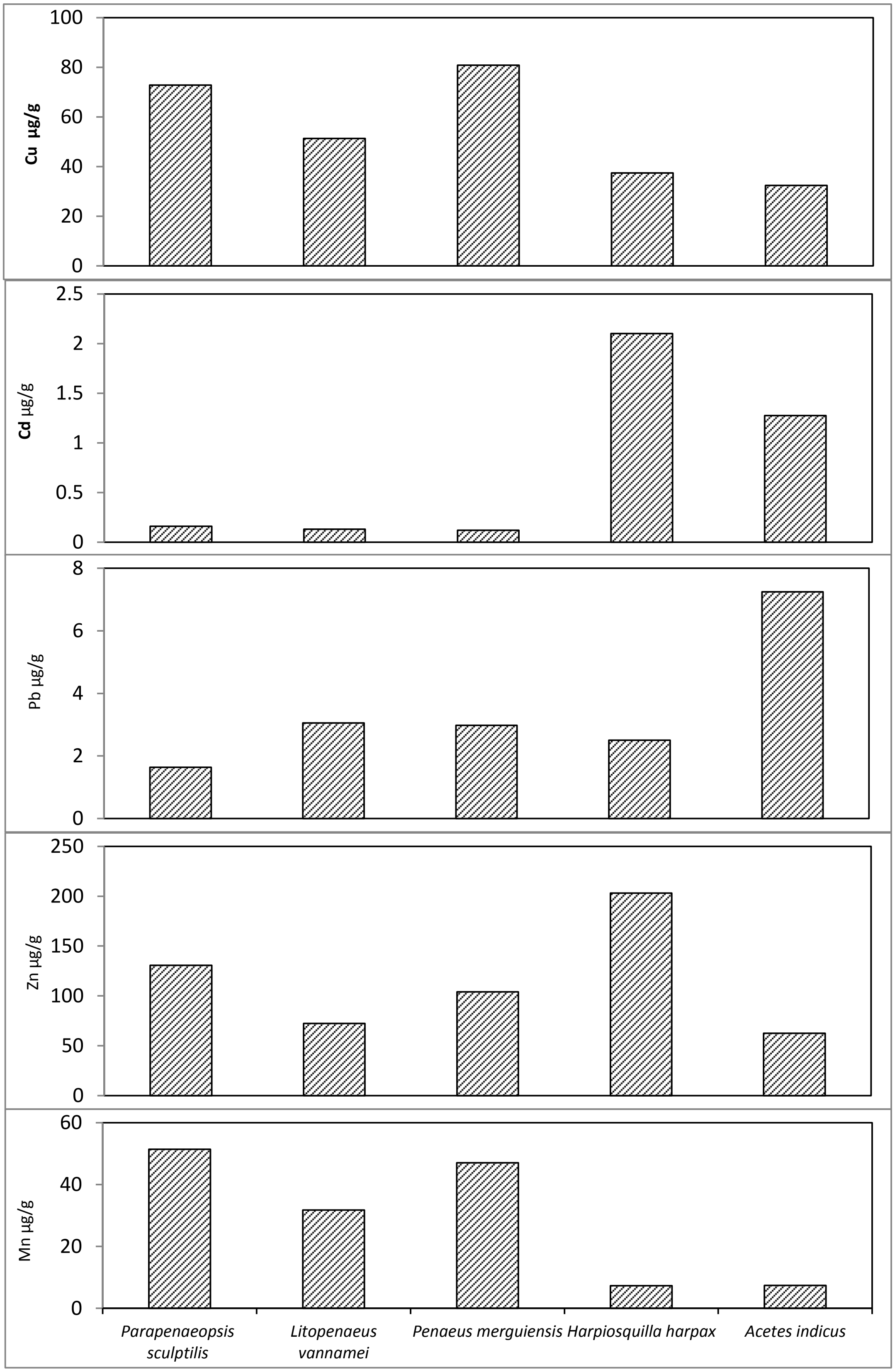


Figure 6.3 Concentration of Mn, Zn, Pb, Cd and Cu in the muscle tissues of five different species of marine shrimp

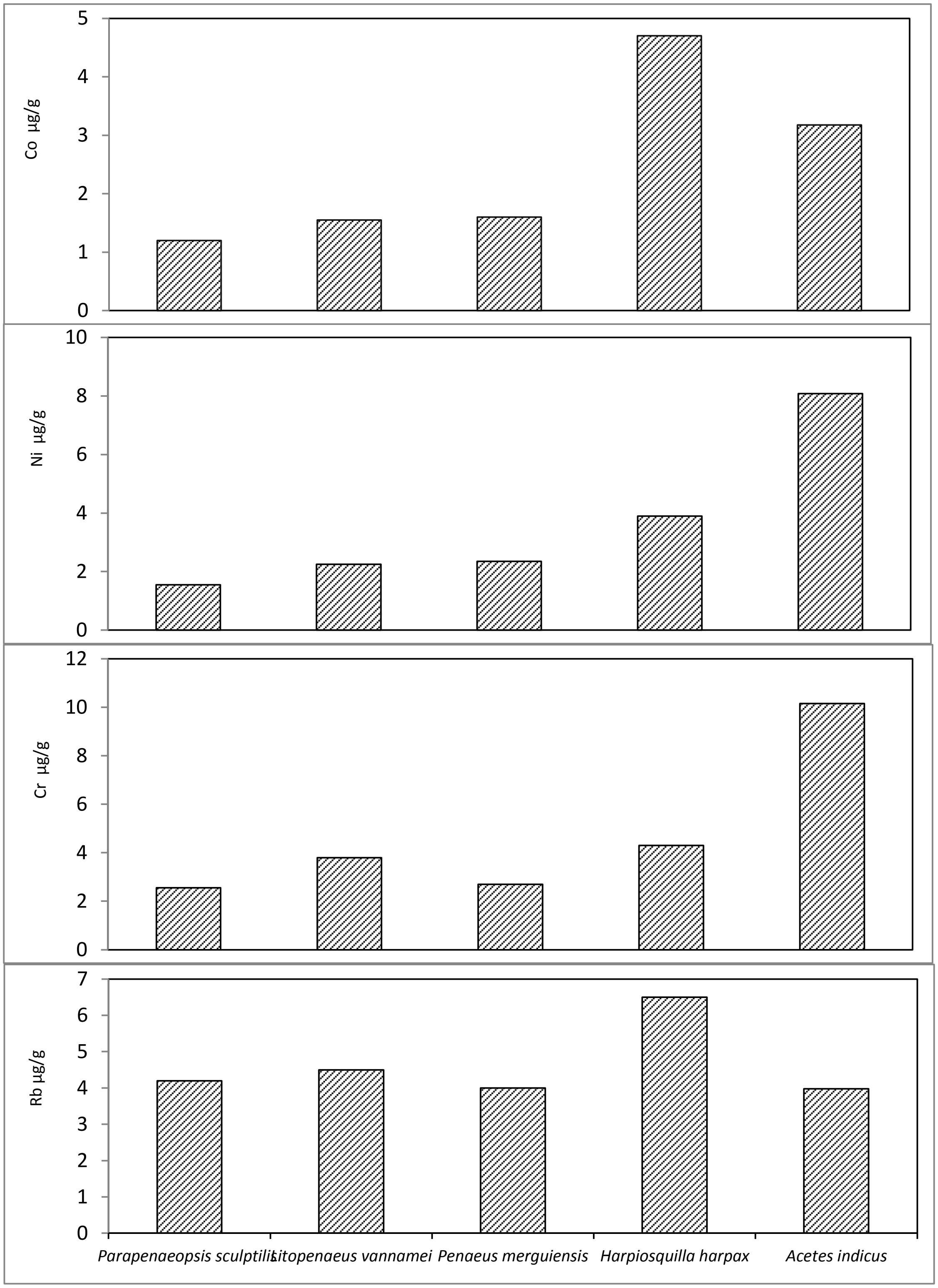


Figure 6.4 Concentration of Rb, Cr, Ni and Co in the muscle tissues of five different species of marine shrimp

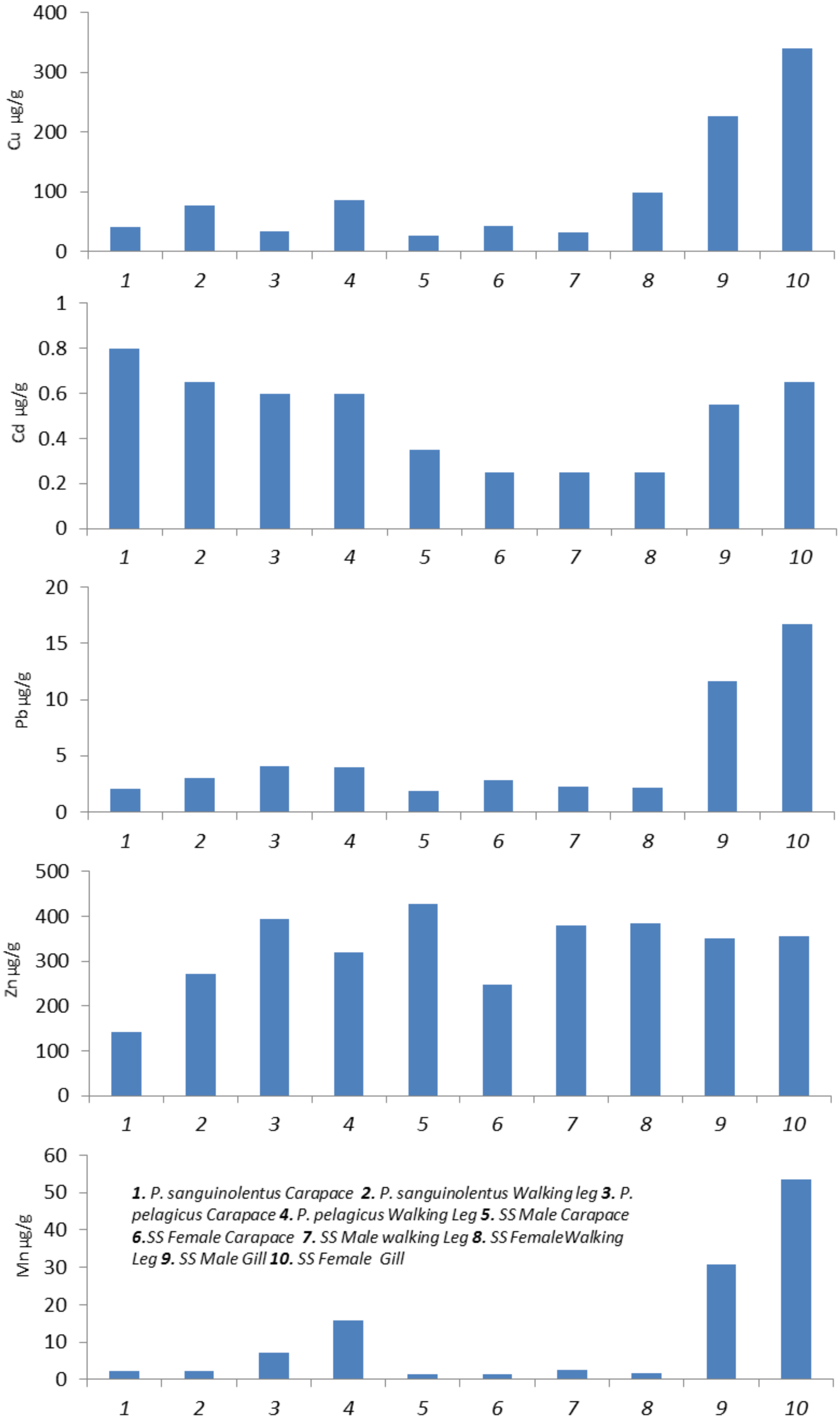


Figure 6.5 Concentration of Mn, Zn, Pb, Cd and Cu in three different crab species and their organs

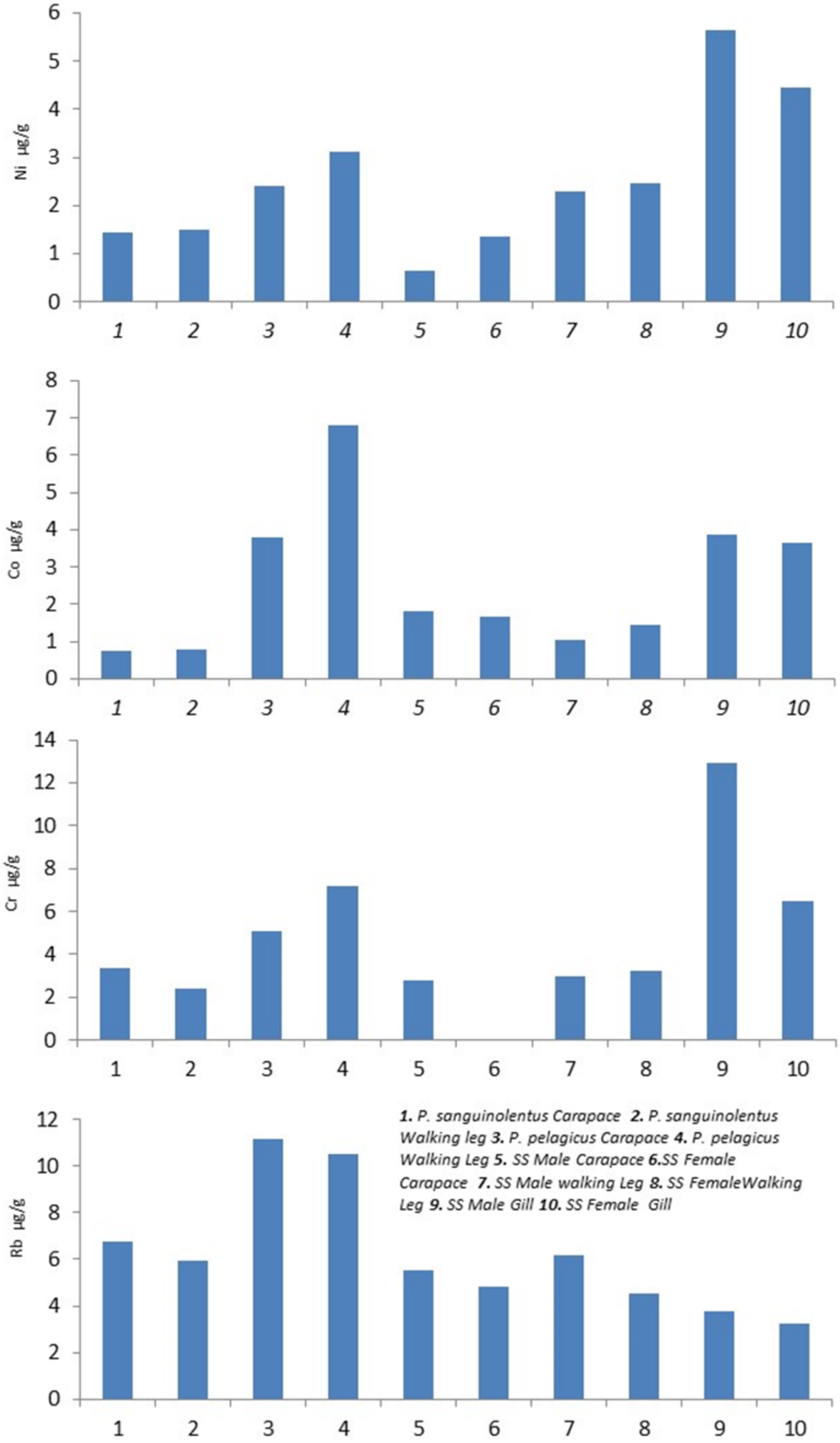


Figure 6.6 Concentration of Rb, Cr, Co and Ni in three different crab species and their organs

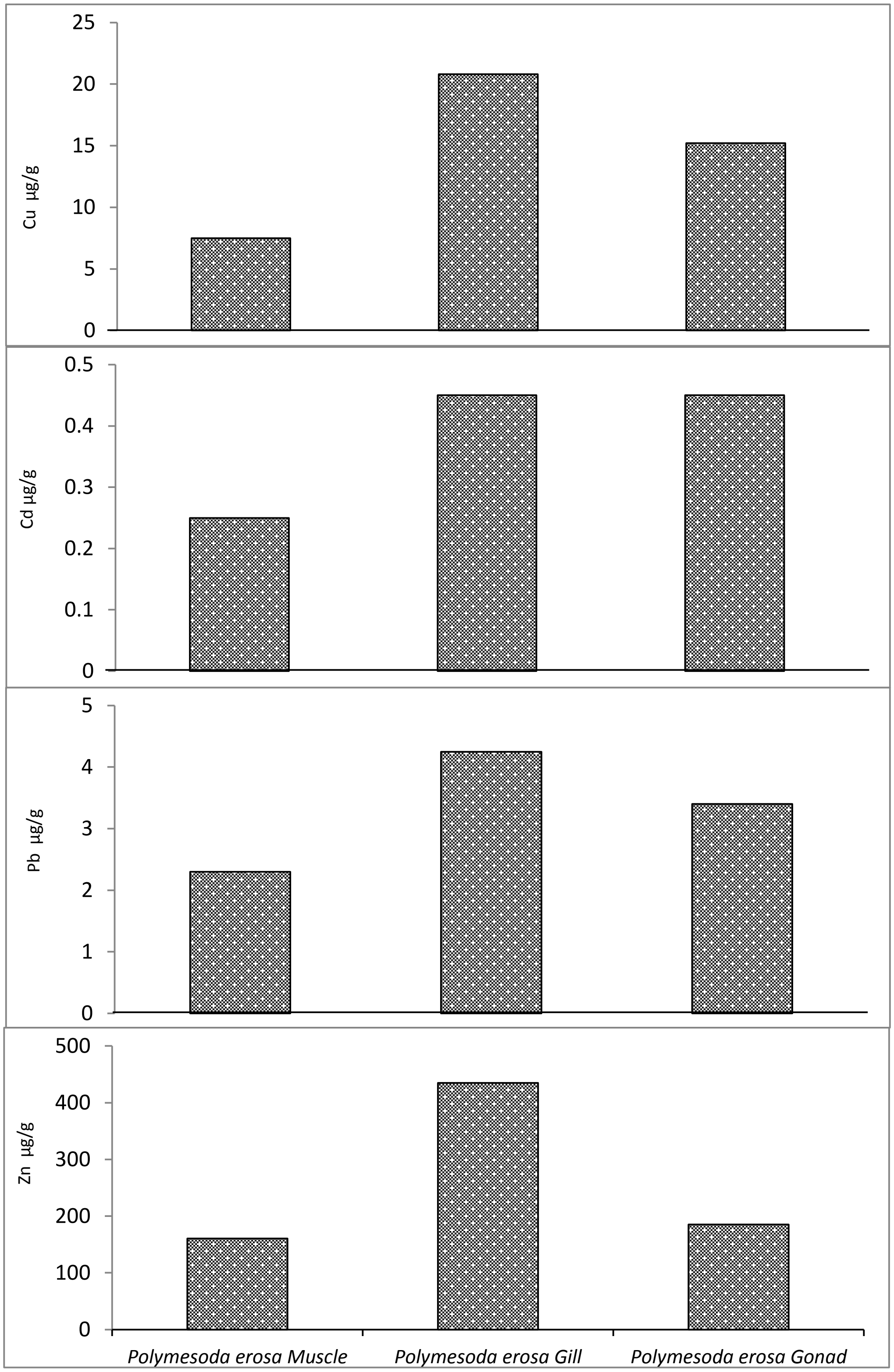


Figure 6.7 Concentration of Cu, Cd, Pb and Zn in three different organs of bivalve Polymesoda erosa

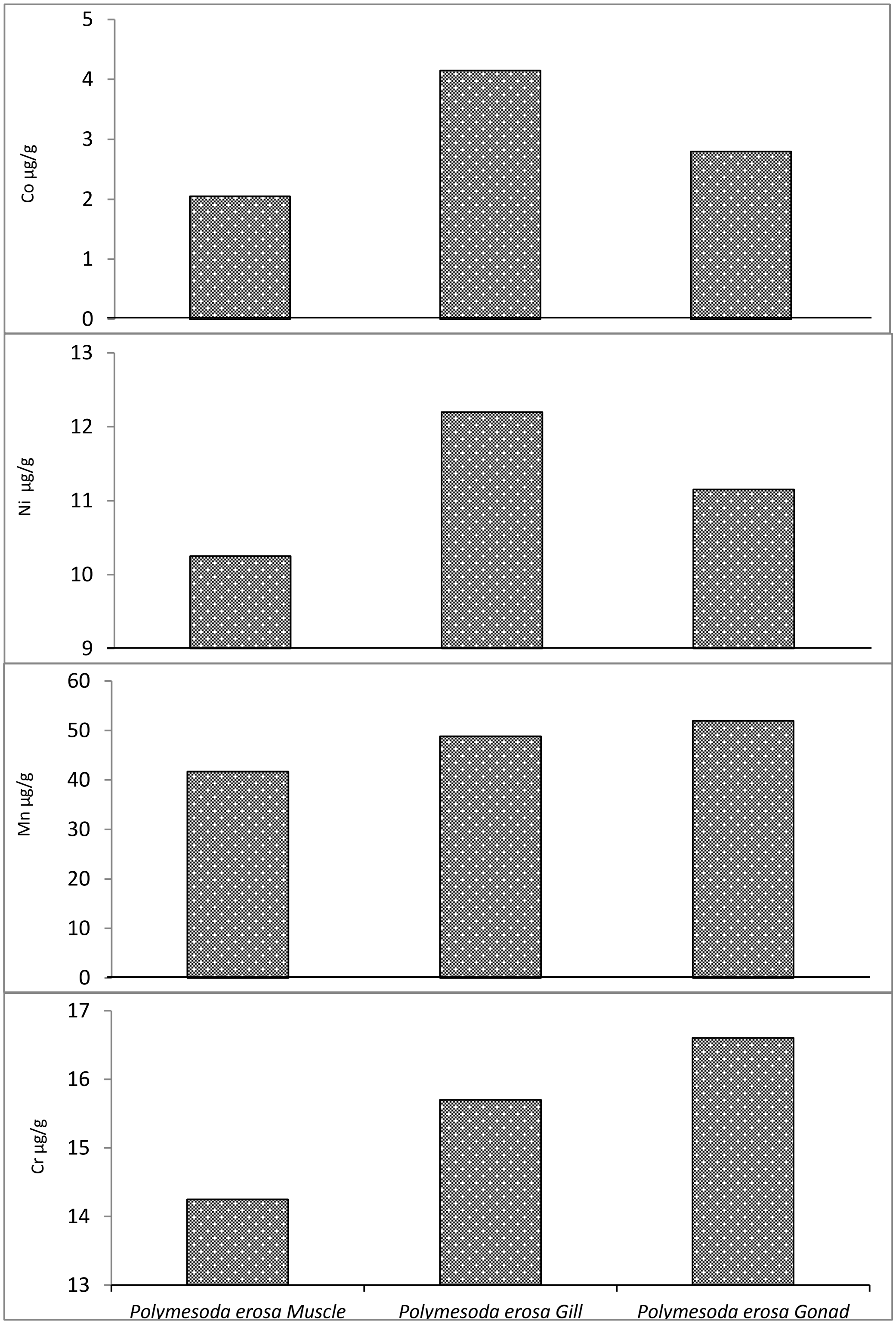


Figure 6.8 Concentration of Co, Ni, Mn and Cr in three different organs of bivalve Polymesoda erosa

Table 6.1 Concentration of elements in the aquatic organism collected from the Miri Coast (µg/g; dry weight)

Biota	Organs	Cr	Mn	Co	Ni	Cu	Zn	Rb	Cd	Pb
Carcharhinus leucas	Muscle	4.6	0.4	6.5	4.1	13.3	71.0	9.5	0.6	2.4
	Gill	7.3	9.1	8.1	13.6	16.4	153.0	6.7	0.6	4.2
	Liver	4.4	5.9	6.2	2.3	27.5	84.0	1.8	0.5	20.0
	Gonad	8.0	7.5	9.2	4.3	23.1	200	7.0	2.7	3.1
Scomberomorus lineolatus	Muscle	4.5	0.7	0.8	1.2	8.5	20.2	2.9	0.2	1.7
	Gill	6.6	20	2.2	2.2	17.0	86.5	0.6	0.6	5.7
	Liver	4.5	4.5	0.9	1.0	16.4	102	2.0	3.4	1.3
	Gonad	2.4	6.6	0.7	1.3	16.9	27.3	2.5	2.4	1.8
Sphyraena qenie	Muscle	1.2	1.0	0.0	0.8	8.7	43.0	3.4	0.3	1.9
	Gill	5.8	15.4	2.9	4.5	12.9	137.5	1.7	0.0	9.8
	Liver	1.9	7.0	BDL	1.3	65.5	301.0	1.9	4.5	1.0
	Gonad	2.45	5.3	0.2	2.2	15.9	160.0	2.4	1.4	2.2
Setipinna tenuifilis	Muscle	ND	3.6	ND	ND	9.9	36.6	ND	0.4	2.6
	Gill	ND	73.0	ND	ND	8.8	73.0	ND	0.8	6.7
	Liver	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Gonad	ND	4.7	ND	ND	13.3	79.2	ND	0.6	1.2
Psettodes erumei	Muscle	ND	3.8	ND	ND	9.0	17.3	ND	0.7	1.7
	Gill	ND	32.7	ND	ND	14.3	126.4	ND	0.9	11.9
	Liver	ND	6.3	ND	ND	36.9	160.8	ND	2.8	0.8
	Gonad	ND	4.15	ND	ND	14.83	77.4	ND	0.51	0.5
Trichiurus lepturus	Muscle	ND	3.4	ND	ND	9.0	25.3	ND	0.6	0.6
	Gill	ND	10.9	ND	ND	13.0	29.4	ND	0.35	2.05
	Liver	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Gonad	ND	ND	ND	ND	ND	ND	ND	ND	ND
Otolithes ruber	Muscle	ND	1.55	ND	ND	12.4	16.9	ND	0.3	1.6
	Gill	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Liver	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Gonad	ND	5.75	ND	ND	22.75	79.2	ND	0.7	4.25
Shrimp										
Parapenaeopsis sculptilis	Muscle	2.5	51.3	1.2	1.5	72.8	130.8	4.2	0.1	1.6
Litopenaeus vannamei	Muscle	3.8	31.7	1.5	2.2	51.3	72.4	4.5	0.1	3.0
Penaeus merguiensis	Muscle	2.7	47.0	1.6	2.3	80.8	104.2	4	0.1	2.9
Harpiosquilla harpax	Muscle	4.3	7.3	4.7	3.9	37.4	203	6.5	2.1	2.5
Acetes indicus	Muscle	10.1	7.4	3.1	8.0	32.4	62.4	3.9	1.2	7.2
Crabs										
Portunus sanguinolentus	Carapace	3.3	2.2	0.7	1.4	41.9	142.4	6.7	0.8	2.0
	Walking Leg	2.4	2.2	0.8	1.5	76.6	273	5.9	0.6	3.0
Portunus pelagicus	Carapace	5.1	7.2	3.8	2.4	33.5	394	11.2	0.6	4.1
	Walking Leg	7.2	15.9	6.8	3.1	85.7	319	10.5	0.6	4
Scylla serrate Male	Carapace	2.8	1.4	1.8	0.6	27.1	428.7	5.5	0.3	1.9
	Walking Leg	2.9	2.5	1.0	2.3	32.8	379.6	6.1	0.2	2.2
	Gill	12.9	30.8	3.8	5.6	240	350	3.7	0.5	11.6
Scylla serrate Female	Carapace	0.0	1.2	1.6	1.3	43.2	247.5	4.8	0.2	2.8
	Walking Leg	3.2	1.8	1.4	2.4	98	384.2	4.5	0.2	2.1
	Gill	6.5	53.5	3.6	4.4	340	356.5	3.2	0.6	16.7
Bivalve										
Polymesoda erosa	Muscle	14.2	41.7	2.0	10.2	7.5	160.5	ND	0.2	2.3
	Gill	15.7	48.8	4.1	12.2	20.8	435	ND	0.4	4.2
	Gonad	16.6	51.9	2.8	11.1	15.2	185	ND	0.4	3.4

BDL-Below Detection Limit; ND-Not Detected

Table 6.2. Morphometric measures of the studied marine organisms from the Miri coast

Fish Species	English/ common name	Length (cm)	Weight (g)	Habitat	Feeding nature	Climate
Carcharhinus leucas	Bull Sharks	56.4	930.25	Semi-pelagic	Carnivorous (feeds on bony fishes, crabs, shrimps, sea snails, rays etc.)	Tropical & Sub-tropical
Scomberomorus lineolatus	Spanish Mackerel	27.2	166.80	Pelagic-neritic	Carnivorous (feeds on fishes)	
Sphyraena qenie	Barracuda	29.5	280.5	Pelagic-Demersal - Reef -associated	Carnivorous (feeds on snappers, groupers, small tunas and anchovies)	
Setipinna tenuifilis	Common hairfin anchovy	14.6	23.66	Pelagic-neritic	Carnivorous (feeds on prawn, copepods, crustacean larvae, mollusks and fishes)	
Psettodes erumei	Indian Halibut	22.9	146.98	Pelagic-Demersal	Carnivorous (feeds on small fish and benthic invertebrates)	
Trichiurus lepturus	Largehead hairtail/ Ribbon fish	36.8	79.01	Bentho-pelagic	Carnivorous (feed mainly on fishes and occasionally on squids and crustaceans)	
Otolithes ruber	Tigertooth croaker	18.6	75.93	Bentho-pelagic	Carnivorous (feeds on fishes, prawns and other invertebrates)	
Shrimps						
Parapenaeopsis sculptilis	Rainbow shrimp	15.2	19.45	Benthic	Omnivores (algae, plankton matter, and tiny fishes)	Tropical & Sub-tropical
Litopenaeus vannamei	Whiteleg Shrimp	11.8	7.83	Benthic	Omnivores (algae, plankton matter and tiny fishes)	
Penaeus merguiensis	Banana Shrimp	11.7	8.08	Benthic	Omnivores (algae, plankton matter and tiny fishes)	
Harpiosquilla harpax	Silver Mantis Shrimp	10.5	15.06	Benthic	Omnivores (algae, plankton matter and tiny fishes)	
Acetes indicus	Bubuk	2.1	0.40	Benthic	Omnivores (algae, plankton matter and tiny fishes)	

Crabs						
Fish Species	**English/ common name**	**Length (cm)**	**Weight (g)**	**Habitat**	**Feeding nature**	**Climate**
Portunus sanguinolentus	Blood-spotted swimming crab	14.1	177.07	Benthic	Omnivores (algae, molluscs, worms, other crustaceans, fungi, bacteria and detritus)	Tropical & Sub-tropical
Portunus pelagicus	Blue Swimming Crab	8.9	102.54	Benthic	Omnivores (algae, molluscs, worms, other crustaceans, fungi, bacteria and detritus)	
Scylla serrate	Mud Crab	8.2	112.27	Benthic	Omnivores (algae, molluscs, worms, other crustaceans, fungi, bacteria and detritus)	
Bivalve						
Polymesoda erosa	Mud Clam/Lokan	7.6	68.82	Sessile (attached to hard surfaces)	Filter Feeders (planktons and algae)	Tropical & Sub-tropical

6.6.3 **Distribution of trace/heavy metals**

6.6.3.1 ***Chromium***

Chromium in Fish

Results showed Cr concentrations in fish organs varied from 1.20 to 8.01 μg g^{-1}. Among the species and the organ tissues, the highest Cr level was recorded in the gonad tissue of *Carcharhinus leucas* (13.6 μg g^{-1}) and the lowest value was observed in the muscle tissues of *Sphyraena qenie* (0.85 μg g^{-1}). Cr accumulation in organs of the studied fish were not similar to the data reported in other publications (Table 6.3). Cr concentration in fish muscles was in the order (highest – lowest); *Carcharhinus leucas* > *Scomberomorus lineolatus* > *Sphyraena qenie*. In these species, Cr concentration in the muscles varied from 1.20 to 4.60 μg g^{-1} with an average of 3.45 μg g^{-1}. These values were higher compared to those reported in similar studies from other locations, for example: the Mediterranean Sea, (1.28 – 1.60 μg g^{-1}), Kalay et al. (1999); the Masan Bay, Korea (0.18 – 0.25 μg g^{-1}), Kwon and Lee (2001); Black sea (0.06 – 0.84 μg g^{-1}), Topcuoğlu et al. (2002); Parangipettai coast, India (0.41 to 1.56 μg g^{-1}), Lakshmanan et al. (2009); and Malacca strait, Malaysia (0.55μg g^{-1}), Alama et al. (2012).

Table 6.3 Accumulation of Chromium in the different organs of fish sp.

Fish Species	**Cr accumulation sequence**
Carcharhinus leucas	Gonad > Gill > Muscle > Liver
Scomberomorus lineolatus	Gill > Liver > Muscle > Gonad
Sphyraena qenie	Gill > Gonad > Liver > Muscle

Chromium in Crustaceans

Chromium content in the shrimp muscles varied between 2.55 and 10.15 μg g^{-1} with an average value of 4.70 μg g^{-1}. Chromium was higher in *Acetes indicus* (10.15 μg g^{-1}) and lower in *Parapenaeopsis sculptilis* (2.55 μg g^{-1}) and its abundance was observed in decreasing order as *Acetes indicus* > *Harpiosquilla harpax* > *Litopenaeus vannamei* > *Penaeus merguiensis* > *Parapenaeopsis sculptilis.* The average Cr level in the shrimp muscles were higher than the values reported from other parts of the world; i.e. the Southeast coast of India (0.61μg g^{-1}), Sivaperumal et al. (2007); Malacca Strait, Malaysia

(0.29 μg g^{-1}), Alama et al. (2012); and Malacca and Kedah, Malaysia (*Acetes indicus* sp; 0.59 – 1.34 μg g^{-1}), Rahouma et al. (2013).

The observed Cr concentration in the crab species was in the range of 2.40 to 12.90 μg g^{-1} with an average of 4.64 μg g^{-1}. In the three species of crabs analyzed, the highest Cr content was recorded in *Scylla serrata* followed by *Portunus pelagicus* and *Portunus sanguinolentus*. The highest Cr concentration was observed in the gills followed by the walking legs and carapace muscles of all three species. Chromium concentration in the crabs from Miri region was higher than the values reported from Iskenderun Bay, Turkey (Blue crab *Callinectes sapidus;* 0.20 to 0.55 μg g^{-1}), Türkmen et al. (2006); Mediterranean Lagoons (muscle and gill tissues of *Callinectes sapidus* sp 0.03 to 0.08 μg $g^{-}1$; 0.04 to 0.10 μg g^{-1} respectively) and the Kuwait coast (*Portunus pelagicus* sp; 0.47 μg g^{-1}), Al-Mohanna and Subrahmanyam (2001). The average Cr content in the muscle tissues of crab species from the Miri region was 3.37 μg g^{-1}.

Chromium in Bivalve

The Cr concentration in *Polymesoda erosa* ranged from 14.25 to 16.6 μg g^{-1} with an average of 15.5 μg g^{-1}. The highest accumulation was noticed in the gonads followed by the gills and the muscles. Cr concentration was observed in the muscles of *Polymesoda erosa* as 14.25 μg g^{-1}.

6.6.3.2 ***Manganese***

Manganese in Fish

The Mn concentration in the analyzed fish organs varied between 0.40 (muscle of *Carcharhinus leucas*) and 32.75 μg g^{-1}(gills of *Psettodes erumei*). In all the fish species, Mn concentration was in the order (from highest to lowest) gills, gonads, liver and muscle (Table 6.4). The Mn concentration in the analyzed fish muscles was in the order of *Psettodes erumei* > *Setipinna tenuifilis* > *Trichiurus lepturus* > *Otolithes ruber* > *Sphyraena qenie* > *Scomberomorus lineolatus* > *Carcharhinus leucas*. For these species, the average Mn in the muscles was 2.06 μg g^{-1}; which was lower compared to the values reported from the Langkawi Islands, Malaysia (16.80 to 24.35 μg g^{-1}), Irwandi and Farida (2009); East coast of India (2.90 μg g^{-1}), Kumar et al. (2012); Mumbai coast, India (3.47

μg g^{-1}), Velusamy et al. (2014), but higher than values reported from the Black Sea (0.56 – 0.69 μg g^{-1}), Topcuoğlu et al. (2002); Parangipettai coast, India (0.31 – 1.20 μg g^{-1}), Raja et al. (2009).

Table 6.4 Accumulation of Manganese in the different organs of fish sp.

Fish Species	Mn accumulation sequence
Carcharhinus leucas	Gill > Gonad > Liver > Muscle
Scomberomorus lineolatus	Gill > Gonad > Liver > Muscle
Sphyraena qenie	Gill > Gonad > Liver > Muscle
Setipinna tenuifilis	Gill > Gonad > Muscle
Psettodes erumei	Gill > Gonad > Liver > Muscle
Trichiurus lepturus	Gill > Muscle
Otolithes ruber	Gonad > Muscle

Manganese in Crustaceans

The Mn concentration in the marine shrimp muscles varied between 7.30 and 51.35 μg g^{-1} with an average of 28.97 μg g^{-1}. The highest and lowest concentration (51.35 and 7.30 μg g^{-1}) was recorded in *Parapenaeopsis sculptilis* and *Harpiosquilla harpax* respectively. The Mn concentration in the analyzed muscles of marine shrimp was in the order of *Parapenaeopsis sculptilis* > *Penaeus merguiensis*> *Litopenaeus vannamei* > *Acetes indicus* > *Harpiosquilla harpax*. The observed values of Mn (7.30 - 51.35 μg g^{-1}) in the shrimp tissues was higher than the values reported for brown shrimp from the coast of Turkey (6.00 - 15.00 μg g^{-1}), Bat et al. (2013); shrimp and lobster species from the Bay of Bengal, Bangladesh (3.10 – 15.20 μg g^{-1}), Hossaina and Khan (2001) and *Acetes indicus* sp from Peninsular Malaysian waters (2.61 – 6.95 μg g^{-1}), Rahouma et al. (2012).

Mn concentration in the crabs was in the range of 1.25 to 53.55 μg g^{-1} with an average of 28.98 μg g^{-1}. In the three species of crabs analyzed, the highest Mn was recorded in *Scylla serrata* followed by *Portunus pelagicus* and *Portunus sanguinolentus*. The highest Mn accumulation is in the gill tissues followed by the walking legs and lowest in the carapace muscles. The average Mn content for the edible tissues of crab was 4.32 μg g^{-1}, which was higher than the those reported for crab *Portunus pelagicus* from the Kuwait coast (0.95 μg g^{-1}); Al-Mohanna and Subrahmanyam (2001); and lower than the value reported for *Scylla serrata* from the Mahanadi estuary, India (12.70 μg g^{-1}), Mohapatra et al. (2009).

Manganese in Bivalve

The Mn concentration in *Polymesoda erosa* was recorded in the range of 41.70 to 51.95 μg g^{-1} with an average of 47.5μg g^{-1}. The highest accumulation was noticed in the gonads followed by the gills and the lowest level was observed in the muscle. The Mn content in the foot muscle of *Polymesoda erosa* was lower than the values reported for similar species from the Mandovi estuary, west coast of India (at 53.9 μg g^{-1}) (Gawade et al. 2013).

6.6.3.3 *Cobalt*

Cobalt in Fish

The Co concentration in the analyzed fish organs varied between BDL (below detection limit) to a maximum of 9.20 μg g^{-1}. Among the species and the organs analyzed, the maximum concentration was recorded in the gonads of *Carcharhinus leucas* as 9.20 μg g^{-1} and the lowest concentration was detected in the muscle of *Scomberomorus lineolatus* as 0.5 μg g^{-1}. In the analyzed fish species, a higher Co accumulation was noticed in the gills followed by the gonads, liver and muscle (Table 6.5). The Co concentration in the analyzed fish muscle was found in the order of *Carcharhinus leucas* > *Scomberomorus lineolatus* > *Sphyraena qenie*.

The concentration of Cobalt in fish muscles varied between BDL and 6.50 μg g^{-1} with an average of 2.33 μg g^{-1}. The observed values of Co in fish tissues were higher than the values reported from Masan Bay, Korea (0.02μg g^{-1}), Kwon and Lee (2001); Gulf of Cambay, India (0.24 μg g^{-1}), Reddy et al. (2007); Black Sea coast (0.05 – 0.40 μg g^{-1}), Topcuoğlu et al. (2002); Parangipettai coast, India (0.05 – 0.28 μg g^{-1}), Raja et al. (2009); Iran (0.61 to 0.91 μg g^{-1}), Hosseini et al. (2015) but lower than the values reported from the southwest coast of India (3.64 – 11.80 μg g^{-1}), Rejomon et al. (2010).

Table 6.5 Accumulation of Cobalt in the different organs of fish sp.

Fish Species	**Co-accumulation sequence**
Carcharhinus leucas	Gonad > Gill > Liver > Muscle
Scomberomorus lineolatus	Gill > Liver > Gonad > Muscle
Sphyraena qenie	Gill > Gonad > Liver > Muscle

Cobalt in Crustaceans

The Co concentration in the shrimp muscles varied between 1.20 and 4.70 μg g^{-1} with an average of 2.44 μg g^{-1}. The Co concentration was recorded highest in *Harpiosquilla harpax* (4.70 μg g^{-1}) and the lowest in *Parapenaeopsis sculptilis* (1.20 μg g^{-1}). The Co concentration in the analyzed muscles of marine shrimp was in the order of *Harpiosquilla harpax* > *Acetes indicus* > *Penaeus merguiensis* > *Litopenaeus vannamei* > *Parapenaeopsis sculptilis.* The Co concentration in shrimp tissues was higher than the values reported for brown shrimp from the Turkish coast (0.24 – 0.61 μg g^{-1}); Bat et al. (2013) and lower than the values reported from the southwest coast of India (8.50 – 19.00 μg g^{-1}), George et al. (2011).

In the three species of crabs analyzed, the highest Co concentration was observed in *Portunus pelagicus* followed by *Scylla serrata* and *Portunus sanguinolentus*. The highest Co was accumulated in the walking legs followed by the gills and the carapace muscles. The Co concentration was in the range of 0.70 to 6.80 μg g^{-1} with an average of 2.56 μg g^{-1}. The mean concentration of Co in the analyzed edible tissues (carapace and walking leg) of crab species is 2.26 μg g^{-1}. This average value was higher than the value reported for crabs from the Persian Gulf (0.53 to 0.61 μg g^{-}1); Hosseini et al. (2014).

Cobalt in Bivalve

The Co concentration in *Polymesoda erosa* was in the range of 2.05 to 4.15 μg g^{-1} which was lower than the values reported for similar species from the Mandovi estuary-west coast of India (26 μg g^{-1}); Gawade et al. (2013). The highest accumulation was noticed in the gills followed by the gonads and the muscle tissue.

6.6.3.4 ***Nickel***

Nickel in Fish

The Ni concentration in the fish organs varied between 0.85 and 13.6 μg g^{-1}, with an average of 3.24 μg g^{-1}. Among the species and the organ tissues measured, the maximum and minimum Ni content was observed in the gills of *Carcharhinus leucas* and the muscles of *Sphyraena qenie* as 13.6 μg g^{-1} and 0.85 μg g^{-1} respectively. The concentration of Ni in fish muscles varied between 0.85 and 4.10 μg g^{-1} with an average value of 2.06 μg g^{-1}. The Ni concentration was more abundant in the gills followed by the gonads, liver and muscle (Table 6.6). In the fish muscles the order of concentration was (highest to lowest) *Carcharhinus leucas* > *Scomberomorus lineolatus* > *Sphyraena qenie*. The observed values of Ni (0.85 – 4.10 μg g^{-1}) in fish muscles was higher than those observed from Masan Bay, Korea (0.02 μg g^{-1}), Kwon and Lee (2001); Antarctic waters (0.11 – 0.12 μg g^{-1}), Honda et al. (1987); Parangipettai coast, India (0.38 – 1.54 μg g^{-1}), Raja et al. (2009) but lower than values reported for Ni from the Mediterranean Sea (4.25 – 6.07 μg g^{-1}), Kalay et al. (1999); southwest coast of India (6.06 – 13.92 μg g^{-1}), Rejomon et al. (2010) and Iran (49.40 – 54.10 μg g^{-1}), Hosseini et al. (2015).

Table 6.6 Accumulation of Nickel in the different organs of fish sp.

Fish Species	Ni accumulation sequence
Carcharhinus leucas	Gill > Gonad > Muscle > Liver
Scomberomorus lineolatus	Gill > Gonad > Muscle > Liver
Sphyraena qenie	Gill > Gonad > Liver > Muscle

Nickel in Crustaceans

The Ni concentration in the shrimp muscles varied between 1.55 and 8.07 μg g^{-1} with an average of 3.62 μg g^{-1}, with the highest and lowest values found in *Acetes indicus* and *Parapenaeopsis sculptilis* respectively. The Ni concentration in the muscles of marine shrimps was in the order of *Acetes indicus* > *Harpiosquilla harpax* > *Penaeus merguiensis* > *Litopenaeus vannamei* > *Parapenaeopsis sculptilis.* The present observed values of Ni can be compared with values reported for marine shrimp and lobster species from Bay of Bengal, Bangladesh (2.8 to 8.9 μg g^{-1}), Hossaina and Khan (2001); and higher than the values observed for *Penaeus indicus* shrimps from Thane – Bassein creek, India (0.01-0.08 μg g^{-1}), Krishnamurti and Nair (1999). However, the values were lower than those reported from the Cochin coast, India (10.6 to 24.7 μg g^{-1}), George et al. (2011).

In the three species of crabs analyzed, higher Ni concentration was observed in the *Scylla serrata* followed by *Portunus pelagicus* and *Portunus sanguinolentus*. The maximum Ni accumulation was in the gills followed by the walking legs and the carapace muscles. The Ni concentration in the different organ tissues of crabs was in the range of

0.65 to 5.65 μg g^{-1} with an average of 2.53μg g^{-1}. The average concentration of Ni in the edible tissues of crab species was 1.9 μg g^{-1}, which was higher than the reported values for *Scylla serrata* crab from the Thane creek, India (0.04-0.09 μg g^{-1}), Krishnamurti and Nair (1999); Blue crab *Callinectes sapidus* from Iskenderun Bay, Turkey (0.66 to 1.59 μg g^{-1}), Türkmen et al. (2006) but lower than the reported values from Queensland, Australia (8.90 to 26.8 μg g^{-1}), Mortimer and Cox (1999).

Nickel in Bivalve

The Ni concentration in *Polymesoda erosa* was in the range of 10.25 and 12.20 μg g^{-1}, with an average value of 11.20 μg g^{-1}. The highest accumulation was in the gills followed by the gonads and muscle tissue. The average Ni content in the muscles of *Polymesoda erosa* was lower than the values reported from the Mandovi estuary, west coast of India (14 μg g^{-1}); Gawade et al. (2013) but higher than from the west coast of Peninsular Malaysia (2.61 to 7.76 μg g^{-1}, Yap et al., 2014).

6.6.3.5 ***Copper***

Copper in Fish

The Cu concentration in fish muscles varied between 8.50 and 13.30 μg g^{-1}. Among the species and the organ tissues, the liver of *Sphyraena qenie* had the highest concentration (65.50 μg g^{-1}) and the lowest concentration was observed in the muscle of *Scomberomorus lineolatus* (8.50 μg g^{-1}). In the fish species; (*Carcharhinus leucas*, *Sphyraena qenie* and *Psettodes erumei*) the accumulation of Cu showed the same sequence as liver > gonads > gills > muscles. The sequence of Cu concentration in all organs of the fish species is listed in (Table 6.7). The Cu concentration in the fish muscles was in the order (highest to lowest) *Carcharhinus leucas* > *Otolithes ruber* > *Setipinna tenuifilis* > *Trichiurus lepturus* > *Psettodes erumei* > *Sphyraena qenie* > *Scomberomorus lineolatus*. The Cu concentration in the fish muscles was higher than the values reported for the marine fish from, the Mediterranean Sea (3.40 - 5.88 μg g^{-1}), Kalay et al. (1999) but lower than the values reported from Poompuhar, SE coast of India (20.48 μg g^{-1}), Prasath and Khan (2008); Langkawi Island, Malaysia (11.48 to 13.95μg g^{-1}), Irwandi and Farida (2009).

Table 6.7 Accumulation sequence of Cu in the different organs of the fish sp.

Fish Species	Cu accumulation sequence
Carcharhinus leucas	Liver > Gonad > Gill > Muscle
Scomberomorus lineolatus	Gonad > Liver > Gill > Muscle
Sphyraena qenie	Liver > Gonad > Gill > Muscle
Setipinna tenuifilis	Gonad > Gill > Muscle
Psettodes erumei	Liver > gonad > Gill > Muscle
Trichiurus lepturus	Gill> Muscle
Otolithes ruber	Gonad > Muscle

Copper in Crustaceans

The Cu concentration in the shrimp muscles varied between 32.42 and 80.87 µg g^{-1}. The highest and lowest concentration of Cu was recorded in *Penaeus merguiensis* (80.87 µg g^{-1}), and *Acetes indicus* (32.42 µg g^{-1}) respectively. The Cu concentration in the analyzed muscles of marine shrimp was in the order: *Penaeus merguiensis* > *Parapenaeopsis sculptilis* > *Litopenaeus vannamei* > *Harpiosquilla harpax* > *Acetes indicus*. The average Cu concentration of all the shrimp muscles was 54.98 µg g^{-1}. This value was higher than the reported values for marine shrimp muscles from the coastal waters of Peninsular Malaysia (0.80-24.00 µg g^{-1}), Ismail et al. (1995); Kochi coast, India (28.60-46.80 µg g^{-1}), George et al. (2011) but lower than the values reported in the *Penaeus merguiensis* from the Javanese coast, Indonesia (5-120 µg g^{-1}), Everaarts et al. (1989); and in the tiger prawns (*Penaeus monodon*) from Sabah, Malaysia (12.80-159 µg g^{-1}); Awaluddin et al. (1992).

Maximum Cu content in the three species of crabs analyzed was detected in the *Scylla serrata* followed by the *Portunus pelagicus* and *Portunus sanguinolentus*. The maximum Cu accumulation was in the gills followed by the walking legs and carapace muscle. The Cu concentration in all organs was in the range of 27.10 to 340 µg g^{-1}. When compared with the sex ratio, the female crab of the *Scylla serrata* species accumulated more Cu in their organs compared to male crabs. The average values of Cu in muscle (54.86µg g^{-1}) was less than the values reported from the *Portunus pelagicus* species from the Kuwait coast (123.80µg g^{-1}), Al-Mohanna and Subrahmanyam (2001); Mahanadi estuary, India, (117.20µg g^{-1}) Mohapatra et al. (2009); and the Pahang Malaysia (6.38 – 79.83µg g^{-1}), Kamaruzzaman et al. (2012).

Copper in Bivalve

The Cu concentration in *Polymesoda erosa* was in the range of 7.50 to 20.80 μg g^{-1}, with the decreasing order as gill > gonad > muscle. The Cu concentration in the bivalve *Polymesoda erosa* was lower (at 14.5 μg g^{-1}), compared to the values reported for the same species from Selangor and Johor in peninsular Malaysia (15.70 and 36 μg g^{-1}), Edward et al. (2009) but higher than the values reported for *Polymesoda erosa* muscle tissues from the west coast of Peninsular Malaysia (1.86 to 3.58 μg g^{-1}), Yap et al. (2014).

6.6.3.6 ***Zinc***

Zinc in Fishes

The Zinc concentration was the highest compared to all elements analysed in the different species of fishes. Its concentration in the different species of fish organs showed wide fluctuations, ranging from 16.90 to 301.00 μg g^{-1}. Among the species and the organs, the *Sphyraena qenie* liver had the highest concentration of Zn, and the lowest value was observed in the muscle of *Otolithes ruber*. The accumulation sequence of Zn in all the organs of the fish species is shown in Table 6.8 with a sequence of liver > gill > gonad > muscles, the same pattern in as *Scomberomorus lineolatus* and *Psettodes erumei*. The liver and gonads are the main target organs which accumulate higher Zn concentration compared to gills and muscle.

The Zn concentration in the analyzed fish muscles was recorded in the order of (highest to lowest) *Carcharhinus leucas* > *Sphyraena qenie* > *Setipinna tenuifilis* > *Trichiurus lepturus* > *Scomberomorus lineolatus* > *Psettodes erumei* > *Otolithes ruber*. The mean Zn concentration in the muscle tissues of fish species was 32.92 μg g^{-1}, which was similar to the average values reported from the Gulf of Cambay, India (38.54 μg g^{-1}), Reddy et al. (2007) but higher than the values reported from Peninsular Malaysia (2.30 – 6.50 μg g^{-1}), Babji et al. (1979); and Parangipettai, SE coast of India (0.10 – 0.80 μg g^{-1}), Lakshmanan et al. (2009). However, the observed average Zn in the fish muscles along the Miri coast was lower than the values reported for Zn in the marine fishes from Langkawi Island, Malaysia (49.39 μg g^{-1}), Irwandi and Farida (2009), Poompuhar coast, India (156.78 μg g^{-1}), Prasath and Khan (2008); and Malacca, Malaysia (49.39 μg g^{-1}), Alama et al. (2012).

Table 6.8 Accumulation of Zinc in the different organs of fish sp.

Fish Species	**Zn accumulation sequence**
Carcharhinus leucas	Gonad > Gill > Liver > Muscle
Scomberomorus lineolatus	Liver > Gill > Gonad > Muscle
Sphyraena qenie	Liver > Gonad > Gill > Muscle
Setipinna tenuifilis	Gonad > Gill > Muscle
Psettodes erumei	Liver > Gill > Gonad > Muscle
Trichiurus lepturus	Gill > Muscle
Otolithes ruber	Gonad > Muscle

Zinc in Crustaceans

The Zn concentration in the shrimp muscles varied between 62.43 and 203.00 µg g^{-1} with the highest concentration of (203.0 µg g^{-1}) in *Harpiosquilla harpax* and the lowest at (62.42 µg g^{-1}) in *Acetes indicus*. The average concentration of Zn in the muscles of marine shrimps in the present study was 114.56 µg g^{-1}. The Zn concentration was in the order (highest-lowest) of *Harpiosquilla harpax* > *Parapenaeopsis sculptilis* > *Penaeus merguiensis* > *Litopenaeus vannamei* >*Acetes indicus.* The Zn concentration in shrimp muscles was similar to the values reported from the coastal waters of Malaysia (68 to 186 µg g^{-1}), Patimah and Dainal (1993) and higher than the values reported from Peninsular Malaysia (5.00 – 16.00 µg g^{-1}), Ismail et al. (1995); Kenya coast (106.00 µg g^{-1}), Everaarts and Nieuwenhuize (1995); Gulf of Mexico (107.00 µg g^{-1}), Vazquez et al. (2001); Cochin coast, India (44.80 – 88.70 µg g^{-1}), George et al. (2011) and from the Indonesia coast (2.13 µg g^{-1}), Soegianto et al. (1999). However, the average value of Zn in the shrimp muscles along the Miri coast was lower than the average values reported from Sunderbans, India (1184.00 µg g^{-1}), Guhathakurta and Kaviraj (2000).

In the three species of crabs analyzed, the highest Zn concentration was noticed in the organs of *Scylla serrata* followed by *Portunus pelagicus* and *Portunus sanguinolentus*. The highest Zn accumulation was in the carapace muscles followed by the walking legs and gills. The distribution of Zn in different organs differed between the studied species. The Zn concentration (muscle and gill tissue) was in the range of 142.41 and 428.72 µg g^{-1}, which was lower than the values reported in the different body parts of *Scylla serrata* sp. from Pahang, Malaysia (325.39 – 523.21 µg g^{-1}), Kamaruzzaman et al. (2012). The observed values of Zn in the edible tissues of *Portunus pelagicus* was higher than the observed values reported in the same species from the Kuwait coast (206.00 µg g^{-1}), Al-Mohanna and Subrahmanyam (2001) and *Scylla serrata* species from the Mahanadi estuary, India (287.60 µg g^{-1}), Mohapatra et al. (2009).

Zinc in Bivalve

The Zn concentration in the organs of *Polymesoda erosa* was in the range of 160.50 to 435.01 µg g^{-1}. The highest accumulation was found in the gills followed by the gonads and muscle. Zinc in the muscle tissues of *Polymesoda erosa* from the Miri coast was lower compared to the same species from Selangor and Johor from Peninsular Malaysia (343.00 and 368.00 µg g^{-1}), Edward et al. (2009) but higher than the values reported from the west coast of Peninsular Malaysia (104.00 to 154.00 µg g^{-1}), Yap et al. (2014).

6.6.3.7 ***Rubidium***

Rubidium in Fish

The Rb concentration in the analyzed fish organs varied between 0.65 and 9.50 µg g^{-1}. Among the species and the organs, the maximum concentration was recorded in the muscle of *Carcharhinus leucas* (9.50 µg g^{-1}), and the lowest value was in the gills of *Scomberomorus lineolatus* (0.65 µg g^{-1}). The Rb accumulation was the highest in muscle, followed by the gonad, liver and gill (Table 6.9). The Rb concentration in the muscle was in the order (highest - lowest); *Carcharhinus leucas* > *Sphyraena qenie* > *Scomberomorus lineolatus*. In *Scomberomorus lineolatus* and *Sphyraena qenie* the accumulation pattern is in the same order as muscle > gonad > liver > gill. The concentration of Rb in fish muscle varied between 0.65 and 9.50 µg g^{-1} with an average value of 5.28 µg g^{-1}. These values were higher than the values reported for the muscles of five sturgeon species from the Caspian Sea (2.21 to 3.12 µg g^{-1}), Pourang et al. (2005); and the Jamaican coast (0.61 to 1.03 µg g^{-1}), Hoo Fung et al. (2013) but lower than the values reported from the Bay of Bengal, Bangladesh (3.28 to 27.85 µg g^{-1}), Sharif et al. (1991).

Table 6.9 Accumulation of Rubidium in the different organs of fish sp.

Fish Species	Rb accumulation sequence
Carcharhinus leucas	Muscle> Gonad > Gill > Liver
Scomberomorus lineolatus	Muscle > Gonad > Liver > Gill
Sphyraena qenie	Muscle > Gonad > Liver > Gill

Rubidium in Crustaceans

The Rb concentration in the shrimp muscles varied between 3.98 and 6.50 μg g^{-1} with an average of 4.64 μg g^{-1}. The highest concentration was in *Harpiosquilla harpax* and the lowest in *Acetes indicus*. Rb concentration in the muscle tissues was in the order (highest - lowest); *Harpiosquilla harpax* > *Litopenaeus vannamei* > *Parapenaeopsis sculptilis* > *Penaeus merguiensis* > *Acetes indicus.*

In the three species of crab analyzed, higher Rb concentration was noticed in the *Portunus pelagicus* followed by *Portunus sanguinolentus* and *Scylla serrata* with a range of 3.25 to 11.2 μg g^{-1}. The highest Rb is accumulated in the carapace tissues followed by the walking legs and gills of all the studied crabs. The average concentration of Rb in the analyzed edible tissues (carapace and walking legs) of crab species was 6.90 μg g^{-1}.

6.6.3.8 ***Cadmium***

Cadmium in Fish

The Cd concentration in the fish organs varied between 0.20 and 4.50 μg g^{-1} with an average of 1.17μg g^{-1}. Among the species and the organs studied, the liver of *Sphyraena qenie* showed the highest concentration (at 4.50 μg g^{-1}) with the lowest concentration detected in the muscle of *Scomberomorus lineolatus* (at 0.20 μg g^{-1}). The Cd accumulation sequence was same for *Scomberomorus lineolatus* and *Sphyraena qenie* with liver > gonad > gill > muscles. This differed for *Carcharhinus leucas*, which showed a sequence as; gonad > liver > gill > muscle (Table 6.10). The Cd concentration in the fish muscles was in the decreasing order of; *Psettodes erumei* > *Carcharhinus leucas* > *Trichiurus lepturus* > *Setipinna tenuifilis* > *Sphyraena qenie* > Otolithes *ruber* > *Scomberomorus lineolatus*. The mean Cd content for the muscles is 0.45 μg g^{-1}, which was similar to the values reported from the NE coast of India (0.41μg g^{-1}), Kumar et al. (2012) but lower than the value reported from the coastal fish of Langkawi Island, Malaysia (0.20 to 0.90 μg g^{-1}), Irwandi and Farida (2009) and the NE Mediterranean Sea (1.07 to 1.43 μg g^{-1}), Kalay et al. (1999). However, the average values of Cd in this study exceeded the values reported for fish from Peninsular Malaysia (0.03 – 0.05 μg g^{-1}), Babji et al. (1979).

Table 6.10 Accumulation of Cadmium in the different organs of fish sp.

Fish Species	Cd accumulation sequence
Carcharhinus leucas	Gonad > Gill > Muscle >Liver
Scomberomorus lineolatus	Liver > Gonad > Gill > Muscle
Sphyraena qenie	Liver > Gonad > Gill > Muscle
Setipinna tenuifilis	Gill > Gonad > Muscle
Psettodes erumei	Liver > Gill > Muscle > Gonad
Trichiurus lepturus	Muscle > Gill
Otolithes ruber	Gonad > Muscle

Cadmium in Crustaceans

The Cd concentration in the shrimp muscles varied between 0.12 and 2.10 μg g^{-1} with an average of 0.76 μg g^{-1} with the highest recorded in *Harpiosquilla harpax* (2.10 μg g^{-1}) and the lowest in *Penaeus merguiensis* (0.12 μg g^{-1}). The Cd concentration in the muscle tissues of marine shrimp was in the decreasing order of; *Harpiosquilla harpax* > *Acetes indicus* > *Parapenaeopsis sculptilis* > *Litopenaeus vannamei* > *Penaeus merguiensis* with the average Cd value comparable to *Penaeus monodon* sp from the brackish water of Sundarbans, India (0.74 μg g^{-1}), Guhathakurta and Kaviraj (2000) and lower than the values reported from Sabah, Malaysia (1.60 - 6.10 μg g^{-1}), Awaluddin et al. (1992); Kochi coast, India (3.60 - 9.60 μg g^{-1}), George et al. (2011), and the Javanese coast *Penaeus merguiensis* (0.60 – 13.90 μg g^{-1}), Everaarts et al. (1989) but higher than the values reported from the Malacca Strait of Malaysia for *Penaeus merguiensis* (0.10 μg g^{-1}), Alama et al. (2012) and from the Indonesian coast (0.002 μg g^{-1}), Soegianto and Supriyanto (2008).

In three species of crab, the higher Cd concentration was in the organs of *Portunus sanguinolentus* followed by *Portunus pelagicus* and *Scylla serrata*. The highest concentration was in the carapace muscle followed by the walking legs of *Portunus* *sanguinolentus* and *Portunus pelagicus* sp. whereas in the *Scylla serrata* sp. Cadium accumulated more in the gills. The Cd concentration in all the organs of crab species varied between 0.25 and 0.80 μg g^{-1} with an average of 0.50 μg g^{-1}, which was comparable to the values reported for *Scylla serrata* sp from Pahang, Malaysia (0.05 – 0.78 μg g^{-1}), Kamaruzzaman et al. (2012).

Cadmium in Bivalve

The Cd concentration in *Polymesoda erosa* was in the range of 0.25 to 0.45 μg g^{-1} with the highest accumulation in the gills followed by the gonads, with the lowest level observed in muscle. The Cd concentration in the *Polymesoda erosa* muscle from the Miri coast was low, compared with the levels reported for the same species from Selangor and Johor in Peninsular Malaysia (2.96 and 3.59 μg g^{-1}), Edward et al. (2009) and also from the west coast of Peninsular Malaysia (0.70 to 1.79 μg g^{-1}), Yap et al. (2014).

6.6.3.9 ***Lead***

Lead in fish

The Pb concentration in the fish organs varied between 0.57 and 20 μg g^{-1} with an average value of 3.89 μg g^{-1}. Among the species and the organs, the highest and lowest concentration of Pb was detected in the liver of *Carcharhinus leucas* (20.00 μg g^{-1}), and the gonads of *Psettodes erumei* (0.57 μg g^{-1}) respectively. In most of the fish species, the Pb accumulation (Table 6.11) was in the gills followed by liver, gonad and muscle with the exception of *Carcharhinus leucas* and *Sphyraena qenie*, which showed the highest concentration in the liver. In the case of *Otolithes ruber*, the highest accumulation was in the gonads, followed by muscle. The Pb concentration in the fish muscle was in this decreasing order; *Setipinna tenuifilis* > *Carcharhinus leucas* > *Sphyraena qenie* > *Psettodes erumei* > *Scomberomorus lineolatus* > *Otolithes ruber* > *Trichiurus lepturus*. The concentration of Pb in fish muscle varied between 0.60 and 2.60 μg g^{-1} with an average of 1.81 μg g^{-1}. These values were higher than those observed for the coastal fish from Peninsular Malaysia (0.21 - 0.32 μg g^{-1}), Babji et al. (1979); Langkawi Islands, Malaysia (0.80 to 1.00 μg g^{-1}), Irwandi and Farida (2009); and the Parangipettai coast, South India (0.06 – 1.57 μg g^{-1}), Lakshmanan et al. (2009) but lower than those values for the coastal fish from the Red Sea (4.80 μg g^{-1}), Ismail and Abu-Hilal (2008) and the Mediterranean Sea (4.70 μg g^{-1}), Abdallah (2008). The values obtained in this study were comparable with those found on the edible fishes from the coastal region of Kalpakkam, India (0.40 – 2.29 μg g^{-1}), Biswas et al. (2012).

Table 6.11 Accumulation of Lead in the different organs of fish sp.

Fish Species	Pb accumulation sequence
Carcharhinus leucas	Liver > Gill > Gonad > Muscle
Scomberomorus lineolatus	Gill > Gonad > Muscle > Liver
Sphyraena qenie	Liver > Gonad > Gill > Muscle
Setipinna tenuifilis	Gill> Muscle > Gonad
Psettodes erumei	Gill > Muscle > Liver > Gonad
Trichiurus lepturus	Gill > Muscle
Otolithes ruber	Gonad > Muscle

Lead in Crustaceans

The Pb concentration in the shrimp muscles varied between 1.64 (in *Parapenaeopsis sculptilis*) and 7.25 μg g^{-1} (in *Acetes indicus*) with an average value of 3.48 μg g^{-1}. The Pb concentration in the muscles of marine shrimps were in the decreasing order of; *Acetes indicus* > *Litopenaeus vannamei* > *Penaeus merguiensis* > *Harpiosquilla harpax* > *Parapenaeopsis sculptilis*. The Pb concentration in the muscle tissues of shrimp from the Miri coast was higher than those observed ranges in marine shrimp collected from other coastal waters of Malaysia (0.06 – 5.90 μg g^{-1}), Ismail et al. (1995); and the Cochin coast of India (0.60 – 1.90 μg g^{-1}), George et al. (2011) but lower than the values reported from Peninsular Malaysia (1.68 to 54.00 μg g^{-1}), Patimah and Dainal (1993); Sabah, Malaysia (4.60 – 32.00 μg g^{-1}), Awaluddin et al. (1992) and the Indonesian coast (*Penaeus merguiensis;* 0.02 μg g^{-1}), Soegianto and Supriyanto (2008).

In the three species of crab, a higher Pb concentration was in *Scylla serrata* followed by *Portunus pelagicus* and *Portunus sanguinolentus*. The highest Pb concentration was in the gills followed by the walking legs and carapace muscle. The Pb concentration of all the organs was in the range of 1.9 and 16.7 μg g^{-1} with an average of 3.48 μg g^{-1}. Maximum and minimum Pb concentrations were observed in the gills and carapace muscle tissues of *Scylla serrata* species. The accumulation of Pb in the female crab (*Scylla serrata*) was greater than of the male. The mean Pb content in the edible tissues of the three different species of crabs was in the range of 1.90 to 4.10 μg g^{-1} with an average of 2.78 μg g^{-1}. These values were higher than the values reported for *Portunus pelagicus* from the Kuwait coast (1.90 μg g^{-1}), Al-Mohanna and Subrahmanyam (2001) and in *Scylla serrata* sp from the Mandovi river estuary, India (0.22 μg g^{-1}), Mohapatra et al. (2009) but lower than values reported for *Scylla serrata* sp from Malaysia (1.49 – 7.84 μg g^{-1}), Kamaruzzaman et al. (2012).

Lead in Bivalve

The Pb concentration in *Polymesoda erosa* was in the range of 2.30 to 4.25 μg g^{-1} with an average of 3.30 μg g^{-1}. The highest accumulation was in the gills, followed by the gonads and the lowest level was in muscle. The Pb concentration in the muscle tissues of *Polymesoda erosa* from the Miri coast was lower than the values reported for the same species from Selangor and Johor in Peninsular Malaysia (6.80 and 17.20 μg g^{-1}), Edward et al. (2009) and from the west coast of Peninsular Malaysia (1.89 to 3.41 μg g^{-1}), Yap et al. (2014).

6.7 Discussion

6.7.1 Element/metal concentrations in fish tissues

It was clearly observed in the present study, the accumulation of trace/heavy metals in the tissue organs of demersal fish was higher than pelagic fishes. This may be related to the direct contact with element/metal enriched seafloor sediments, feeding mechanisms and the greater uptake of trace/heavy metal concentrations from zoobenthic predators and the elemental/metal interaction with benthic organisms (Campbell 1988; Yi and Zhang 2012). Metal absorption in aquatic organisms was facilitated by two routes: the digestive tract (dietary exposure via the food chain) and through the gill surface by waterborne exposure (Ptashynski et al. 2002). The concentrations of trace/heavy metals in the fish species studied were in the ranges of Cu, 8.50 to 65.50 μg g^{-1}; Pb, 0.57 to 20.00 μg g^{-1}; Cd, 0.20 to 4.50 μg g^{-1}; Mn, 0.40 to 32.75 μg g^{-1}; Co, BDL to 9.20 μg g^{-1}; Ni, 0.85 to 13.60 μg g^{-1}; Rb, 0.65 to 9.50 μg g^{-1}; Zn, 16.90 to 301.00 μg g^{-1}; and Cr, 1.20 to 7.30

μg g^{-1}. The order of trace/heavy metal accumulation in the different organs of fish species is shown in Table 6.12.

Table 6.12 Trace/heavy metal accumulation in different organs of the analysed fish sp.

Species	Tissue	Order
Carcharhinus leucas	Muscle	Zn > Cu> Rb > Co > Cr > Ni > Pb > Cd > Mn
	Gill	Zn > Cu > Ni > Mn > Co > Cr > Rb > Pb > Cd
	Liver	Zn > Cu > Pb > Co > Mn > Cr > Ni > Rb > Cd
	Gonad	Zn > Cu > Co > Cr > Mn > Rb > Ni > Pb > Cd
Scomberomorus lineolatus	Muscle	Zn > Cu > Cr > Rb > Pb > Ni > Co > Mn > Cd
	Gill	Zn > Mn > Cu > Cr > Pb > Ni > Co > Rb > Cd
	Liver	Zn > Cu > Mn > Cr > Cd > Rb > Pb > Ni > Co
	Gonad	Zn > Cu > Mn > Rb > Cr> Cd > Pb > Ni > Co
Sphyraena qenie	Muscle	Zn > Cu > Rb > Pb > Cr > Mn > Ni > Cd > Co
	Gill	Zn > Mn > Cu > Pb > Cr > Ni > Co > Rb > Cd
	Liver	Zn > Cu > Mn > Cd > Rb > Cr > Ni > Pb > Co
	Gonad	Zn > Cu > Mn > Cr > Rb > Pb > Ni > Cd > Co
Setipinna tenuifilis	Muscle	Zn > Cu > Mn > Pb > Cd
	Gill	Zn > Mn > Cu > Pb > Cd
	Gonad	Zn > Cu > Mn > Pb > Cd
Psettodes erumei	Muscle	Zn > Cu > Mn > Pb > Cd
	Gill	Zn > Mn > Cu > Pb > Cd
	Liver	Zn > Cu > Mn > Cd > Pb
	Gonad	Zn > Cu > Mn > Pb > Cd
Trichiurus lepturus	Muscle	Zn > Cu > Mn > Pb > Cd
	Gill	Zn > Cu > Mn > Pb > Cd
Otolithes ruber	Muscle	Zn > Cu > Pb > Mn > Cd
	Gonad	Zn > Cu > Mn > Pb > Cd

The minimum values were observed in the muscles for Cu, Pb, Cd, Mn, Co, Ni, Zn and Cr with the exception of Rb, which was observed in the gills whilst the maximum values were recorded in the livers for Cu, Cd and Zn, and in the gills for Mn, Cr, Co, Ni and Pb. Zinc and Cu are essential elements for normal metabolic activities, so their accumulation was found to be higher in all the organs of the analyzed aquatic organisms. *Carcharhinus leucas* alone showed the maximum concentration of Co in the gonads and Pb in the liver, which was consistent with findings from the Red Sea, Egypt (El-Moselhy et al. 2014).

From the results, it was clearly observed most of the analyzed elements/metals accumulated in the liver followed by the gills, gonads and muscle. The essential elements Zn and Cu were higher in all the analyzed organs of fish and other aquatic organisms in this study. The element/metal absorption rate varied between the body parts of the fish (muscles, liver, gills and gonads) and is dependent on bioaccumulation, physiology and the feeding habits of the fish (Canli and Atli 2003). Elements/metals choose their body part (organs) depending on their metabolic activity (Ebrahimi-Yazdanabad et al. 2014). Among the different organs of fish, the liver acts as a primary organ for metal storage (Roesijadi 1996; Amiard et al. 2006). The liver plays an important role in the metabolic processes of trace/heavy metals in fish and is related to the natural binding of proteins such as metallothioneins (MT) (Görür et al. 2012). In this case, the liver accumulates more elements/metal than the muscle since it has higher metabolic activity, and it also has a specific function accumulating and transporting elements/metals in the body (Fernandes et al. 2007). The liver also plays a part in detoxification (Filazi et al. 2003; Staniskiene et al. 2006; Pakzad 2013).

Zinc and Cu are essential for the normal growth of aquatic organisms and their enzymatic reactions (Heath 1995; Erdoğrul and Ateş 2006). A higher accumulation of Cu and Zn in the liver indicates these elements have a role in cellular metabolism, where Zn is required for bile secretion (Roesijadi 1996). The Cu and Zn in the liver are necessary in order to fulfill enzymatic and other metabolic demands in organisms together with MT protein (Amiard et al. 2006). The higher concentration of non-essential elements such as Cd was present in the liver tissues of *Scomberomorus lineolatus, Sphyraena qenie* and *Psettodes erumei* as well as Pb in the liver tissues of *Carcharhinus leucas*. The presence of MT proteins in the hepatic tissue has a greater tendency to bind with Cu, Zn and Cd. Most of the studies (Honda et al. 1983; Hernández-Hernández et al. 1990; Adhikari et al. 2009; Irwandi and Farida 2009; Malik et al. 2010; Ebrahimpour et al. 2011; Zhao et al. 2012; Bashir et al. 2013; El-Moselhy et al. 2014) reported accumulation of essential and non-essential metals have occurred more often in the liver followed by the gills, gonads and muscle.

The concentration of metals in the surrounding water is reflected by the gills because the gills have direct contact with the water and suspended materials therein during the respiration process. Due to the process of osmoregulation and gas exchange, the gills act as a barrier to the metal ion exchange from water (Qadir and Malik 2011). Therefore, it is clear metals stored in the gill tissues are gathered mainly from the surrounding water of a particular environment. In addition, the size of the gills in different fish species also controls the level of metal accumulation and levels of metal are higher in larger gilled organisms.

Higher concentrations of Pb and Mn accumulate in the gills, as compared to the other organs. Apart from *Carcharhinus leucas*, the other fish species *Scomberomorus lineolatus, Sphyraena qenie, Setipinna tenuifilis, Psettodes erumei* and *Trichiurus lepturus* had the highest concentration of Pb and Mn in their gills. Similar results of higher accumulation of Pb and Mn in the gill tissues were recorded by several authors (Ismail and Abu-Hilal 2008; Bashir et al. 2013; El-Moselhy et al. 2014). An increase in the Pb and Mn concentration in the water column was due to the diffusion of dissolved/particulate forms of Mn and Pb from several sources such as atmospheric deposition, river runoff and small stream discharges from industrial and plantation sites which then mixes directly with the water and settles to the sea bottom mixing with the original sediments because of oxidative precipitation, where it again re-dissolves due to the reducing condition in the sediments and the high water energy flow from the freshwater contribution. So this is the reason for the enrichment of Mn and Pb along the coast of the study area. A large amount of oxide surfaces for element/metals in the water column are produced due to the rapid cycling of Mn between the oxidative precipitation and reductive dissolution cycles. These oxide surfaces have a high scavenging affinity for manganese oxide surfaces such as Pb (Paulson et al. 1988).

6.7.2 Fish size vs trace/heavy metal accumulation

The body size of the aquatic organisms play an important role in the bioaccumulation of trace/heavy metals. Larger animals accumulate more elements/ metals compared to a smaller size animal, because most of the element/metal accumulation occurs through biomagnification and within the process of the food chain (Beijer and Jernelov 1986). Inter-element correlations between the size (length and weight) and the elements/metals abundance are important because they play a vital role in determining the accumulation of these elements/metals in the muscles and other organs such as the gonads and liver. Due to the lack of elemental analyses, i.e. Co, Ni, Rb and Cr in all the fish species, the remaining elements i.e. Cu, Pb, Cd, Mn and Zn were considered in the inter-elemental correlation for the muscles of seven fish species (Table 6.13). These were assessed by means of the Pearson's correlation coefficients (Rejomon et al. 2010; Merciai et al. 2014)

6.7.3 Inter-elemental relationship in fishes

It is interesting to note the essential elements (Cu and Zn) and the non-essential element (Pb) showed a significant positive correlation with fish size Cu ($r=0.830$, $p < 0.01$); Zn ($r=0.719$, $p < 0.05$) whilst non-essential metals, Cd and Pb did not show any significant correlation with size, however showed a positive relationship between them ($r=1.000$; $p < 0.001$). Many mechanisms can explain the existence of a negative correlation between the fish size and metal concentration; (i.e.) the tissue grows more rapidly than the element/metal intake and/or the relative dilution effect of the lipid content of tissues (Farkas et al. 2003). Thus, the net accumulation of element/metal in an organism depends on the uptake rate and depuration (Canli and Atli 2003). It has been shown that interspecific differences in the metal burden of fish tissues are directly related to the variation in the diet of fishes (Monikh et al. 2013).

Inter-elemental correlation between the size and nine elemental variables were assessed by means of the Pearson's correlation coefficients in the muscles of three fish species (*Carcharhinus leucas, Scomberomorus lineolatus and Sphyraena qenie*) (^{a} $P < 0.01$; ^{b} $P < 0.05$ Table 6.14). With the exception of Cr, the other metals showed significant positive correlations with fish size. Manganese alone showed a strong negative relationship with size. The associations between the various elements noted in the same tissue of fish, may result from similar accumulation behavior of trace elements in fish and their interactions (Kojadinovic et al. 2007). The significant associations between the elements may indicate a common source of origin and its accumulation in the coastal fish.

The strong correlations between essential (Cu *vs* Zn) and non-essential metals (Cd *vs* Pb) in the muscle tissues indicates similar biogeochemical pathways are utilized to allow these particular elements/metals to accumulate in fish. Copper and Zn showed a strong relationship with the toxic elements of Cd and Pb, whereas the strong negative correlation between fish size and Mn suggests concentrations were largely determined by the metabolic process, dietary habitats and swimming behavior of different species. Many authors (Garcia-Montelongo 1994; Pourang et al. 2005; Rejomon et al. 2010; Agah et al. 2010; Rajkowska and Protasowicki 2013; Jonathan et al. 2015) have reported the similar inter-elemental relationships between essential and non-essential elements in the muscles of fish globally.

Generally, elemental correlations are dependent on natural surface coatings, where the main components are Fe and Mn oxides in the water column, which plays important roles in different life cycles due to their specific characteristics of absorption (Dong et al. 2001). The scavenging effect of absorption is supported by the positive association between Mn, Pb and Cd in the muscle tissue (Dong et al. 2001; Arain et al. 2008). Dissolved and particulate forms of trace/heavy metals in the water column are associated with oxide surfaces and enter into aquatic organisms through the gills in addition to the process of the food chain. The enrichment of metals such as Cu, Zn, Pb, Cd and Mn in sediments and water was observed.

Table 6.13 Pearson's Correlation Matrix between trace metals and fish size in seven fish species (n=70) from the Miri coast

	Length	**Weight**	**Cu**	**Pb**	**Cd**	**Zn**	**Mn**
Length	1.000						
Weight	**.880** [a]	1.000					
Cu	**.830** [a]	**.666** [b]	1.000				
Pb	-.046	.236	.148	1.000			
Cd	-.046	.236	.148	**1.000** [a]	1.000		
Zn	**.719** [b]	**.916** [a]	.561	.233	.233	1.000	
Mn	**-.782** [b]	-.631	-.381	.506	.506	-.461	1.000

[a] $P < 0.01$; [b] $P < 0.05$

Table 6.14 Pearson's Correlation Matrix between nine variables and fish size for three fish species (n=30) from the Miri coast

	Length	**Weight**	**Cu**	**Pb**	**Cd**	**Zn**	**Mn**	**Co**	**Ni**	**Cr**	**Rb**
Length	1.000										
Weight	**.998**	1.000									
Cu	**.999**	**.995**	1.000								
Pb	**.953**	**.971**	**.942**	1.000							
Cd	**.953**	**.971**	**.942**	**1.000**	1.000						
Zn	**.924**	**.948**	**.910**	**.996**	**.996**	1.000					
Mn	**-.828**	**-.789**	**-.847**	-.619	-.619	-.551	1.000				
Co	**.990**	**.979**	**.994**	**.901**	**.901**	**.861**	**-.898**	1.000			
Ni	**.983**	**.969**	**.989**	**.881**	**.881**	**.838**	**-.917**	**.999**	1.000		
Cr	.448	.387	.479	.156	.156	.072	**-.872**	.569	.605	1.000	
Rb	**1.000**	**.998**	**.999**	**.954**	**.954**	**.925**	**-.826**	**.990**	**.982**	.445	1.000

Highlighted values are having P value (< 0.05)

6.7.4 Metal concentrations in the Crustaceans

The concentration of elements/metals in muscles for all of the shrimp species was found to be in the range of; Cu, 31.15 to 80.87 μg g^{-1}; Cd, 0.12 to 2.10 μg g^{-1}; Pb, 1.64 to 9.00 μg g^{-1}; Zn, 54.00 to 203 μg g^{-1}; Mn, 4.10 to 51.36 μg g^{-1}; Co, 1.20 to 4.70 μg g^{-1}; Ni, 1.55 to 13.65 μg g^{-1}; Rb 3.97 to 6.50 μg g^{-1} and Cr, 2.55 to 15.10 μg g^{-1}. Table 6.15 presents the order of element/metal accumulation in the muscles of shrimp.

Table 6.15 Trace/heavy metal accumulation in the muscle tissues of Shrimp Sp.

Species	Order
Parapenaeopsis sculptilis	Zn>Cu>Mn>Rb>Cr>Pb>Ni>Co>Cd
Litopenaeus vannamei	Zn>Cu>Mn>Rb>Cr>Pb>Ni>Co>Cd
Penaeus merguiensis	Zn>Cu>Mn>Rb> Pb>Cr>Ni>Co>Cd
Harpiosquilla harpax	Zn>Cu>Mn>Rb> Co>Cr>Ni>Pb>Cd
Acetes indicus	Zn>Cu>Mn>Rb>Cr>Ni >Pb>Co>Cd

The concentration of elements/metals in all the tissues (carapace, walking leg and gill) of the crab species studied was in the range of; Cu, 27.10 to 340.00 μg g^{-1}; Cd, 0.25 to 0.80 μg g^{-1}; Pb, 1.90 to 16.70 μg g^{-1}; Zn, 142.40 to 428.70 μg g^{-1}; Mn, 1.25 to 53.55 μg g^{-1}; Co, 0.75 to 6.80 μg g^{-1}; Ni, 0.65 to 5.65 μg g^{-1}; Rb 3.25 to 11.20 μg g^{-1} and Cr 0.03 to 12.90 μg g^{-1}. Table 6.16 presents the order of element/metal accumulation in the different organs (carapace, walking legs and gill) of crab. The minimum concentration of Cu, Pb, Zn, Mn, Co, Ni and Cr was recorded in the carapace muscle (edible part) and Cd and Rb concentrations were recorded in the walking leg and gill tissues. While maximum values of Cu, Pb, Mn, Ni and Cr were recorded in the gills, Cd, Zn and Rb in the carapace tissues and Co in the walking legs.

Table 6.16 Trace/heavy metal accumulation in different organs of the crab sp.

Species	Tissue	Order
Portunus sanguinolentus	Carapace	Zn > Cu > Rb > Cr > Mn > Pb > Ni > Cd > Co
	Walking Leg	Zn > Cu > Rb > Pb > Cr > Mn > Ni > Co > Cd
Portunus pelagicus	Carapace	Zn > Cu > Rb > Mn > Cr > Pb > Co > Ni > Cd
	Walking Leg	Zn > Cu > Mn > Rb > Cr > Co > Pb > Ni > Cd
Scylla serrate Male	Carapace	Zn > Cu > Rb > Cr > Pb > Co > Mn > Ni > Cd
	Walking Leg	Zn > Cu > Rb > Cr > Mn > Ni > Pb > Co > Cd
	Gill	Zn > Cu > Mn > Cr > Pb > Ni > Co > Rb > Cd
Scylla serrate Female	Carapace	Zn > Cu > Rb > Pb > Co > Ni > Mn > Cd > Cr
	Walking Leg	Zn > Cu > Rb > Cr > Ni > Pb > Mn > Co > Cd
	Gill	Zn > Cu > Mn > Pb > Cr > Ni > Co > Rb > Cd

6.7.5 Variations of elements/metals in different tissue organs of shrimp

For environmental monitoring studies the use of marine shrimp and crabs as bio indicators has been emphasized by several investigators (Ismail et al. 1995; Krishnamurti and Nair 1999; Al-Mohanna and Subrahmanyam 2001; Mohapatra et al. 2009; George et al. 2011; Kamaruzzaman et al. 2012; Rahouma et al. 2012; Hosseini et al. 2014). Crustaceans accumulate metals via two routes; either via, hepatopancreas during feeding or through the gills during respiration. Hepatopancreas plays an important role in the uptake, detoxification and expulsion of metals in crustaceans (Barrento et al. 2009). Element/metal concentration is more predominant in hepatopancreas compared to muscle tissues because of higher metabolic activity in the hepatopancreas tissues. In general, crustaceans accumulate elements/metals directly proportional to the increment in the bioavailability from water and from the food chain (Viswanathan et al. 2013). Many decapods can effectively regulate crustacean’s tissue and body burdens of trace/heavy metals (Rainbow and white, 1989). One of the main regulatory mechanisms is that of molting. It is an excretory mechanism and substantial quantities of elements/metals may be expelled by the molted carapace. Shrimp are considered a vector for transferring the toxic metals to the top level predators in the food chain.

In crabs, a high level of metal concentration is observed in the gill tissues followed by walking legs and carapace muscles. The high content of Cu present in the gills may be because Cu is a component of haemocyanin, a respiratory pigment which takes place in the gills. Similarly, Zn is essential for the synthesis of protein in crabs and the Zn uptake increases during molting. The enrichment of elements such as Cu, Zn, Pb, Mn, Co, Ni and Cr in the gills of crab is because the gills are in direct contact with the surrounding water that can account for the highest content of Cu and Zn and other elements.

6.7.6 The accumulation of elements/metals in crabs by gender

A sex-specific difference in the metal uptake by crabs was also observed in the present study. The female crab of the *Scylla serrata* species accumulates higher levels of elements/metals compared to the male. The variations in accumulation between gender are due to differences in food consumption and/or feeding habits (Beckvar 1996). The male crab mostly feeds on bivalves and fish, whereas the females feed on shrimp, plant root and debris (Williams 1981). Plant roots have an ability to depurate water and sediments carried by tidal waves. This ability prevents the entry of salt particles to the buds, and as such allows accumulation of heavy metals in their cell walls and roots (Bernini et al. 2006). This may explain the higher accumulation of metals in the female crab as they feed predominantly on shrimp and plant roots as opposed to the male. In addition, female crabs are larger than the male in size and they eat more in order to meet the demands of reproduction (Beckvar et al. 1996; Gewurtz et al. 2011). Hosseini et al. (2014) observed similar findings of higher metal concentrations in the female crab (*Portunus segnis)* compared to male because of the feeding behavior.

It is difficult to compare the element/metal concentrations in the same types of tissues in two different species because of several factors, such as their habitat, size, age, feeding nature, physiological tolerance and metabolic reactions (Pourang 1995). The accumulation of trace/heavy metals in the different tissues of aquatic organisms is related to the time of exposure and the concentration of elements/metals in an environment. The *Portunus pelagicus* (Blue swimming crab) which belongs to the *Portunidae* family, showed the highest concentration of Co, Ni, Rb, Cr, Mn and Pb compared to the other species of crabs and this may be related to the feeding habits of this species. *Portunus pelagicus* is *carnivorous* and feeds on slow-moving benthic invertebrates and organic debris. Zinc and Cu are essential elements and are recorded higher in all the organs of crabs. Zinc is essential for protein synthesis and its uptake increases during the molting time (Engel and Brouwer 1987). The high content of Cu in crabs can be explained by its enrichment in the haemolymph which is involved in oxygen transport through its body (Rainbow et al. 2000).

It was observed the Cu and Zn concentration in the sediments of Miri coast exceeded the Upper Continental Crust (McLennan 2001) values (Cu = 25; Zn = 71 µg g^{-1}). Cu and Zn are enriched in sediments and water, which may explain the higher concentrations of Cu and Zn in the gills of the crustaceans, because it enters the body through the process of respiration. Crabs and shrimps are bottom feeders and are generally expected to contain a higher concentration of metals than mobile fish (Ololade et al. 2008). The relationship between trace/heavy metal concentrations in crustaceans and their feeding habits is well established i.e. the Penaeid shrimp; Scelzo (1997). The enrichment of Pb can be attributed to nearby oil extraction operations and atmospheric input from the urban and industrial area and from local forest fire, which are common in Borneo due to their volatile nature. Hosseini et al. (2014) observed an increase in concentrations of Pb, Ni, Co and Cd in the blue crab (*Portunus segnis*) from the Persian Gulf and determined this was due to the petrochemical activities, and the industrial and domestic effluents from the nearby cities.

A higher level of element/metal content in crustaceans was observed in the hepatopancreas tissues compared to other organs. This may be due to the presence of metallothionein protein in hepatopancreas tissue (Dunn et al. 1987). This protein plays an important role in the regulation and detoxification of metals present in this tissue. Metallothionein proteins contain a high percentage of amino acids, nitrogen and sulphur which sequester metals in stable complexes (Hamilton and Mehrle 1986; Roesijadi 1992). In general, the greater accumulation of metals in the hepatopancreas tissue is more likely due to the presence of MT proteins compared to the muscle and gill tissues. In the present study, three tissue organs in the crab were considered, with the metal accumulation greater in the gill tissue followed by the walking legs and carapace muscle tissues.

The possible association between the elements in the muscles of five shrimp species was assessed using Pearson's correlation coefficient (Table 6.17). The essential elements, such as Cu and Mn show a positive relationship with the length, but Zn however, showed a positive correlation with the weight of the shrimp species. The non-essential elements, such as Pb, Ni and Cr showed a significant correlation with the size (length and weight) and this indicates the accumulation of these elements relay was determined by the body size of the shrimp.

Compared to shrimp size (length and weight) and inter-elemental correlation; most of the elements/metals such as Pb ($r = -0.975$; $p < 0.01$), Ni ($r = -0.971$; $p < 0.01$) and Cr ($r = -0.970$; $p < 0.01$) showed a significant negative correlation with the shrimp length. Lead showed a significant negative correlation with weight ($r = -0.886$, $p < 0.05$). Copper showed a strong positive correlation with Mn ($r = 0.961$; $p < 0.01$) and a negative correlation with Cd ($r = -0.758$; $p < 0.05$ respectively). Similar to the behavior of Pb, Cd showed significant negative correlation with Mn ($r = -0.885$; $p < 0.05$) and had a positive correlation with Co ($r = 0.992$; $p < 0.01$). Zinc and Co showed a strong positive correlation with Rb ($r = 0.854$; $r = 0.785$; $p < 0.05$) indicating their association with the fine clay particles within sediments. Manganese showed a strong to moderate negative correlation with Co and Ni ($r = -0.889, -0.791$; $p < 0.05$ respectively). Nickel showed a strong positive correlation with Cr ($r = 0.982$; $p < 0.01$). Similar observations between the essential and non-essential metals are reported by George et al. (2011) in marine shrimp from the southwest coast of India.

The significant correlations between most of the elements in the muscles may reflect a common source (i.e. sediments in this region), and similar accumulation behavior and interactions in the Miri coastal area. A comparable biogeochemical process has been shown to be responsible for the association of essential and non-essential heavy metals in the muscle tissues of shrimp (Pourang et al. 2004; George et al. 2011). Pourang et al. (2005) observed similar elemental interactions in the muscle tissue of fish and shrimp from the Persian Gulf. Lead showed a significant negative correlation with Zn ($r = -0.590$, $p < 0.05$) and Mn ($r = -0.690$; $p < 0.05$) and a high positive correlation with Ni ($r = 0.940$; $p < 0.01$) and Cr (0.962; $p < 0.01$).

Table 6.17 Pearson's Correlation Matrix between size (length and weight) and elements in shrimp muscles (n=50)

	Length	**Weight**	**Cu**	**Pb**	**Cd**	**Zn**	**Mn**	**Co**	**Ni**	**Cr**	**Rb**
Length	1.000										
Weight	**.856**[b]	1.000									
Cu	.736	.406	1.000								
Pb	**-.975**[a]	**-.886**[b]	-.603	1.000							
Cd	-.479	-.047	-.785	.297	1.000						
Zn	.436	.734	-.043	-.590	.569	1.000					
Mn	.763	.434	**.961**[a]	-.607	**-.885**[b]	-.155	1.000				
Co	-.476	-.088	-.772	.283	**.992**[a]	.565	**-.889**[b]	1.000			
Ni	**-.971**[a]	-.719	-.759	**.940**[a]	.591	-.287	-.791	.565	1.000		
Cr	**-.970**[a]	-.749	-.758	**.962**[a]	.480	-.419	-.741	.447	**.982**[a]	1.000	
Rb	.126	.422	-.459	-.339	.762	**.854**[b]	-.534	.785	-.047	-.151	1.000

[a] $P < 0.01$; [b] $P < 0.05$

6.7.7 Metal concentrations in Bivalves

The total concentration of elements/metals in the bivalve (*Polymesoda erosa*) was in the range of: Cu, 7.50 to 20.80 μg g^{-1}; Cd, 0.25 to 0.45 μg g^{-1}; Pb, 2.30 to 4.25 μg g^{-1}; Zn, 160.50 to 435.00 μg g^{-1}; Mn, 41.70 to 51.95 μg g^{-1}; Co, 2.05 to 4.15 μg g^{-1}; Ni, 10.25 to 12.20 μg g^{-1} and Cr, 14.25 to 16.60 μg g^{-1}. Among the analyzed elements/metals, the maximum concentration of Cu, Cd, Pb, Zn, Co and Ni was observed in the gills and Mn and Cr observed in the gonads. All the elements in the muscles were lower compared with other organs. The accumulation of elements/metals in the organs of *Polymesoda erosa* was in the order; gill > gonad > foot muscle. Table 6.18 represents the order of element/metal accumulation in the different organs of *Polymesoda erosa*.

Table 6.18 Trace/heavy metals accumulation in Polymesoda erosa

Species	Tissue	Order
Polymesoda erosa	Foot Muscle	Zn > Mn > Cr > Ni > Cu > Pb > Co > Cd
	Gill	Zn > Mn > Cu > Cr > Ni > Pb > Co > Cd
	Gonad	Zn > Mn > Cr > Cu > Ni > Pb > Co > Cd

6.7.7.1 Metal accumulation in Bivalve tissues

Marine mussels offer a cheap source of protein for human consumption. *Polymesoda erosa* is a bivalve species, which is one of the sessile, benthic filter feeding organisms, commonly present in the estuarine and coastal regions of the Miri coast. Because of its sessile nature, they have a tendency to accumulate larger quantities of trace elements/metals in their body tissues. This species is commonly consumed by humans and is widely utilized as an in situ biomarker in assessing the bioavailability of toxic metal contamination in estuarine and coastal systems (Edward et al. 2009; Gawade et al. 2013; Yap et al. 2014).

The gills of *Polymesoda erosa* accumulate higher concentrations of elements/metals due to the filter feeding habits of bivalves. Zinc concentration was higher in all the organs compared to the other elements/metals. Essential elements are accumulated in higher concentrations in all the organs, whereas non-essential elements (Pb and Cd) are observed to be lower in the edible tissues. The distribution of elements/metals in different organs of bivalves is believed to be related to cellular processes participating in the metal metabolisms (Marigomez et al. 2002). Another possibility is the differences in the affinities of elements/metals to bind to metallothionein in the different organs. Here they are incorporated into lysosomes and thereafter being eliminated by the circulating hemocytes and blood plasma (Roesijadi 1981). Due to the mechanism of internal metal handling, there is a difference in the accumulation and excretion of the metals. This may account for the high or low distribution of elements/metals in different organs of bivalves (Gundacker 1999).

6.7.8 Human Health Risk Assessment

A human health risk assessment was conducted according to the United States Environmental Protection Agency (USEPA 2009) methods. The level of exposure resulting from oral human consumption of particular trace/heavy metals in the fish edible tissues is expressed by calculating the average daily dose (ADD; average daily intake of a specific chemical over a lifetime) has been calculated using the following equation

$$ADD\ (mg/kg/day) = \frac{Cm * IR * EF * ED}{BW * AT}$$

Where, C_m is the mean concentration of element/metal in fish muscle (mg/kg dry wt.), IR is the rate of ingestion (0.0312 kg/day for normal and 0.1424 kg/day for habitual fish consumers), EF is the exposure frequency (365 days/year), ED is the exposure duration over a lifetime (assumed as 70 years), BW is the body weight (assumed as 70 kg for normal adults), and AT is the average lifetime (70 years × 365 days/year). Risk assessment was assessed by calculating the hazard index (HI), which is a noncancer index of adverse health effects from intake of specific trace/heavy metal contaminant in food. HI is expressed as the ratio of the ADD to the oral reference dose (RfD) of the trace/heavy metal according to the following equation (USEPA 2000).

$$Hazard\ Index\ = \frac{ADD}{Oral\ RfD}$$

Where oral RfD is the oral reference dose of trace/heavy metals (mg/kg/days) based on the safe upper level of elements/metal’s oral intake for an adult human with an average body weight of 70 Kg. The oral RfD for Cu, Pb, Zn, Mn, Cd, Ni and Cr is 0.04, 0.00357, 0.3, 0.14, 0.001, 0.02 and 1.5 mg/kg/day, respectively (USEPA 2015), while for Co this is 0.03 mg/kg/day (Finley et al. 2012). HI values < 1.0 indicate adverse health effects are not likely to occur. However, if the ADD of certain trace/heavy metal exceeds its oral RfD and thus the HI > 1.0, it may be presumed adverse health effects are excepted to occur. The sum of HI values gives the cumulative risk effect of all elements/metals (Pawelczyk 2013).

It is essential to know the fish consumption information for assessing the human health effects along with the chemically contaminated fish (Copat et al. 2012). The Hazard Index (HI) is a combined risk calculation package that groups both the element/metal level in fish edible muscles and the consumption rate of these muscles by a human to achieve a hazard classification. The ingestion rates of mean normal and habitual consumers used in this study have been proposed by the USEPA (2015) for the general human population. Results of HI values calculated for the various trace/heavy metals in muscle tissues of fish species in this study is presented in Table 6.19 and Table 6.20. The calculated HI values for all fish muscles are <1 for all the studied trace/heavy metals, indicating humans would not experience any significant health risk at both ingestion rates by consumers except for Pb in *Carcharhinus leucas*, *Sphyraena qenie* and *Setipinna tenuifilis* and for Cd in *Carcharhinus leucas*, *Psettodes erumei* and *Trichiurus lepturus* for habitual fish consumers. Among the heavy metals examined in this study Pb and Cd in certain fish species (Table 6.19) showed the highest value of HI (1>) which may cause chronic effects in humans when these fish are consumed at a greater quantity.

Table 6.19 Indicating HI for muscle consumption calculated at mean ingestion and subsistence rates for Cu, Pb, Zn, Mn and Cd for seven fish species

Fish Sp	**Cu** [a]	**Cu** [b]	**Pb** [a]	**Pb** [b]	**Zn** [a]	**Zn** [b]	**Mn** [a]	**Mn** [b]	**Cd** [a]	**Cd** [b]
Carcharhinus leucas	0.148	0.676	0.300	**1.368**	0.105	0.481	0.001	0.006	0.267	**1.221**
Scomberomorus lineolatus	0.095	0.432	0.218	0.997	0.030	0.137	0.002	0.010	0.089	0.407
Sphyraena qenie	0.097	0.442	0.243	**1.111** [c]	0.064	0.292	0.003	0.015	0.156	0.712
Psettodes erumei	0.100	0.458	0.218	0.997	0.026	0.117	0.012	0.055	0.312	**1.424** [c]
Trichiurus lepturus	0.100	0.458	0.075	0.342	0.038	0.172	0.011	0.049	0.267	**1.221** [c]
Otolithes ruber	0.134	0.610	0.200	0.912	0.025	0.115	0.005	0.023	0.134	0.610
Setipinna tenuifilis	0.110	0.503	0.325	**1.482** [c]	0.054	0.249	0.011	0.052	0.178	0.814

[a] 0.0312 kg/day (mean ingestion rate) [b] (0.1424 kg/day (subsistence ingestion rate)); [c] HI> 1, adverse health effects are excepted to occur.

Table 6.20 Indicating HI for muscle consumption calculated at mean ingestion and subsistence rates for Co, Ni and Cr in three fish species

Fish Sp	**Co** [a]	**Co** [b]	**Ni** [a]	**Ni** [b]	**Cr** [a]	**Cr** [b]
Carcharhinus leucas	0.120	0.549	0.091	0.417	0.001	0.006
Scomberomorus lineolatus	0.033	0.149	0.028	0.127	0.001	0.006
Sphyraena qenie	0.044	0.200	0.019	0.086	0.000	0.002

[a] 0.0312 kg/day (mean ingestion rate) [b] (0.1424 kg/day (subsistence ingestion rate))

6.7.9 Bioaccumulation Factor (BAF)

The bioaccumulation factor of trace/heavy metals in fish muscle has been calculated according to the following equation (Gobas et al. 2009).

$$BAF = \frac{Cm}{Cw}$$

Where, C_m is the mean concentration of element/metal in fish muscle (mg/kg dry.wt) and C_w is the mean concentration of element/metal in seawater. The muscles act as a bio-accumulator organ for all the studied elements/metals in various fish species since fish have a large mass of muscle tissue in which concentrations of the most elements/metals may be regulated (Reinfelder et al. 1998). Generally, the toxic, non-essential metal Pb bioaccumulates least efficiently, while the essential elements (Cu and Zn) are bioaccumulated with a higher efficiency in various fish. In the present study, among the fish examined, the *Carcharhinus leucas* showed a higher bioaccumulation factor for Cu (1095.52), Zn (1519.04), Rb (466.60), Co (114.60) and Cr (125.99) (Table 6.21). The species *Psettodes erumei* showed a higher bioaccumulation factors for Mn (493.51) and Cd (42.71). The *Setipinna tenuifilis* species showed the highest bioaccumulation factor of Pb (21.87). Similar results in the bioaccumulation of trace metals in marine fish were observed by Rejomon et al. (2010) from the south west coast of India.

Table 6.21 Bioaccumulation factors for elements/metals in the various fish species from the Miri coast

Fish Species	**Cu**	**Pb**	**Cd**	**Mn**	**Zn**	**Co**	**Ni**	**Rb**	**Cr**
Carcharhinus leucas	1096	20	37	52	1519	115	47	467	126
Scomberomorus lineolatus	700	15	12	91	433	9	14	142	125
Sphyraena qenie	717	16	21	130	920	0	10	169	32.87
Psettodes erumei	741	15	43	494	370	-	-	-	-
Trichiurus lepturus	741	5	37	442	542	-	-	-	-
Otolithes ruber	988	13	18	201	362	-	-	-	-
Setipinna tenuifilis	815	22	24	468	784	-	-	-	-

- Not detected

Based on the bioavailability of elements/metals in the seawater, the bioaccumulation factors and element/metal content in different species of fish may vary. The quantity and bioavailability of metals in the aquatic environment have been identified as an indirect measure of bioaccumulation of trace/heavy metals in the different tissues of aquatic organisms (Kucuksezgin et al. 2006). The variations in BAF of element/ metals in different fish species might be attributed to different physiological states and inter-specific differences of the studied fish (Rejomon et al. 2010). For this research, monitoring of fish tissue contamination is necessary to indicate an early warning of associated water contamination problems and allows for the proper remedial actions to protect the public health and the environment (Murtala et al. 2012) because fish respond quickly with great sensitivity to fluctuations in the aquatic environment.

In the water column, uptake of elements/metals by marine shrimp and crabs depends upon their bioavailability (Carvalho et al. 1999). The range of BAF for studied shrimp species were Cu, (2670.92-6661.45); Zn, (1335.58-4348.18); Mn, (948.05-6669.81); Rb, (195.24-319.25); Cr, (69.84-278.01); Ni, (17.68-92.12); Co, (21.16-82.86); Cd, (7.32-128.13) and Pb (13.79-60.97) (Table 6.22). The range of BAF for studied crab species were Cu, (2232.29-28006.59); Zn, (3046.64-9172.02); Mn, (162.34-6954.55); Rb, (159.63-550.10); Cr, (0.74-353.33); Co, (13.22-119.89); Pb, (15.98-140.44); Ni, (7.42-64.45) and Cd, (15.25-48.81) (Table 6.23). The BAF of Cu, Pb, Mn, Ni and Cr elements were higher in gill tissues whereas Cd, Zn and Rb were more in carapace muscles. The BAF value of Co alone was higher in the walking legs.

The ranges of BAF for the studied bivalve species were Cu, (617.79-1713.34); Zn, (3433.89-9306.80); Mn, (5415.58-6746.75); Cr, (390.30-454.67); Ni, (116.93-139.17); Co, (36.14-73.17); Pb, (19.34-35.74) and Cd, (15.25-27.89) (Table 6.24). Generally, essential elements such as Cu, Zn and Mn are bioaccumulated in higher efficiency, while the toxic non-essential elements Pb and Cd are bioaccumulated at a lower efficiently in all the analyzed crustacean and bivalve species. Similar observations of the higher efficiency of essential elements and a lowest occurrence of non-essential metals in the muscles were noticed in the shrimp tissues from the southwest coast of India (George et al. 2011). Sadiq (1992) suggested the metal bioaccumulation in the crabs was affected by the biochemical composition of sediments and properties of interstitial seawater. The level of metal bioaccumulation in aquatic organisms may vary greatly with individual species and depends on the absorption and elimination process, exposure time and environmental factors such as dissolved organic matter (Hare and Tessier 1996; Hashmi et al. 2002). The major factors, which contribute to the accumulation of trace/heavy metals in shrimp are their life cycle, habitat, feeding nature, ecology and its physiological efficiency (Zhou et al. 2008).

Table 6.22 Bioaccumulation factors for elements/metals in the various shrimp Sp.

Shrimp Species	**Cu**	**Cd**	**Pb**	**Zn**	**Mn**	**Co**	**Ni**	**Rb**	**Cr**
Parapenaeopsis sculptilis	5999	10	14	2798	6670	21	18	206	70
Litopenaeus vannamei	4232	8	26	1549	4122	27	26	221	104
Penaeus merguiensis	6661	7	25	2229	6109	28	27	196	74
Harpiosquilla harpax	3081	128	21	4343	948	83	44	319	118
Acetes indicus	2671	78	61	1336	968	56	92	195	278

Table 6.23 Bioaccumulation factors for elements/metals in the various crab Sp.

Crab Species	**Cu**	**Cd**	**Pb**	**Zn**	**Mn**	**Co**	**Ni**	**Rb**	**Cr**
Portunus sanguinolentus Carapace	3451	49	17	3047	292	13	17	332	92
Portunus sanguinolentus Waking leg	6314	40	26	5841	292	14	17	292	66
Portunus pelagicus Carapace	2759	37	34	8430	935	67	27	55	140
Portunus pelagicus Waking Leg	7059	37	34	6825	2065	120	35	516	197
SS Male Carapace	2232	21	16	9172.	182	32	7	273	77
SS Male Walking Leg	2706	15	19	8122	331	19	26	302	81
SS Male Gill	19769	334	97	7488	4006	68	64	184	353
SS Female Carapace	3558	15	26	5295	162	29	15	236	1
SS Female Walking Leg	8072	15	18	8220	234	26	28	223	87
SS Female Gill	28007	37	140	7627	6955	64	51	159	178

Table 6.24 Bioaccumulation factors for elements/metals in the bivalve

Polymesoda erosa	**Cu**	**Cd**	**Pb**	**Zn**	**Mn**	**Co**	**Ni**	**Cr**
Muscle	618	15	19	3434	5416	36	117	390
Gill	1713	27	36	9307	6344	73	139	430
Gonad	1252	27	29	3958	6747	49	127	455

6.7.10 **Hazard Level**

Among the analyzed metals, Pb and Cd are classified as non-essential toxic metals, which causes health hazards. Various agencies such as the FAO (1983); the WHO (1989); and the EC (2001) prescribed maximum residual limits for human consumption. The food standards for fish set by the FAO (1983) and the WHO (1989) are in wet weight based-concentrations (Table 6.25). For comparing with food standards, the elements/metal concentrations in the tissues of aquatic organisms in this study (Table 6.1), needed to be converted into wet weight by dividing them by factors ranging from 4 to 6 (Khan et al. 1987; Romeo et al. 1999; Rejomon et al. 2010). In this study, overall a factor 4.54 (i.e. 78% moisture) was adopted. The food standards for trace elements/metals in shrimp were unavailable, so a comparison it with those of fish was done.

By using this factor, the derived wet weight based concentrations of Cu, Cd, Pb, Ni, Cr and Cr in the muscles of analyzed aquatic organisms (fish and crustaceans) from the Miri coast fell below the maximum permissible limits (MPLs) of the WHO (1989) and the FAO (1983), whereas for Mn it was slightly above the acceptable level for crustaceans. However, compared to the European food standards (EC 2001) for fish (edible part) (i.e. 0.2-0.4 μg/g for Pb and 0.05-0.10 μg/g for Cd), Pb and Cd concentration were lower but were slightly exceeded in the gills of crabs. “The food standards for bivalves set by the FAO are 10.0-30.0, 40.0-100.0, 2.0 and 1.0-6.0 μg/g wet weight for Cu, Zn, Cd and Pb respectively” (Wagner and Boman 2004; George et al. 2013). The derived wet weight concentrations of Cu, Zn, Cd and Pb in bivalve were well below the FAO limits. From these results, the examined aquatic organisms were not associated with chemical hazards in their muscles and are safe for human consumption.

Table 6.25 Maximum Permissible Limit (MPL) of trace/heavy metals in fish muscles ($\mu g\ g^{-1}$ wet weight) according to National and International Guidelines values.

Standard’s	**Cu**	**Cr**	**Pb**	**Cd**	**Zn**	**Ni**	**Mn**
WHO 1989	30	50	2	1	100	0.5-1	1
MFR 1985	30	-	2	1	100	-	-
FAO, 1983	30	-	0.5	0.5	40	-	-
USEPA, 2000	120	8	4	2	120	-	-
EC, 2001	-	-	0.2 0.4	0.05-0.10		-	-

WHO-World Health Organization; MFR-Malaysian Food Regulation; FAO-Food and Agricultural Organization; USEPA-United States Environmental Protection Agency; EC-European Commission.

6.7.11 Comparison with other literatures

Analyzing the bioaccumulation of heavy metals in the aquatic organism is important because most of the world's population depend upon seafood as a nutritional source. Fish and shellfish contain poly-unsaturated fatty acids, vitamins and nutrients which are biologically important for human health and help in reducing cardiovascular diseases (Kromhout et al. 1985). Most research has been focused on edible muscle tissue. It is well known, muscle tissues are an active site for the binding of trace/heavy metal accumulation and transformation (Elnabris et al. 2013). In a contaminated aquatic ecosystem, the concentration of elements/metals in fish tissue organs may exceed the maximum permissible limits for human consumption and may cause severe health effects.

To evaluate the public health risk of seafood consumed from the Miri coast, the results of element/metal concentration in the muscle tissue were compared with the maximum permissible limits (MPL) established by national and international organizations (Table 6.25); as well as the reported values in similar commercially important fish species (Table 6.26), shrimp (Table 6.27), crabs (Table 6.28) and bivalve (Table 6.29). The present study results were comparable with the reported values from other parts of the world. There were some exceptions with some of the studies reporting lower or higher values that the present study for the same species.

The results reported in the literature from national and international coastal waters were compared with the present study and the results were relatively close to or somewhat higher than the obtained data for similar species of fish. A detailed discussion of each element/metal compared with other researchers was explained earlier. The essential elements (Cu and Zn) and the toxic non-essential metals (Cd, Pb and Cr) were below the maximum permissible limit of the WHO (1989), the FAO (1983) and the MFR (1985) in the muscles but slightly exceeded in other organs (liver and gills). Thus, the variations in elemental concentration in different tissue organs of crab depend upon the geographical location and might be due to the differences in ecological and geological processes taking place in that particular study area. So it is safe to consume the edible muscles of the aquatic organisms collected from the Miri coast and they do not pose any serious threats to consumers.

Table 6.26 Comparison of trace/heavy metals concentration in muscle tissues ($\mu g\ g^{-1}$ dry weight) of commercially important fishes with values taken from open literature

Area	**Weight**	**Mn**	**Cu**	**Cr**	**Pb**	**Cd**	**Zn**	**Co**	**Ni**	**Rb**	**References**
Peninsular Malaysia	Wet wt	–	–	–	0.21-0.32	0.03-0.05	2.3-6.5	–		–	Balaji et al. (1979)
Antartic water	Dry wt	–	1.92-2.65	–	0.05-0.13	0.22-0.23	9.35-10.10	–	0.11-0.12		Honda et al. (1987)
Bay of Bengal	Dry wt	5.00-11.14	3.33-4.68	-	1.67-2.58	0.01-0.16	18.86-33.89	-	6.43-7.57	3.28-27.85	Sharif et al. 1991
Mediterranean Sea	Dry wt	–	3.40–5.88	1.28–1.60	7.33-9.11	1.07–1.43	16.1–31.4	–	4.25-6.07	–	Kalay et al. (1999)
Masan B ay, Korea	Dry wt	–	0.18-0.84	0.02-0.9	0.04-0.15	0.00–0.03	6.33–12.86	–	0.00-0.03	–	Kwon and Lee (1999)
Black Sea	Dry wt	0.69 –3.56	1.01–4.54	<0.06–0.84	<0.05-0.60	<0.02–0.24	25.7–44.2	<0.05-0.40	<0.01-2.04	–	Topcuoğlu et al. (2002)
Iskenderun Bay, Turkey	Dry wt	–	0.66–1.98	1.03–1.79	–	–	8.99–2.18	–	–	–	Yilmaz (2003)
Caspian Sea,	wet wt	0.32-0.56	1.22-1.91	0.31-0.40	0.004-0.037	0.001-0.006	17.95-24.47	0.002-0.009		2.21-3.12	Pourang et al. (2005)
Calicut, India	Wet wt	0.5	2.8	0.6	0.13	0.1	6	–	–	–	Sankar et al. (2006)
Mumbai, India	Wet wt	–	0.31	0.78	0.08	0.02	8.36	–	–	–	Mishra et al. (2007)
Mozambigue Channel	Wet wt	0.06	0.15	–	0.03	0.25	9.92	–	–	–	Kojadinovic et al. (2007)
Gulf of Cambay, India	Dry wt		2.37		1.09	0.23	38.24	0.24	–	–	Reddy et al. (2007)
Alexandria, Egypt	Dry wt	–	4	–	1.4	1.9	16.7	–	–	–	Abdallah (2008)
Gulf of Aqaba, Red Sea	Dry wt	–	0.97	–	4.8	0.97	9.13	–	–	–	Ismail and Abu-Hilal (2008)
Parangipettai, India	Dry wt	0.31–1.20	0.12–0.31	0.65–0.92	–	0.18–0.54	14.1–33.5	0.05-0.28	0.38-1.54	–	Raja et al. (2009)
Langkawee, Malaysia	Dry wt	24.35	0.01	–	1.1	0.9	49.39	–	–	–	Irwandi and Farida (2009)
SW coast, India	Dry wt	–	2.06-3.62	–	0.23-0.56	1.25-6.38	24.4-84.30	3.64-11.8	6.06-13.92	–	George et al. 2010
East coast of India	Wet wt	2.9	5.7	–	–	0.41	21.9	–	–	–	Kumar et al. (2012)
Kalpakkam Coast, India	Dry wt	0.5-8.8	0.8-6.5	0.24-1.78	0.04-2.29	–	14.3-27.9	–	–	–	Biswas et al. (2012)

Area	Weight	Mn	Cu	Cr	Pb	Cd	Zn	Co	Ni	Rb	References
Malacca, Malaysia	Dry wt	–	1.21	0.55	1.5	0.14	41.84	–	–	–	Alama et al. (2012)
Palestine	Wet wt	0.376-0.834	0.251-0.907	–	Nd-0.552	Nd-0.090	3.705-20.535	–	0.453-0.978	–	Elnabris et al. (2013)
Jamaica coast	Dry wt	0.01-0.32	42.80-772.00	0.02-0.06	13.80-177.00	4.24-8.70	3.55-5.76	-	-	0.61-1.03	Fung et al. (2013)
Mumbai Harbor, India	Dry wt	3.47	2.46	0.47	0.12	0.19	38.54	–	–	–	Velusamy et al. (2014)
Iran	Dry wt	–	8.23	–	2.21	0.73		1.15	52.01	–	Hosseini et al. (2015)
Santa Maria Bay, Mexico	Dry wt	0.105	0.059	0.175	0.086	0.021	1.161	0.057	0.197	–	Jonathan et al. 2015
Carcharhinus leucas	Dry wt	0.4	13.3	4.6	2.4	0.6	71	6.5	4.1	9.5	Present Study
Scomberomorus lineolatus	Dry wt	0.7	8.5	4.55	1.75	0.2	20.25	0.5	1.25	2.9	Present Study
Sphyraena qenie	Dry wt	1	8.7	1.2	1.95	0.35	43	0	0.85	3.45	Present Study
Psettodes erumei	Dry wt	3.8	9	–	1.75	0.7	17.3	_	_	_	Present Study
Trichiurus lepturus	Dry wt	3.4	9	–	0.6	0.6	25.35	_	_	_	Present Study
Otolithes ruber	Dry wt	1.55	12	–	1.6	0.3	16.9	_	_	_	Present Study
Setipinna tenuifilis	Dry wt	3.6	9.9	–	2.6	0.4	36.65	_	_	_	Present Study

Table 6.27 Comparison of element/ metal concentrations (µg g-1 dry weight) in the muscle tissues of shrimp from the Miri Coast with other regions

Location	**Species**	**Cu**	**Cd**	**Pb**	**Zn**	**Mn**	**Co**	**Ni**	**Cr**	**Rb**	**References**
Java Sea	*Penaeus merguiensis*	5-120	0.6-13.9	–	26-109	–	–	–	–	–	Everaarts and Swennen (1987)
Coast Malay Peninsula	*Penaeus sp*	60-130	0.2-0.9	0.7-3.4	60-85	–	–	–	–	–	Everaarts et al. (1989)
Sabah, Malaysia	*Penaeus monodon*	12.8 -159	1.6-6.1	4.6-32	–	–	–	–	–	–	Awaluddin et al. (1992)
Malaysia	*Penaeus monodon*	32-99	0.21-49	1.68-54	68-186	–	–	–	–	–	Patimah & Dainal (1993)
Kenya coast	*Penaeus sp*	45-90	1.1-8.5	0.1-0.6	49-102	–	–	–	–	–	Everaarts and Nieuwenhuize (1995)
Malaysia	*Penaeus monodon*	0.8 -24	0.09-0.8	0.06-5.9	5.0-16.0	–	–	–	–	–	Ismail et al. (1995)
Mumbai coastal water	*Parapenaeopsis sculptilis*	10.5-37.8	0.001-1.5	0.01-0.07	9.2-85.0	–	–	0.004-0.009	–	–	Krishnamurti and Nair (1999)
Mumbai coastal water	*Parapenaeopsis hardwickii*	22.6-30.5	0.03-1.2	0.01-0.07	64.7-130.2	–	–	0.008-0.03	–	–	Krishnamurti and Nair (1999)
Sundarbans, India	*Penaeus monodon*	–	0.74	32.1	1184	–	–	–	–	–	Guhathakurta and Kaviraj (2000)
Bay of Bengal, Bangladesh	*Penaid Shrimp & Spiny Lobster*	12.2-75.6	0.2-0.6	0.8-3.8	17.5-105.1	3.1-15.2	–	2.8-8.9	1.7-4.9	–	Hossain et al. (2001)
The Gulf of Mexico	*Penaeus setiferus*	17.3	6.11	7.73	107	–	–	–	–	–	Vazquez et al. (2001)
Peninsular Malaysia	*Acetes indicus*	–	0.68-1.25	2.51-8.76	75.1-129	–	–	–	–	–	Yap et al. (2004)
India	*Penaeus sp*	8.19	0.095	0.5	17.76	–	–	–	0.61	–	Sivaperumal et al. (2007)
Indonesia	*Penaeus merguiensis*	1.166	0.0002	0.022	2.13	–	–	–	–	–	Soegianto and Supriyanto (2008)
Cochin Kerala, India	*Shrimp*	28.6 -46.8	3.6-9.6	0.6-1.9	44.8-88.7	–	8.5 -19	10.6 -24.7	–	–	George et al. (2011)
Malacca and Kedah, Malaysia	*Acetes indicus*	–	0.02-0.83	0.17-1.29	34.25-45.79	2.61-6.95	–	–	–	–	Mustafa et al. (2012)
Malacca strait, Malaysia	*Penaeus merguiensis*	12.06	0.1	1	42.41	–	–	–	0.29	–	Lubna Alam et al. (2012)
Malacca, Johor & Terengganu Malaysia	*Acetes indicus*	39.37-56.09	0.04-0.76	0.07-0.59	29.18-46.34	0.89-1.77	–	–	0.59 - 1.34	–	Mustafa et al. (2013)
Miri coast, Sarawak	*Parapenaeopsis sculptilis*	72.83	0.16	1.64	130.8	51.36	1.2	1.55	2.55	4.2	Present study
Miri coast, Sarawak	*Litopenaeus vannamei*	51.38	0.13	3.05	72.4	31.74	1.55	2.25	3.8	4.5	Present study
Miri coast, Sarawak	*Penaeus merguiensis*	80.87	0.12	2.98	104.2	47.04	1.6	2.35	2.7	4	Present study
Miri coast, Sarawak	*Harpiosquilla harpax*	37.4	2.1	2.5	203	7.30	4.7	3.9	4.3	6.5	Present study
Miri coast, Sarawak	*Acetes indicus*	32.42	1.275	7.25	62.42	7.45	3.17	8.075	10.15	3.97	Present study

Table 6.28 Comparison of element/metal concentrations (μg g^{-1} dry weight) in the muscle tissues of crabs from the Miri Coast with the other regions

Coast	**Sample**	**Cu**	**Cd**	**Pb**	**Zn**	**Mn**	**Co**	**Ni**	**Rb**	**Cr**
Miri Coast	*P. sanguinolentus Carapace*	41.9	0.8	2.05	142.4	2.25	0.75	1.45	6.75	3.35
Miri Coast	*P. sanguinolentus Waking leg*	76.65	0.65	3.05	273	2.25	0.8	1.5	5.95	2.4
Miri Coast	*P. pelagicus Carapace*	33.5	0.6	4.1	394	7.2	3.8	2.4	11.2	5.1
Miri Coast	*P. pelagicus Waking Leg*	85.7	0.6	4	319	15.9	6.8	3.1	10.5	7.2
Miri Coast	*S. serrata Male Carapace*	27.1	0.35	1.9	428.7	1.4	1.8	0.65	5.55	2.8
Miri Coast	*S. serrata Male Waking Leg*	32.85	0.25	2.25	379.6	2.55	1.05	2.3	6.15	2.95
Miri Coast	*S. serrata Male Gill*	240	0.55	11.6	350	30.85	3.85	5.65	3.75	12.9
Miri Coast	*S. serrata Female Carapace*	43.2	0.25	2.85	247.5	1.25	1.65	1.35	4.8	0.027
Miri Coast	*S. serrata Female Waking Leg*	98	0.25	2.15	384.2	1.8	1.45	2.45	4.55	3.2
Miri Coast	*S. serrata Female Gill*	340	0.65	16.7	356.5	53.55	3.65	4.45	3.25	6.5
Kuwait Coast[1]	*P. pelagicus Carapace*	14	–	0.7	46	0.98	–	–	–	0.51
Kuwait Coast[2]	*Portunus pelagicus*	123.8	–	1.9	206	0.95	–	–	–	0.47
Worldwide[3]	*Portunus pelagicus*	70	–	1	80	1	–	–	–	0.69
Persian Gulf [4]	*Portunus segnis Muscle*	–	0.15-0.38	0.43 - 0.71			0.53-0.62	14.5-17.3	–	–
Persian Gulf [4]	*Portunus segnis Hepatopancreas*		0.61-0.88	2.2 - 2.5			0.91-1.20	20.40-31.90		
Persian Gulf [4]	*Portunus segnis Gill*		0.43 -0.51	1.10 – 1.50			0.63- 0.71	15.40 – 20.20		
Mediterranean Lagoons[5]	*Callinectes sapidus*	5.38-11.7	0.03-0.08	–	13.9-20.1	0.15-2.98		0.24-0.45	–	0.05-0.13
Nigeria[6]	*Callinectes sapidus*	0.03-2.75	0.08-4.0	–	0.02-6.06	–	–	–	–	0.03-30.03
Denmark[7]	*Carcinus maenas muscle*	7.3-16	0.002-0.006	–	51-52	2.5-6.3	–	–	–	–
Denmark[7]	*Carcinus maenas Gill*	12 - 16	0.05 -0.06	–	9.30 – 9.40	15 - 32	–	–	–	–
Australia[8]	*Callinectes sapidus*	15.8-28.9	0.001	–	63.1-83.4	1.20-2.80		0.10-0.30		0.09-0.73
Vietnam[9]	*Somaniathelphusa sinensis*	62	–	–	420	28	–	–	–	–
Chilika Lagoon, India[10]	*Scylla serrata*	124	–	0.18	280	12	–	–	–	–
Mahandi Estuary, India[11]	*Scylla serrata*	117.2	–	0.22	287.6	12.7	–	–	–	–
Malaysia[12]	*Scylla serrata*	6.38-79.38	0.05-0.78	1.49-7.84	325.39-523.21	–	–	–	–	–

[1]Anderlini et al. (1982), [2](2001), [3]Bryan (1976), [4]Hosseini et al. (2014), [5]Mutlu et al. (2011), [6]Olowu et al. (2010), [7]Bjerregaard and Depledge (2002), [8]Mortimer and Cox (1999), [9]Brauer et al. (2001), [10]Mohapatra et al. (2007), [11]Mohapatra et al. (2009), [12]Kamaruzzaman et al. (2012)

Table 6.29 Element/metal concentrations ($\mu g\ g^{-1}$ dry wt.) in bivalve samples from the Miri coast with other regions

Sample, Location	Cu	Cd	Pb	Zn	Mn	Co	Ni	Cr	References
Muscle	7.5	0.25	2.3	160.5	41.70	2.05	10.25	14.25	Present Study
Gill	20.8	0.45	4.25	435	48.85	4.15	12.2	15.7	Present Study
Gonad	15.2	0.45	3.4	185	51.95	2.8	11.15	16.6	Present Study
Polymesoda erosa, Sungai Sepang	15.70	2.96	6.80	343.00	_	_	5.07	_	Edward et al. (2009)
Polymesoda erosa, Malacca	5.91	4.23	11.60	249.00	_	_	4.29	_	Edward et al. (2009)
India	–	0.5	2.2	46.6	42.2	12.4	–	_	Gawade et al. (2013)
Malaysia	1.96	4.33	0.89	5.38	_	_	9.10	_	Yap et al. (2014)

6.8 Summary

The element/metal concentration was higher in the demersal species compared to pelagic because of their bottom-dwelling habits. On the basis of the results obtained it can be concluded the level of elements/ metals (Cu, Cd, Pb, Zn, Mn, Co, Ni, Cr and Rb) in the edible muscle tissues (on wet weight basis) of all the analyzed marine life from the Miri coast are below the MPLs of national and international seafood guideline values with a few exceptions. The accumulation of trace/heavy metals in the muscle tissues of the aquatic organisms in this study was comparable or below the concentrations reported for similar commercially important species globally. Inter-elemental correlations were observed between the essential and non-essential metals along with fish size. Most of the analyzed metals except Cr showed significant correlation with fish size (length and weight). Likewise, all the metals except Rb showed a positive correlation with the shrimp length and weight.

The body size (length and weight) of the aquatic organisms plays a significant role in the bioaccumulation of trace/heavy metals in their muscles and other organs. The accumulation of elements/metals varied between the species and the organs due to specific factors like age, size, genetic tendency, habitat, feeding nature, the swimming behavior of different species and the geological process of the study area. It also depends upon the bioavailability of elements/metals in the particular ecosystem and the exposure time spent by the organism in that ecosystem with the contaminated water and sediments.

The analyzed elements were noticed in all the organs and the maximum concentration was recorded in the liver tissues followed by the gills, gonads and muscles. The differences in concentration of element/metal in various tissues were due to the presence of metal-binding proteins such as metallothioneins. The liver has the capacity to absorb a large amount of metallothioneins, which is responsible for the metabolic activities and accumulation of elements/metals in the liver tissues. These proteins are involved in the binding of essential metals and detoxifying non-essential toxic metals. The maximum metal accumulation was noticed in the liver tissue. In the case of crabs, a higher accumulation was observed in the gill tissues, because the gills are responsible for the respiration and gaseous exchange and have direct contact with the surrounding turbid water; so it accumulates more concentration. The accumulation of metals in female crabs is greater compared to males because female crabs are normally larger in size and feed more to meet the increasing demands of reproduction.

The bioaccumulation Factor calculation suggests the essential elements were accumulated at a higher efficiency than non-essential elements in all aquatic organisms of this study. According to the Hazard Index calculation, none of the elements will pose any adverse health effects to humans for both ingestion rates proposed by USEPA, except for Pb and Cd in certain fish species for habitual consumers. From the wet weight, the examined aquatic organisms are not associated with vulnerable metal content in their muscle and safe for human consumption.

Chapter 7 **Land Use / Land Cover (LULC) and Shoreline Change**

This chapter provides the information on shoreline changes with reference to sediment accretion and erosion pattern and the land use/land cover (LULC) effects in Miri city for the past 51 years.

7.1 **Introduction**

The Earth's surface features are undergoing rapid change due to natural processes and anthropogenic activities. The surface of the Earth includes a variety of natural and artificial geographical features such as ecosystems, landforms, human settlements and engineered constructions. LULC analysis is a general term which is used to depict earth surface cover, whether it is natural or manmade. According to the Food and Agricultural Organisation (FAO 1997, 1999a), land cover is the observed physical and biological cover of the earth's land, as vegetation or man-made features and land use is the total of arrangements, activities, and inputs that people undertake in a certain land cover type. Assessment of changes in LULC in different time periods attained more importance in the last few decades and a number of studies have been conducted to assess the spatial patterns of land use / land cover (Xiubin 1996; Carlson and Arthur 2000; Lambin et al. 2003; Tan et al. 2010; Mendoza-González et al. 2012; Avelar and Tokarczyk 2014; Khan et al. 2015). The causes of land use / land cover changes can be either natural influences or sometimes human activities.

LULC of an area is influenced by human development activities or other changes taking place in the region. The temporal changes in LULC in an area can be assessed by using historical maps and more recently, aerial photos or satellite images (Mas 1999; Shalaby and Tateishi 2007; Yang et al. 2010). The advancement of satellite imaging technology and geographical information systems (GIS) made the process of change detection quicker and more accurate than in the past. Temporal images available from a number of satellites with different spatial and spectral resolutions have complemented the effective assessments of LULC made by human activities and natural phenomenon, as well as helping to predict future LULC changes in the region (Veldkamp and Lambin 2001). LULC studies can be adopted to monitor major environmental problems such as deforestation, sea-level rise, watershed management, acidification, forest fires, greenhouse effects, eutrophication and desertification by using different resolutions of satellite images (Fonji and Taff 2014). High resolution satellite images are normally used to monitor biodiversity loss of an area to distinguish small contrasting areas. LULC analysis is an important techniques used by many professionals for proper planning and sustainable management of land resources. LULC can also be applied to monitor changes of the Earth's terrestrial surface due to climate change, loss in biodiversity and the impact of pollution on terrestrial and aquatic environments (Berlanga-Robles and Ruiz-Luna 2002).

Coasts are the narrow stretch of land, which serves as the contact zone between the ocean and land forms, which are highly dynamic natural systems where ocean processes dominate over land processes. Studies related to coastal geomorphology include coastal change analysis and LULC changes in defined coastal areas over a period of time. Describing coastal regions through coastal geomorphological analysis and mapping has rapidly gained acceptance in more recently (Blodget et al. 1991; Boak and Turner 2005; Hapke et al. 2010). Changes in shorelines can be caused by natural as well as human induced development activities and increases the risk factor for coastal communities (Malini and Rao 2004). Shoreline changes is an environmental concern when considering development projects such as harbors, jetties, ports, embankment facilities, etc. Monitoring shoreline changes is necessary in the short term and long term basis, either seasonally or annually to provide efficient data on erosion and deposition in regards to coastal zone management and to improve sustainable shoreline management plans (Kankara et al. 2014).

In the present study, the LULC changes of a 713 km^2 area, which included a 74km coastal belt adjacent to Miri was analyzed for a period covering 51 years using two different datasets. Information relating to the LULC of the study area was extracted from two sources, a topographic sheet for the year 1963 (scale 1:50,000), produced by the Department of Survey and Mapping, Malaysia and for more recent LULC information, from a Landsat 8 operational land imager (OLI) sensor image acquired on 23rd May 2014. Since the area is characterized as a tropical rainfall region there was some difficulty in obtaining a cloud-free image of the study area. The image chosen for the present study is comparatively cloud free and was used for further analysis.

7.2 Results and Discussion for LULC

7.2.1 LULC – 1963

The LULC details for the year 1963 were generated from topographical maps by interpreting the general surveyed LULC types which clearly depicted an approximate boundary. The various LULC types identified from the topographical maps were artificial surfaces, settlements (urban / semi-urban area), plantation (rubber), forest (primary and secondary), grass lands, swamps, river/ water bodies, tidal/barrier islands, beaches or tidal flats and rocky cliff beaches. The distribution of identified LULC classes are represented in Figure 7.1 and tabulated in Table 7.1. The distribution of LULC areas in the particular time period provides information about the spatial distribution of various kinds of LULC. Among the delineated LULC types, primary forest covers more than 66% followed by secondary forest at 27% and swampland at 3% of the total area. All other LULC classes together cover less than five percent of the total study area. Furthermore, during 1963, plantation activities such as rubber and coconut were taking place and rubber plantations in particular covered more than 1% of the total study area. The information extracted from the year 1963 act as the base line information for further analysis of LULC changes which have taken place in the study area.

Table 7.1 LULC types during 1963

Land use / land cover	**Area (km^2)**	**Area (%)**
Artificial surfaces	0.089	0.01
Settlements / urban/semi-urban	5.05	0.71
Coconut plantations	0.28	0.04
Rubber plantations	9.53	1.34
Grassland	1.89	0.26
Primary forests	471.77	66.11
Secondary forests	191.41	26.82
Swamps	21.9	3.07
River / Water body	6.79	0.95
Tidal / Barrier island	0.6	0.08
Beaches / Tidal flats	4.04	0.57
Rocky cliff beaches	0.22	0.03
Total	**713.56**	**100**

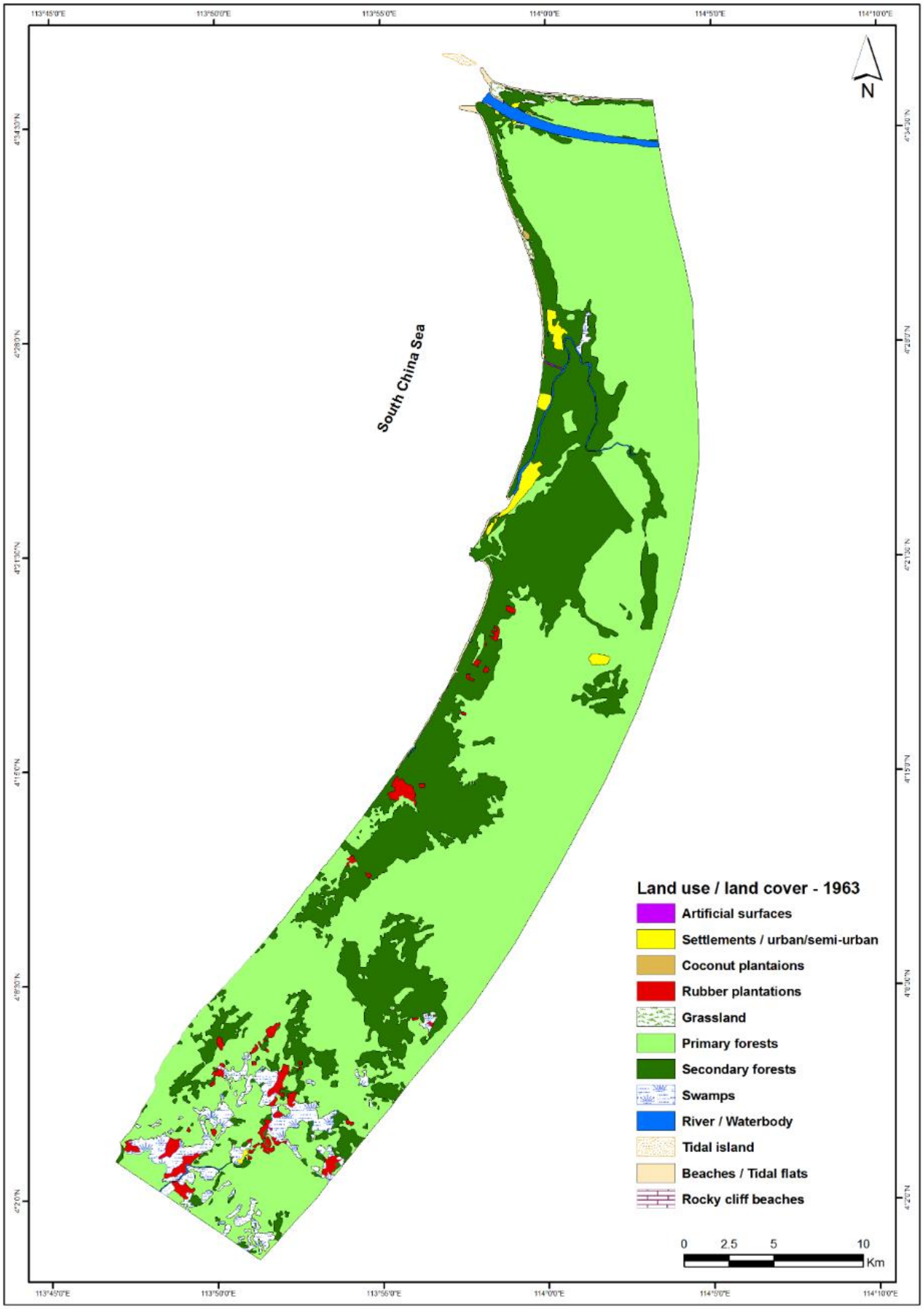


Figure 7.1 LULC map of the year 1963 (source: Topographical map by Dept. of Survey and Mapping, Malaysia.

7.2.2 LULC – 2014

Assessment of the temporal pattern of LULC in the study area was facilitated with the use of recently available satellite imagery (Landsat image 2014). The interpretation of satellite images started with keeping the LULC data of 1963 as the base line information. The major types of LULC identified from the satellite images were artificial surfaces, settlements (urban / semi-urban area), plantations (oil palm and chili), forests (primary and secondary), grass lands, swamps, river/ water body (lakes), tidal/barrier islands, beaches or tidal flats, rocky cliff beaches, house-hold agriculture, cleared areas, afforested areas, secondary mixed forests with oil palms and golf courses. Few new types of LULC were introduced during this time and other existing LULC areas were totally changed to other types. Table 7.2 LULC in 2014, shows the LULC types identified during 2014 with the area covered by each type and spatial distribution is shown in Figure 7.2. Among the LULC identified for 2014, the majority of the area is covered by secondary forest mixed with oil palm (45%) followed by settlements (urban + semi-urban 19%), oil palm plantations (14%) and afforested areas (11%) also noted was the extent of remaining primary forest was reduced to 3% while secondary forest is 2% of the total area.

Table 7.2 LULC in 2014

Land use / Land cover	**Area (km^2)**	**Area (%)**
Artificial surfaces	2.29	0.32
Settlements / urban/semi-urban	136.68	19.16
Oil Palm plantations	104.98	14.72
Primary forests	26.56	3.72
Secondary forest	14.33	2.01
River / Water body	8.31	1.17
Tidal / Barrier islands	0.95	0.13
Beaches / Tidal flats	1.82	0.26
Rocky cliff beaches	1.21	0.17
Chilly plantation	0.08	0.01
House-hold agriculture	1.06	0.15
Golf courses	1.46	0.20
Cleared areas	1.48	0.21
Afforested areas	84.61	11.86
Secondary mixed forest with oil palms	327.38	45.90
Coconut plantations	-	-
Rubber plantations	-	-
Grassland	-	-
Swamps	-	-
Total	**713.56**	**100**

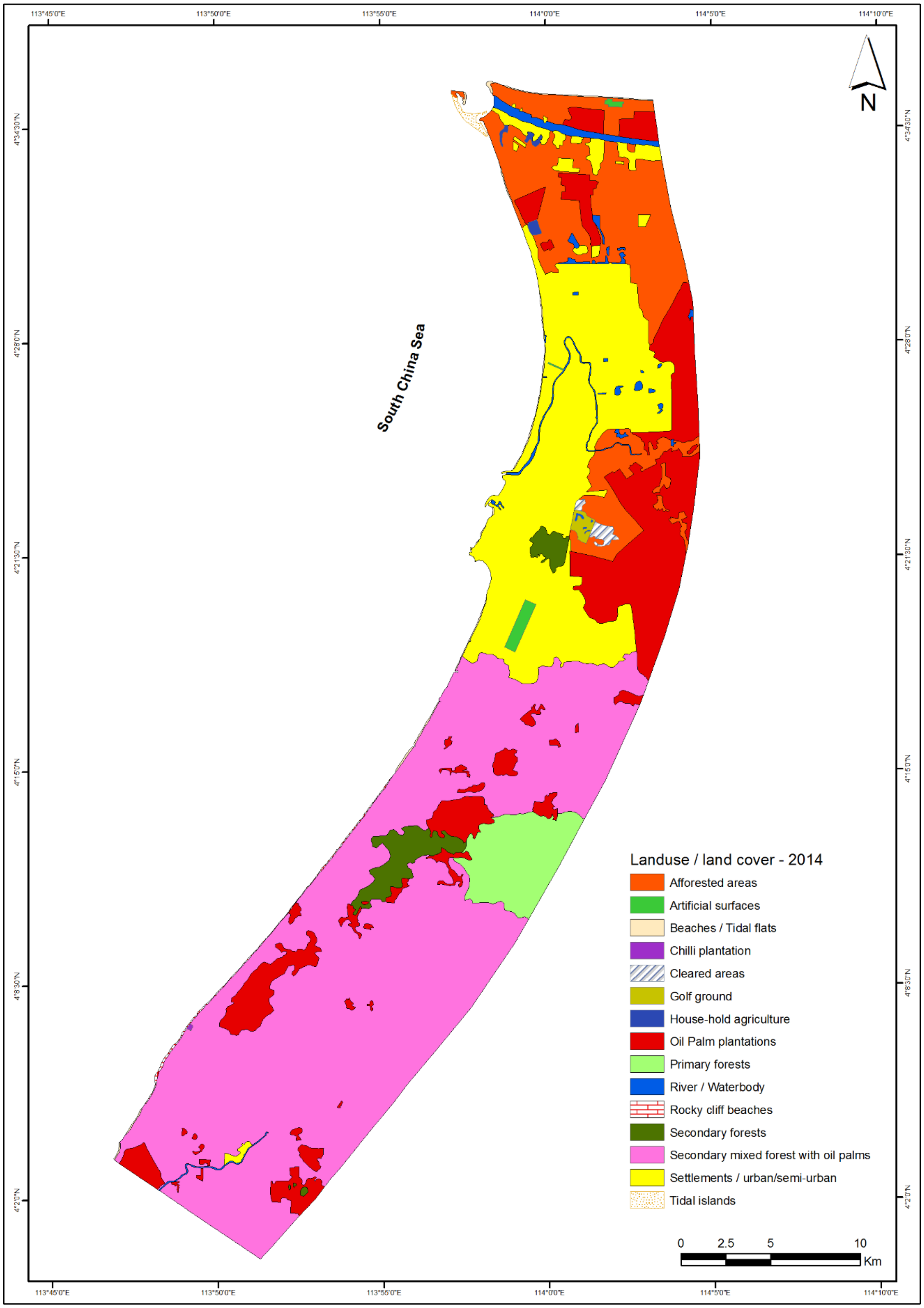


Figure 7.2 LULC map of the year 2014 (Source: Landsat 8, OLI image acquired on 23/5/2014)

7.2.3 LULC analysis – (1963 to 2014)

The changes in the LULC in an area can be analyzed by cross comparing the different time periods of LULC maps. In the present study, in order to identify intensity and significance of LULC changes for the last 51 years (1963 to 2014), LULC maps of both years were overlaid in the ArcGIS software using the analysis support tools. This process facilitated the assessment of spatial changes for different types of LULC from one time period (1963) to more recent times (2014) and also provided the area statistics of each class. The area calculation derived from the overlay analysis is given in Table 7.3. In 2014, few new classes of LULC types were identified and occupying 91% of the total area. While comparing the LULC maps (1963 and 2014), it become quickly apparent, the most obvious changes occurred to the primary and secondary forest cover types. Primary forests, which covered nearly 90% of the total area in 1963, were reduced to 5% of the total area by 2014.

Primary and secondary forests have given way to oil palm plantations, settlement (urban / semi urban) developments, afforestation and secondary mixed forests with oil palm. During the 19th century, under British rule, rubber and oil palm were introduced in Peninsular Malaysia. Consequently, forest cover in the Peninsular Malaysia was reduced from 73% in the early 1950s to ~51% by 1982 (Brookfield and Byron 1990). This forest conversion process continued as primary forest areas were cleared by logging companies for timber and replanted in oil palm plantations which has emerged as a major commercial crop. The distribution of changes in LULC during the time period covered was calculated in percentages and any variations were indicated as plus (increase) or minus (decrease) (Table 7.3) and the major changes during the time period is shown in Figure 7.3. The results of this comparison point towards the destruction of tropical primary forests for conversion to oil palm plantations in the area, which ultimately contributes to environmental changes in the area.

Table 7.3 showing the changes in LULC during 1963 – 2014

Land use / Land cover	**Area % (Year 1963)**	**Area % (Year 2014)**	**Percentage of Changes 1963 to 2014**
Artificial surfaces	0.01	0.32	+0.31
Settlements / urban/semi-urban	**0.71**	**19.16**	**+18.46**
Oil Palm plantations	**-**	**14.72**	**+14.72**
Primary forests	**66.11**	**3.72**	**-62.39**
Secondary forest	**26.82**	**2.01**	**-24.82**
River / Water body	0.95	1.17	+0.21
Tidal islands	0.08	0.13	+0.05
Beaches / Tidal flats	0.57	0.26	-0.31
Rocky cliff beaches	0.03	0.17	+0.14
Chilly plantation	-	0.01	+0.01
House-hold agriculture	-	0.15	+0.15
Golf ground	-	0.20	+0.20
Cleared areas	-	0.21	+0.21
Afforested areas	**-**	**11.86**	**+11.86**
Secondary mixed forest with oil palms	**-**	**45.90**	**+45.90**
Coconut plantations	0.04	-	-0.04
Rubber plantations	1.34	-	-1.34
Grassland	0.26	-	-0.26
Swamps	3.07	-	-3.07

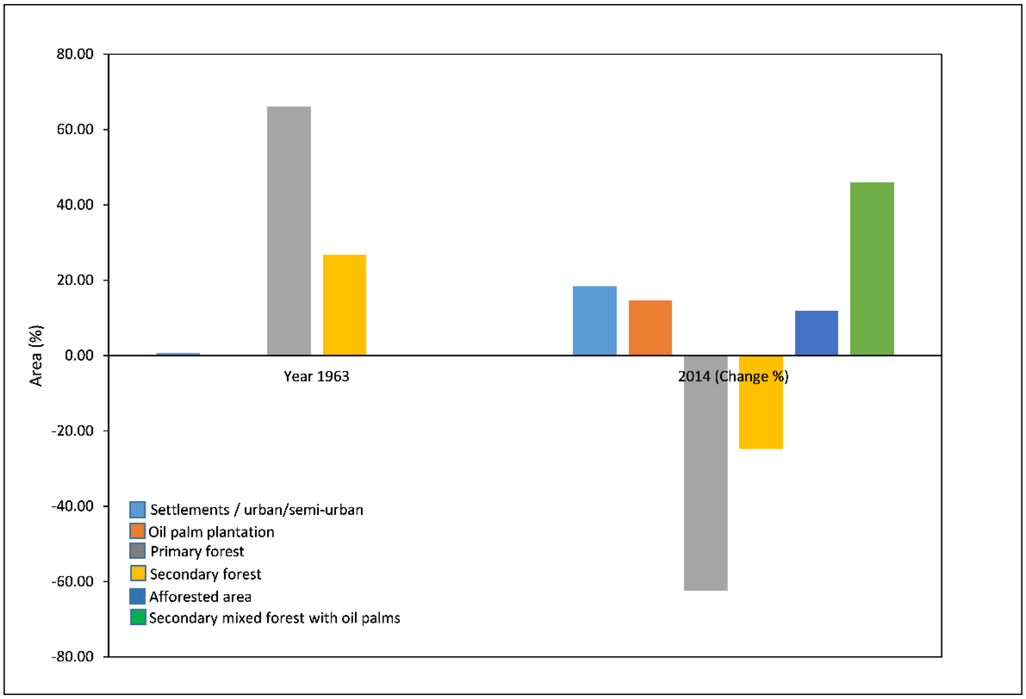


Figure 7.3 Graph showing major changes in the LULC during 1963 to 2014

7.3 Results and Discussion for shoreline changes

Based on the analysis techniques used in the present study, the changes in the shoreline are assessed in two different approaches. In the first analysis, shoreline changes between the years was carried out and in the second approach, total changes from the base year i.e., 1963, until the final year of analysis in 2014, was performed. The results show spatially significant changes occurred along the Miri coast, including both erosion and accretion and can be attributed to natural and man-made activities. In order to make the assessment easy and more understandable, the shoreline of the study area is divided into 6 regions / beaches (A. Baram River estuary, B. Miri River estuary, C. Tanjong Lobang beach, D. Esplanade beach, E. Hawaii beach and F. Bungai beach) shown in Figure 7.4

The simple overlay analysis of shorelines at different years shows variations from year to year and also from the base year to respective temporal years. This facilitated the identification of erosion and accretion zones along the shoreline and their quantification through estimation of area under each class. Some areas of the shoreline when compared to the shoreline in 1963, have expanded outward indicating accretion and in other areas the shoreline has contracted inland indicating erosion.

7.3.1 Shoreline changes during individual years

The characteristics of the shoreline during the periods studied were assessed by comparing the fluctuations between shorelines in respective years. This provided cumulative shoreline variable maps of compared timeframes with prominent erosion and accretion zones along the total stretch of the study area. Area statistics were calculated for each timeframe to understand the variability in shoreline changes (Table 7.4)

Table 7.4 Quantification of erosion and accretion between different years

Year	**Erosion***	**Accretion***
1963-1988	634.04	215.87
1988-1991	147.19	356.18
1991-2001	660.87	464.12
2001-2014	291.97	709.73

* All units are in Acres.

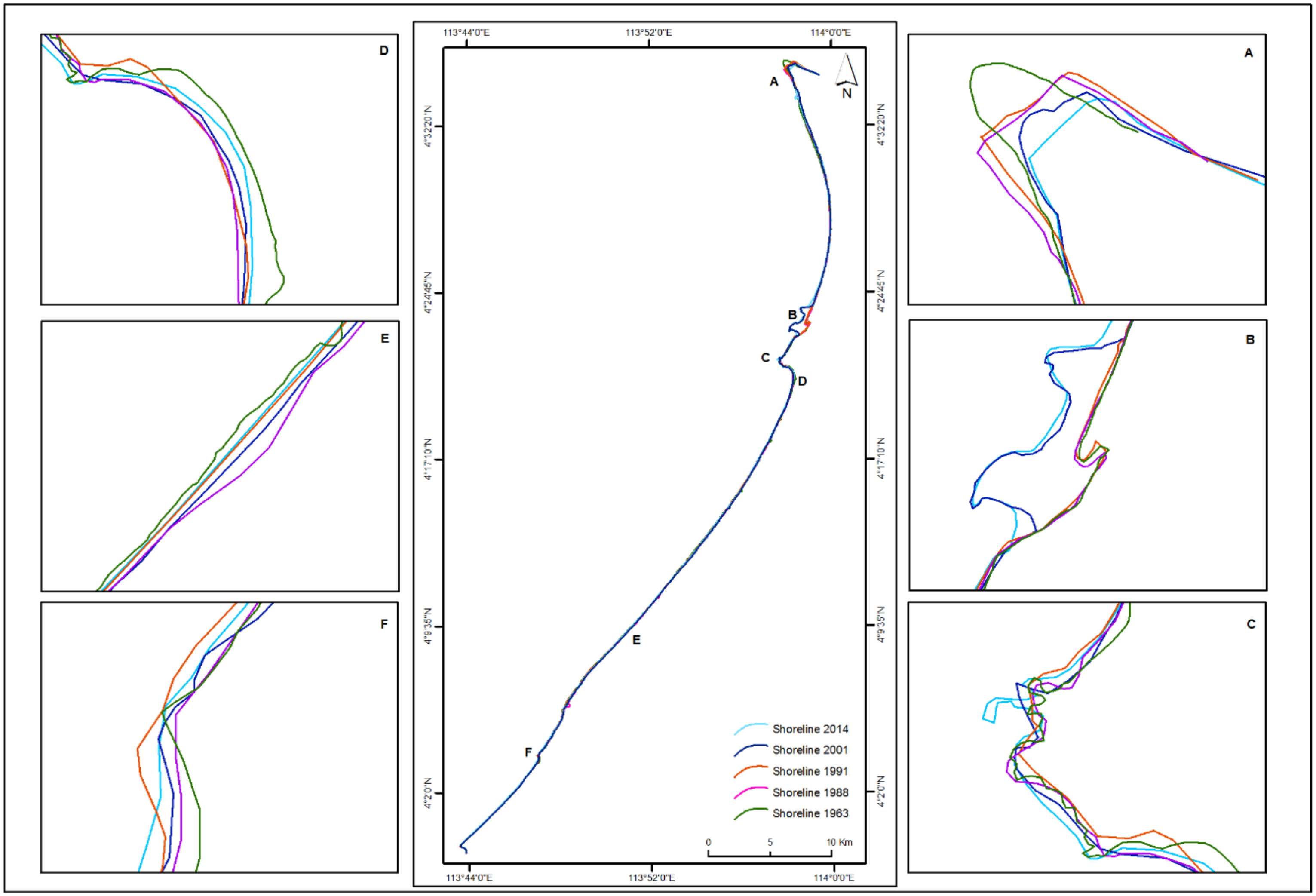


Figure 7.4 Shoreline for the four time periods with selected segments (A. Baram River estuary, B. Miri River estuary, C. Tanjong Lobang beach, D. Esplanade beach, E. Hawaii beach and F. Bungai beach).

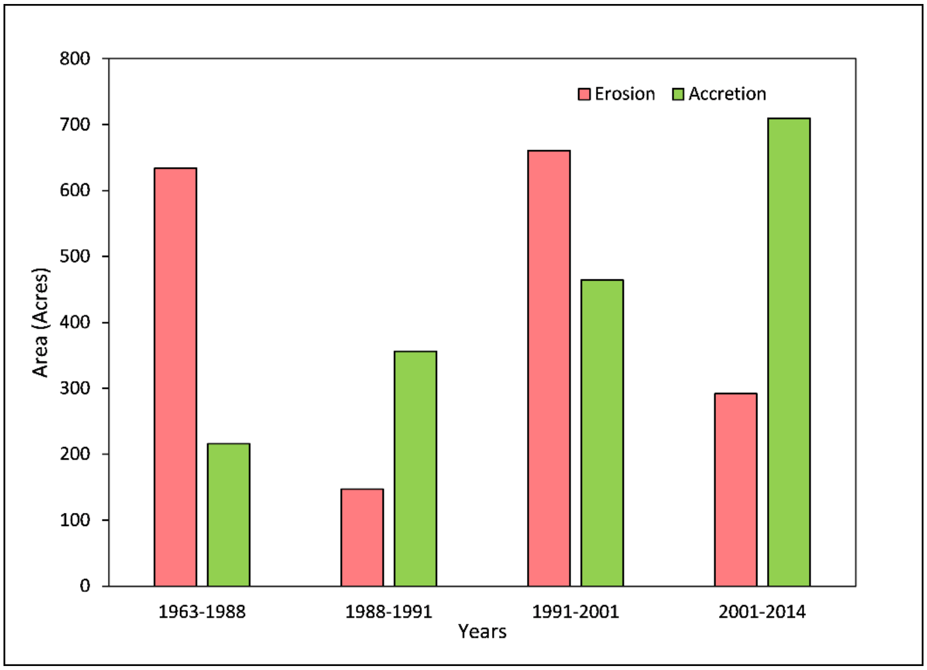


Figure 7.5 Shoreline erosion and accretion rates between the years

The periodic changes of the study area due to erosion and accretion were clearly defined in Figure 7.5. During the period from 1963 – 1988, erosion and accretion varied from 634 to 215 acres respectively. Similarly, the erosion and accretion of the shoreline area between the years 1988 and 1991 show a reversed pattern with less erosion (147 acres) and high accretion (356 acres). However, during the period from 1991 – 2001, the eroded area was larger more compared to the accretion area. During this period, several rock revetment programmes (along the Lutong-Kualabaram Road) and construction of a parallel breakwater structure (at Miri River mouth) was carried out along shoreline, which escalated the process of erosion and accretion simultaneously. The effects of these activities were reflected in the analysis as accretion totaled 464 acres and erosion totaled a maximum of 660 acres. (While analyzing the entire stretch of shoreline in the study area, the shoreline protection measures covered approximately 25km, from the Baram River mouth to Marina Bay. These measures have augmented the erosion in unprotected areas and depositions between the parallel breakwater structures). This supports the concept of decades of erosion and accretion along the shoreline. This concept is again reinforced by assessing the areas eroded and accreted during 2001 – 2014. During this period, erosion was down to 291 acres with increased accretion of 709 acres, and this can be attributed to large scale land reclamation which took place at the Marina Bay, located near the Miri River estuary. During the analyzed time frame, maximum erosion was recorded between the period of 1991 and2001 (660 acres) and the maximum accretion was during 2001-2014 (709 acres). The spatial analysis of erosion and accretion classified the Baram River mouth area as the area of maximum erosion and the Miri River estuary area as the point of maximum accretion. The Kampong Baraya beach shows a trend of erosion, whereas the Esplanade beach, Tanjong beach and Bungai beach areas shows evidence of shoreline accretion in varying degrees.

7.3.2 Shoreline changes from the base (1963) year

The second approach analyzed the changes of the entire shoreline from the base year, which provides an historical perspective of the erosional and accretion processes which have taken place along the total stretch of the study area with regards to natural and man-made changes. In order to generate the statistics and also assess the spatial changes, individual shoreline areas from respective years are cross compared with the base shoreline map and the results of the analysis is shown in Table 7.5 and Figure 7.6.

Table 7.5 Quantification of variation in erosion and accretion from the base (1963) years

Base Year	Change Years	Erosion*	Accretion*
1963	1988	634.04	215.87
	1991	447.32	234.61
	2001	816.25	545.23
	2014	546.72	723.35

*All units are in Acres.

The results show similar characteristics of shoreline changes between different times the comparison of the shoreline in 1988 with the base year, shows more erosion than accretion at 634 and 215 acres respectively. The analysis reveals a major change in the Kualabaram region (the shape of the Baram River mouth itself changed), which reflects greater erosion taking place. But shoreline characteristics from 1991 was entirely different compared to 1988 and the base year 1963, showing decreased erosion at 447 acres and slightly increased accretion at 234 acres. At the same time, the comparison of the base year shoreline with 2001data showed erosion of shoreline peaked with an area of 816 acres and accretion of 545 acres. This correlates with the shoreline protection measures implemented in selected stretches such as rock revetments and breakwaters, which exaggerates both processes of erosion and accretion by intervening in the natural process of ocean currents. The highest rate of accretion (723 acres) in 2014 also had a comparatively higher rate of erosion (547 acres). The rate of accretion shows an increasing trend during 2001 -2014, since more coastal areas have been reclaimed in the Miri River estuary area. These reclamation projects have caused erosion in other areas along the shoreline due to the differential wave action. A closer examination and cross comparison of the analyzed results of both approaches shows a natural cycle of decades reversal in erosion and accretion along the shoreline studied. Earlier, during the period from 1963 to 2001, ocean currents determined the erosion and accretion process and followed a more natural general pattern of coastal processes, whereas after 2001 human induced activities (such as rock revetments, construction of groins and breakwater structures) along the shoreline has changed the total scenario by changing the natural erosion and accretion processes.

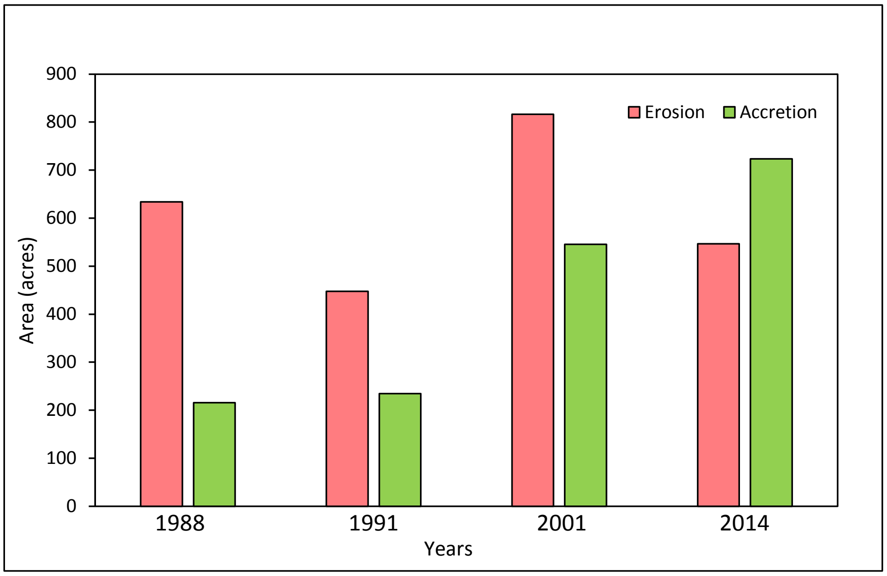


Figure 7.6 Shoreline erosion and accretion rates from the base year 1963

7.3.3 Shoreline changes during the period of 1963 - 2014

An attempt has been made to detect the total spatial changes in shoreline for the past 51years (1963 to 2014) with the help of GIS. The major changes were identified and the total area of erosion and accretion was also calculated. During the period of 51 years, a total of 547 acres of shoreline was eroded and 723 acres of shoreline was accreted. This facilitated the identification and differentiation of natural (strong waves) and man-made changes (seawall construction, groins and breakwaters) along the total length of the shoreline studied. Figure 7.7 shows the major areas of erosion and accretion in the study region during the cumulative period of assessment. The data, shows the maximum variation of either erosion or accretion of the shoreline is concentrated at four major beach areas selected; the Baram River mouth, the Miri River estuary, Tanjong Lobang beach and Esplanade beach. The maximum change in shoreline characteristics and shape was observed in two areas, the Baram River outlet and the Miri River mouth regions. The first is the site of maximum erosion and the latter is the site of maximum accretion.

Close examination of changes in the Baram River estuary region indicates the changes of shoreline to natural to man-made by its shape itself (Figure 7.8). The Baram River, drains into the South China Sea at Kualabaram, and serves as the main means of transportation for timber, sand and rock from regions upstream. The increased sediment delivered by the Baram River into the confluence point may disrupt the efficient navigation of big ships by reducing the depth of the river delta through sediment deposit (this is seen at the dynamic spit in the river mouth with an elongated shape). In order to make navigation efficient and safer, frequent dredging activities and shoreline protection measures were implemented in the area by the port authorities (DID, 2009). This extended the shoreline into the South China Sea to transform the original shape into a comparatively straight shoreline with protective measures against erosion (Figure 7.9).

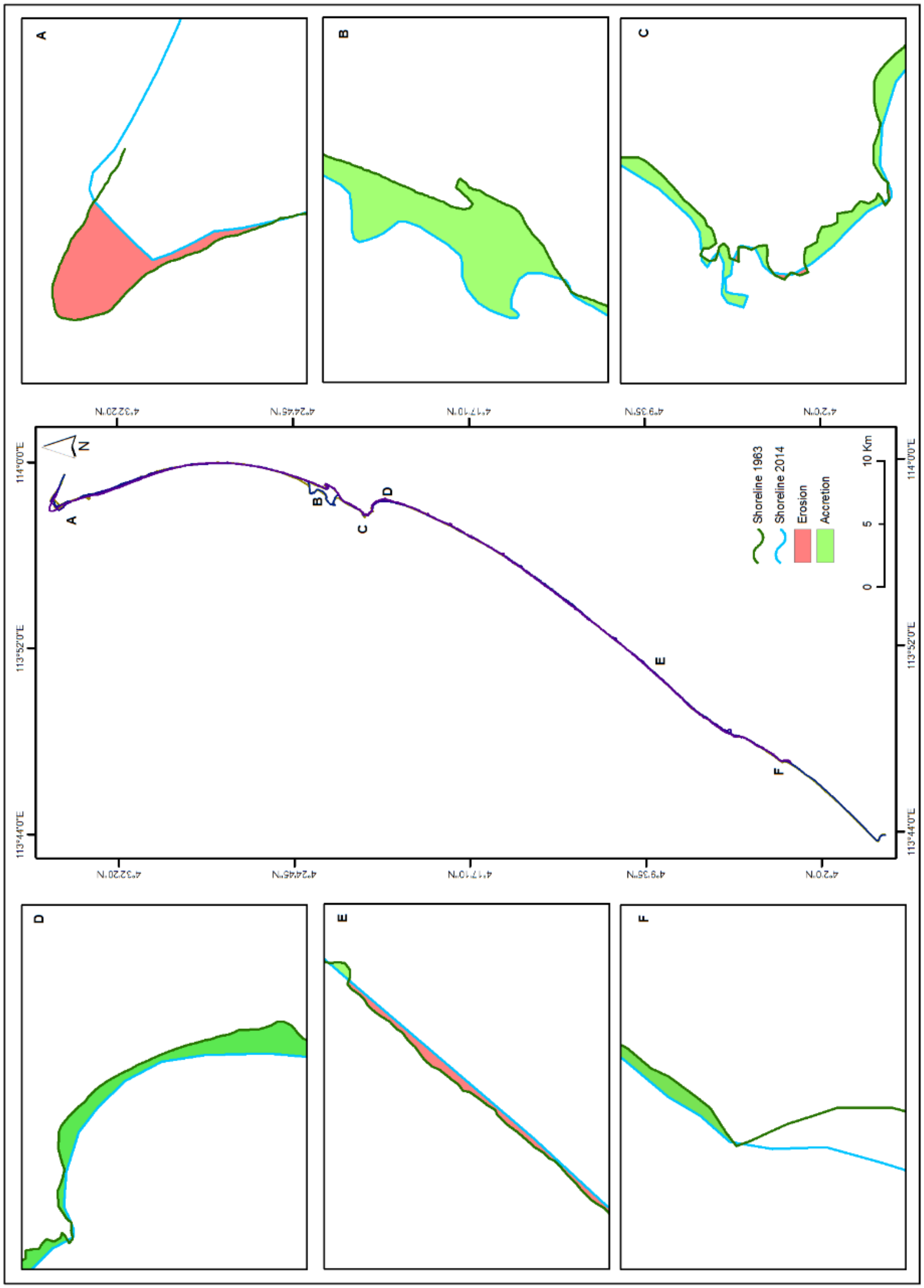
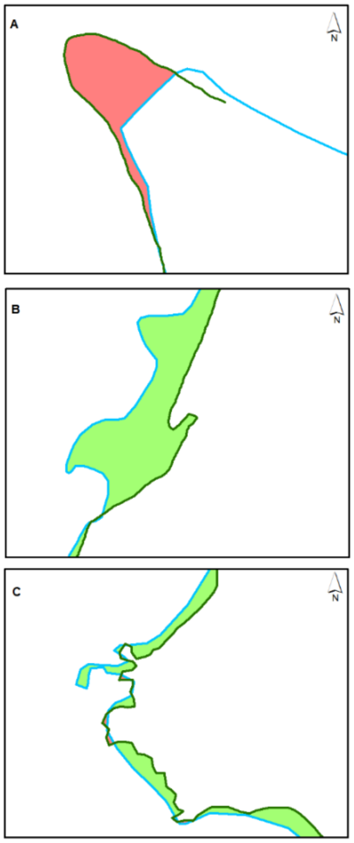


Figure 7.7 Showing major changes in shoreline during the period of 1963 – 2014 (A. Baram River estuary, B. Miri River estuary, C. Tanjong Lobang beach, D. Esplanade beach, E. Hawaii beach and F. Bungai beach).

A study carried out by Tang and Lee (2010) classified the Miri-Kualabaram highway and Marina Bay resort areas as category 1 (high erosion zones causing higher level of threats to infrastructure and facilities along the shoreline) based on the guidelines proposed by the Department of Irrigation and Drainage (1988), from the findings of the National Coastal Erosion Study programme (1986). Similar to the Baram River mouth region, the Tusan Cliffs nearby (Kampong Baraya beach) showed continued erosion caused by strong ocean wave action. Many sandstone cliffs have eroded, in particular shale beds have eroded more rapidly than sandstone cliffs in a short span of time due to wave erosion and also by cliff retreat owing to rainfall induced gully erosion from the land surface (Figure 7.10). This classified as shoreline erosion caused by natural processes.

The Miri River estuary region exhibit the combined effect of natural and man-made factors, which contribute to shoreline accretion. The construction of parallel breakwater structures and the reclamation of land for the Marina Bay projects (2001-2014) were the main man-made activities observed along the Miri coast in the last decade. This construction activity at the Miri River estuary region has changed the natural balance of erosion and accretion through the extended introduction of wave protectors in the sea and increased the accretion process along one side of the extended river mouth. The characteristic shape of the shoreline studied indicates an open concavity towards the South China Sea. This indicates the presence of spatially separated open bays in the region. The open bay shape act as zones of higher erosion through the littoral drift. The mechanism behind the erosion is the powerful waves which interact with the shoreline in an inclined angle (varying with a range of 35 to 45^0), which scoop the material in the wash and backwash zones (Tang and Lee 2010). This eroded material is deposited near the break waters or extended structures, which reduce the sediment carrying capacity of waves by obstructing the path. While looking in to other regions south of Kampong Baraya, the shoreline seems unbroken with little concavity towards the South China Sea. Shorelines in these regions undergoes receive frequent strong wave events, which results in the retreat of shorelines through cliff formation (Tusan beach) and associated landward extension of beaches. The eroded sediments are carried away by the seasonal longshore drifts into different directions.



Natural + Man-made
(Kualabaram estuary)

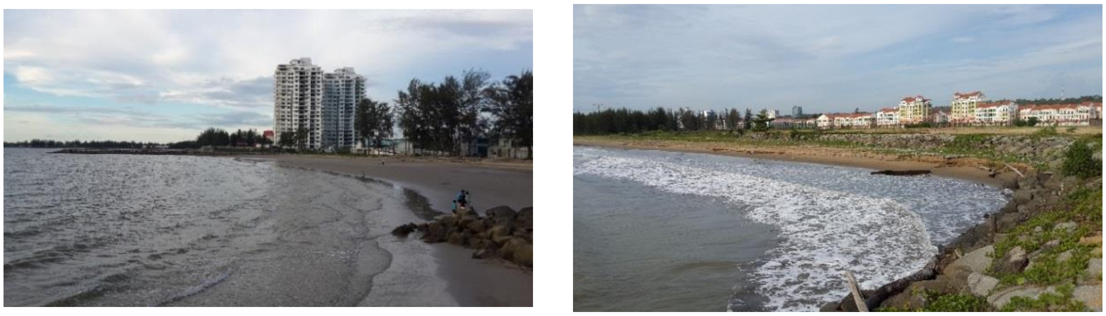
Man-made
(Miri estuary)

Natural
(Tanjong beach)

Figure 7.8 Showing major areas of erosion and accretion (natural, man-made and combine) during the period of 1963-2014

Rock revetment Miri – Kualabaram Road

Rock revetment near Lutong beach



Rock revetment and groins in Tanjong beach

Rock revetment in Marina bay

***Figure 7.9* Rock revetment projects in the shoreline of Miri**

Erosion due to strong waves near Kampong Baraya beach

Erosion due to strong waves near Tanjong beach

Shale beds are eroded more than sandstone cliffs

Cliff retreat and rainfall induced gully erosion

***Figure 7.10* Effect of erosion in the shoreline of Miri**

7.4 Summary

An attempt has been made to characterize the shoreline in the study area through the assessment of LULC patterns and shoreline changes over a period of 51 years (1963 to 2014). Major changes in LULC have been recorded in the conversion of primary forests and secondary forests, which occupied more than 90% of the total area in 1963 and decreased to 5% in 2014. These changes can be attributed to the development of different new classes of LULC in 2014. During this 51 year period, a rapid increase in the number of settlements in the urban and semi-urban areas, the introduction of oil palm plantations, afforestation and secondary forest with oil palms have all taken place. Urban development (the expansion of Miri city, Lutong area, along with the new formal and informal settlement areas in Kualabaram and Taman Tunku) and oil palm plantations have caused the greatest changes in the existing LULC of this region. Similar trends in LULC changes were also noticed along the shoreline of the region which has either eroded or accreted. Shoreline change detection over the different time periods show a decade cyclic reversal of erosion and accretion along the shoreline of Miri. Man-made changes along the shoreline, particularly near the Miri River mouth (Marina bay area), rapidly expanded after the year 2001 as construction of seawalls, groins, breakwater structures and reclamation activities occurred. Whereas the coupled effect of natural and man-made factors were the cause of the erosion and accretion process along the shoreline of Tanjong Lobang and Esplanade beaches.

The assessment of shoreline erosion and accretion within the different periods showing the maximum erosion of 660 acres which was observed during the period of 1991-2001 and the maximum accretion was observed from 2001-2014 with 709 acres of shoreline. While comparing the base line information from the year 1963 with assessments from later years the years 2001 and 2014 show the maximum erosion of 816 acres and accretion of 723 acres respectively. This can be attributed to the implementation of rock revetments, groins and breakwater structures along the eroding beaches, during the period of 1991-2001. Simultaneously, a large quantity of sediment input from the Baram River, carried by the long-shore currents were deposited along the beaches wherever the break water structures were present. The reclamation of the sea area near the Miri River estuary for the development of the Marina Bay project also contributed to the higher rate of accretion during 2001-2014. The total shoreline changes during the last 51 years, show more accretion than erosion with variable effects by natural, man-made or combined factors. During the study period a total of 546 acres of shoreline was eroded and 723 acres of shoreline were constructed or accreted. The spatial pattern of shoreline changes during the period facilitated the identification of four major zones of erosion and accretion along the total stretch of shoreline studied i.e., the Baram River mouth (erosion), Miri River estuary, Tanjong beach and Esplanade beach (accretion). The long-shore currents, strong waves (natural) were amplified by manmade intervention in the form of construction of the Resort city and sports complex at Marina bay, development of recreational areas (Bungai and Tanjong beach) and dredging activities at the Kualabaram River mouth (human activities) are major causes of the erosion/deposition process along the Miri coast. The present findings of the study serve as the background information for the planning of future developmental activities by the coastal management board, environmental protection department and sustainable development authorities.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

Water, sediment, and aquatic organisms (fish, shrimp, crabs and bivalves) were collected along a 74 Km stretch of coast during the monsoon and post-monsoon seasons. Considering the mobility and bioavailability of trace metals in the water column, the water samples were analyzed after filtration through Whatman No.1 filter paper which also included the particulate form of metals < 11 µm. The water column chemistry was found to be influenced by the Baram and Miri Rivers and several smaller rivers/streams. The concentrations of trace metals in the water column can be ranked in the following decreasing order: Monsoon: Fe > Pb > Ni > Co > Zn > Rb > Cd > Cu > Mn; Post-monsoon: Pb > Ni > Co > Zn > Cr > Fe > Cd > Cu > Rb > Mn.

In order to analyze the distribution of metals between the water column and the sediments, the partition coefficient (K_d) was calculated for all the trace metals. On average, the K_d values of Cu, Pb, Zn and Mn exhibit the following order in different fractions: exchangeable > reducible > oxidizable; Cd, Co and Ni values are in the order exchangeable > oxidizable > reducible. The K_d value of Fe is higher in the reducible fraction followed by exchangeable and oxidizable fractions. Of all these elements/metals analyzed, Cu in the exchangeable fraction showed the highest affinity to accumulate in the sediments which is followed by Cd, Zn, Mn, Pb=Ni, Co, Fe. The changes in environmental conditions can greatly affect the exchange of Cu, Pb, Zn and Mn between water and sediment since these metals are in the exchangeable fraction and most mobile.

The association of elements/metals in the exchangeable fraction can be ranked as Cu > Zn > Mn > Pb > Co > Fe > Ni > Cd > Cr during the monsoon and Cu > Zn > Pb > Mn > Cd > Co > Fe > Ni > Cr during the post-monsoon. Copper and Zn were dominant in the exchangeable fraction, Pb and Cd were dominant in the non-residual fraction (F1+F2+F3) for both seasons. The highest proportion of Cd was in the oxidizable fraction, whereas Fe, Co, Ni and Cr were dominantly in the residual fraction for both seasons. Therefore, Fe, Co, Ni and Cr, cannot easily remobilize under normal conditions. Major proportions of Cu, Cd, Pb and Zn are associated with the non-residual fraction, indicating higher mobility. The results revealed that sulphide oxidation within the river basin was the main source for Cu, Zn, Co, Ni which are leached out from the source region, transported, and delivered to the South China Sea by the Baram River. The distribution of Cu, Zn, Cr, and Ni was influenced by the riverine supply as well as sulphide oxidation occurring within the coastal sediments. Lead and Cd were found to be contributed by atmospheric fallout.

Based on the geo-accumulation index and contamination factors, the beach sediments are contaminated by Cu and Zn and may pose adverse biological threats to aquatic organisms in the near future which was further confirmed by the RAC values. The analyzed elements were compared with SQGs values such as, ERL and ERM, to evaluate the degree of contamination connected with biological effects. Lead and Cr are observed less frequently than ERL, whereas Cd, Ni and Zn values are between ERL and ERM for both seasons; Cu exceeds the ERM values, and the biological adverse effect of Cu is 7% during the monsoon and 45% during post-monsoon. The trace metals are comparable with the UCC values, except Cu and Zn in all locations for both seasons.

In aquatic organisms, the greatest concentration of elements/metals was noticed in the liver followed by the gills, gonads and muscles. The difference in the concentrations of elements/metals in various tissues was due to the presence of metal-binding proteins such as metallothioneins. Bioaccumulation factors suggest the essential elements (Cu and Zn) are accumulated with higher efficiency and non-essential elements (Pb and Cd) are bio-accumulated least efficiently in all aquatic organisms of this study. Due to the greater concentration of Cu and Zn in the water and sediment column, aquatic organism accumulates higher concentrations in their tissues. The body size (length and weight) of the aquatic organisms play a significant role in the bioaccumulation of elements in their muscles and other organs. The accumulation of elements/metals varied between the species and their organs due to other factors such as the age, size, habitat, feeding nature, swimming behavior and the geographical nature of the study area.

Based on the human health risk assessment index, humans would not experience any significant health risks at either ingestion rates by consumers. Lead and Cd in certain fish species showed HI (1>) could cause some health effects in humans if the contaminated fish were consumed at greater quantities. According to national and international seafood guidelines, the level of trace/heavy metals (Cu, Cd, Pb, Zn, Mn, Co, Ni, Cr and Rb) in the muscles of all the analyzed species of fish, shrimp, crab and bivalve were below the MPLs of the WHO (1989), MFR (1985) and FAO (1983) on wet weight basis.

In order to assess the effect of urbanization along the Miri coast, changes in the LULC were studied. Major changes in the LULC have been recorded in the conversion of primary forests into secondary forests. Primary and secondary forests together occupied more than 90% of the total area in 1963 but forest clearing resulted in a decline to 5% in 2014. Shoreline change detection, over the different time periods, showed a 10-year cyclic reversal of erosion and accretion processes along the shoreline of Miri. The man-made changes in the shoreline were observed to be the greatest after 2001 as construction of seawalls, groins, breakwater structures and reclamation activities along the shoreline, in particular near the Miri River outlet (Marina bay area), took place. The total shoreline changes during the last 51 years showed more accretion than erosion, with variable effects of natural, man-made and combined factors.

To conclude, the overall aim of the research is achieved by investigating the bioavailable trace/heavy elements in the studied compartments through the proposed standard protocols. The degree of trace/heavy metal contamination, enrichment and the potential toxicological significance in seawater, sediments and marine biota from the Miri coast are still under the permissible limits of environmental guideline values. Except for Cu and Zn, all the remaining elements were below the SQG values. Natural processes are the dominating factors, which control the geochemistry of the elements in water and sediments. The studied elements would not pose any serious threat to the environment which was clearly demarcated by the multivariate statistical analysis and risk assessment calculations. Even though there are differences in the level of metals between the species and organs, no metal was above the maximum permissible limit of national and international standards. Provided the current ecosystem is maintained and does not deteriorate any further, the health and safety risks to humans and other species is within the acceptable range.

8.2 Recommendations:

- Within the purview of this work, trace elements toxicity was not obvious in the biota. However, two things should be considered here: i) the city is expanding and waste generation is on the rise; ii) there is a possibility for the trace elements exceeding the recommended level in the biota in the near future. Thus, a regular monitoring frame work should be established for assessing trace elements toxicity in the coastal sediments.
- Coastal areas are being converted into settlements and other manmade developments, thus these impacts on coastal morphology should be monitored periodically.

8.3 Future directions for research

- This study showed evidence of accumulation of trace elements especially, Cu and Zn, in fish, crabs, bivalves and shrimp. These elements have not reached toxic levels in the biota, compared to national and international standards. Based on lithology, earlier literature and geochemical processes observed occurring along the coast, there is a potential for other toxic elements like As and Hg to increase in the environment. The level of these metals in the biota should be studied.
- Sexual differences in metal accumulation was found in crabs. Similar studies should be conducted on fish and shrimp.
- Sulphide oxidation was one of the dominant processes responsible for leaching of Cu and Zn from the sedimentary formations of the study area. The same process is thought to occur in marine sediments along the south western segment. During such a process, iron, manganese and other trace elements may be released to the water column and transported to the open ocean. Mineralogical and pore water studies of core sediments collected from this area may prove to be very useful tools in deciphering the inherent mechanisms of these processes. Further, additional studies would also be useful in the quantification of trace elements, remobilization and its export to the open ocean.
- Desorption of Cd from riverine particulates can be studied by collecting water and suspended sediments in the estuarine region of the Baram river. Also, the data in this study indicated evidence for the removal of water column Cd by phytoplankton where enough phosphate is available. Though this method of Cd removal is widely reported

for open oceanic regions, this may be the first study pointing out the prevalence of such a mechanism in coastal areas. This aspect should be further explored.

- Trace metal association with suspended matter should be studied since a large percentage of suspended sediments are delivered by rivers. Their dynamics upon entering the estuarine and coastal ecosystem can be thoroughly understood by estimation of their partition coefficient between water and suspended load. While such a work should point out the direction or pathways of elemental mobility, it should also be useful to infer their destiny. Suspended particle sizes ranges widely and influence the chemistry of seawater. A clear understanding of this process could also pave the way for elemental accumulation in the biota.
- This study clearly showed the influence of sediment dynamics on elemental distribution with the dominance of fine sand in the south-western segment and silt being predominant in the northeast segment. Such grain size distribution has the chance of being affected by future changes in the geomorphology and hydrological regime. In this respect, this study was able to demonstrate the accretion/erosion of the coastal area and its periodicity. The linkages between geomorphology and trace elements distribution in the sediments is an interesting and still unexplored area for future research. Such dynamism in sediment distribution is not only controlled by river input, but other processes such as littoral currents, waves and tidal levels may also play important roles. Exploration of the linkages among all these factors is an important aspect of coastal management for a coastal town like Miri in the years ahead.
- Determine seasonal variations of elements and their bioaccumulation in aquatic organisms from marine, estuarine and riverine species through a systematic study on fish age and size *vs* elemental accumulation.
- Carrier phase analysis: linkages between source rock and sediments with geochemical relationships.

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Partition coefficient Kd=sediment/water Exchangeable fraction (monsoon season)								
Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn
BUN 01	14.30	40.73	133.75	16.28	33.11	0.37	2.33	0.39
BUN 02	10.86	0.03	0.00	0.05	0.02	2.21	0.31	2.25
BUN 03	12.40	0.05	0.00	0.03	0.02	2.53	0.35	3.31
BUN 04	16.95	0.06	0.00	0.02	0.01	3.72	0.41	3.41
KBR 01	17.45	0.02	0.01	0.01	0.03	2.84	0.63	1.34
KBR 02	16.10	0.02	0.01	0.04	0.04	2.67	0.67	1.40
KBR 03	16.58	0.03	0.01	0.04	0.03	2.83	0.67	1.48
HWB 01	16.05	0.03	0.00	0.09	0.03	2.88	0.63	1.11
ESP 01	24.67	0.01	0.01	0.02	0.04	3.35	0.67	3.76
ESP 02	25.12	0.02	0.01	0.02	0.04	3.42	0.71	3.43
ESP 03	25.17	0.01	0.01	0.03	0.05	3.54	0.78	2.63
ESP 04	24.36	0.02	0.00	0.04	0.04	3.65	0.70	3.16
ESP 05	30.22	0.02	0.00	0.05	0.04	3.63	0.63	1.83
TLB 01	20.49	0.01	0.00	0.06	0.00	2.99	0.36	0.76
TLB 02	23.01	0.03	0.00	0.05	0.01	3.45	0.39	0.92
MRE 01	12.92	0.03	0.00	0.02	0.01	2.37	0.86	3.51
MRE 02	8.65	0.04	0.00	0.01	0.00	1.57	0.44	1.24
MRE 03	8.69	0.04	0.00	0.01	0.00	1.78	0.35	0.73
MRE 04	11.31	0.01	0.00	0.01	0.00	2.26	0.36	1.00
PSU 01	17.75	0.02	0.00	0.07	0.00	2.57	0.37	1.42
PSU 02	16.76	0.01	0.00	0.07	0.00	2.59	0.41	1.52
LUT 01	22.67	0.02	0.00	0.02	0.02	3.59	0.72	1.90
LUT 02	22.67	0.02	0.00	0.00	0.02	3.73	0.75	1.73
LUT 03	28.00	0.01	0.00	0.00	0.01	3.99	0.65	1.15
FLC 03	17.96	0.01	0.00	0.00	0.02	2.55	0.71	1.22
KUB 01	18.87	0.01	0.00	0.02	0.01	3.52	1.18	0.52

Partition coefficient Kd=sediment/water Reducible fraction (monsoon season)								
Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn
BUN 01	2.01	0.02	0.00	0.05	0.02	0.21	1.54	1.71
BUN 02	1.80	0.02	0.00	0.04	0.01	0.20	1.49	1.14
BUN 03	2.13	0.02	0.00	0.05	0.01	0.24	1.50	1.39
BUN 04	2.03	0.03	0.00	0.01	0.00	0.22	1.32	0.66
KBR 01	1.43	0.01	0.01	0.01	0.02	0.17	1.61	0.75
KBR 02	1.35	0.02	0.01	0.03	0.03	0.14	1.68	0.87
KBR 03	1.20	0.01	0.01	0.04	0.03	0.22	1.47	0.83
HWB 01	1.19	0.03	0.01	0.07	0.04	0.14	1.33	0.68
ESP 01	2.86	0.03	0.00	0.00	0.03	0.23	1.35	1.10
ESP 02	2.44	0.02	0.01	0.02	0.03	0.18	1.34	0.97
ESP 03	2.26	0.02	0.00	0.02	0.03	0.18	1.50	0.72
ESP 04	2.42	0.03	0.00	0.04	0.04	0.20	1.17	0.55
ESP 05	1.72	0.03	0.00	0.04	0.03	0.15	1.09	0.45
TLB 01	2.92	0.01	0.00	0.05	0.00	0.29	0.60	0.31
TLB 02	3.20	0.02	0.00	0.05	0.00	0.33	0.56	0.27
MRE 01	2.13	0.05	0.00	0.02	0.01	0.26	2.21	1.01
MRE 02	1.40	0.04	0.00	0.01	0.00	0.19	1.16	0.51
MRE 03	1.26	0.04	0.00	0.02	0.01	0.18	0.90	0.31
MRE 04	1.25	0.02	0.00	0.01	0.01	0.17	0.77	0.41
PSU 01	1.90	0.03	0.00	0.08	0.00	0.14	1.05	0.33
PSU 02	2.05	0.02	0.00	0.07	0.00	0.18	0.88	0.34
LUT 01	2.33	0.03	0.00	0.00	0.00	0.21	1.12	0.41
LUT 02	2.38	0.04	0.00	0.00	0.01	0.23	1.19	0.39
LUT 03	2.03	0.02	0.00	0.00	0.00	0.20	0.91	0.24
FLC 03	1.65	0.03	0.00	0.00	0.00	0.18	1.54	0.43
KUB 01	2.31	0.02	0.00	0.00	0.01	0.25	1.17	0.24

Partition coefficient Kd=sediment/water Oxidizable fraction (monsoon season)

Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn
BUN 01	0.26	0.00	0.03	0.07	0.06	0.13	0.21	0.95
BUN 02	0.22	0.01	0.03	0.06	0.06	0.11	0.20	0.80
BUN 03	0.43	0.01	0.02	0.06	0.06	0.13	0.21	0.73
BUN 04	0.34	0.01	0.03	0.04	0.04	0.14	0.25	1.77
KBR 01	0.28	0.00	0.03	0.04	0.07	0.11	0.18	0.33
KBR 02	0.25	0.00	0.03	0.07	0.08	0.11	0.18	0.40
KBR 03	0.15	0.01	0.03	0.08	0.06	0.10	0.16	0.47
HWB 01	0.22	0.01	0.03	0.08	0.08	0.11	0.20	0.44
ESP 01	0.43	0.01	0.03	0.02	0.06	0.10	0.15	0.80
ESP 02	0.37	0.01	0.03	0.04	0.07	0.09	0.15	0.63
ESP 03	0.36	0.00	0.01	0.05	0.07	0.11	0.15	0.25
ESP 04	0.36	0.01	0.01	0.05	0.08	0.10	0.13	0.27
ESP 05	0.42	0.01	0.01	0.07	0.07	0.11	0.13	0.21
TLB 01	0.37	0.00	0.01	0.08	0.02	0.09	0.07	0.26
TLB 02	0.38	0.01	0.01	0.07	0.02	0.18	0.06	0.24
MRE 01	0.35	0.01	0.00	0.04	0.03	0.12	0.21	0.49
MRE 02	0.19	0.02	0.01	0.03	0.03	0.09	0.11	0.24
MRE 03	0.26	0.01	0.01	0.02	0.04	0.09	0.09	0.25
MRE 04	0.18	0.02	0.01	0.01	0.04	0.08	0.08	0.25
PSU 01	0.31	0.02	0.01	0.09	0.02	0.09	0.11	0.17
PSU 02	0.42	0.01	0.01	0.11	0.03	0.10	0.10	0.13
LUT 01	0.34	0.01	0.03	0.00	0.05	0.12	0.16	0.14
LUT 02	0.48	0.01	0.02	0.00	0.04	0.13	0.17	0.12
LUT 03	0.36	0.01	0.03	0.03	0.04	0.12	0.14	0.18
FLC 03	0.23	0.00	0.03	0.02	0.04	0.11	0.19	0.20
KUB 01	0.34	0.00	0.02	0.02	0.05	0.10	0.14	0.08

Partition coefficient (Kd)=sediment/water for Exchangeable fraction (POM season)

Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr
BUN 01	45.558	0.102	0.014	0.015	0.010	2.918	16.606	1.550	0.060
BUN 02	44.762	0.101	0.012	0.011	0.013	3.398	22.067	1.360	0.031
BUN 03	48.691	0.054	0.012	0.019	0.011	3.769	21.430	1.749	0.023
BUN 04	40.496	0.160	0.012	0.012	0.008	3.349	20.895	1.443	0.006
KBR 01	25.193	0.078	0.014	0.016	0.012	2.171	14.905	2.287	0.043
KBR 02	21.912	0.096	0.012	0.002	0.011	1.956	13.268	1.643	0.052
KBR 03	31.377	0.133	0.014	0.006	0.016	2.953	15.679	2.191	0.026
HWB 01	20.985	0.072	0.014	0.001	0.013	1.889	12.109	1.370	0.022
ESP 01	16.033	0.077	0.013	0.012	0.019	1.939	13.687	2.122	0.033
ESP 02	13.410	0.078	0.013	0.009	0.018	1.828	14.569	1.279	0.026
ESP 03	38.268	0.119	0.005	0.012	0.007	3.403	26.886	2.374	0.016
ESP 04	13.465	0.065	0.005	0.020	0.003	1.779	16.308	2.720	0.003
ESP 05	15.294	0.078	0.009	0.014	0.006	2.043	16.034	1.822	0.011
TLB 01	14.922	0.114	0.009	0.011	0.004	2.076	18.194	1.238	0.009
TLB 02	12.299	0.055	0.011	0.004	0.010	2.044	12.213	0.450	0.048
PVR 01	7.486	0.036	0.004	0.015	0.012	1.139	20.000	2.619	0.118
MRE 01	10.905	0.031	0.005	0.003	0.021	1.718	20.948	1.129	0.093
MRE 02	5.777	0.046	0.007	0.000	0.008	0.947	16.371	1.314	0.087
MRE 03	8.920	0.062	0.009	0.011	0.007	1.363	15.785	1.346	0.105
MRE 04	11.761	0.044	0.009	0.010	0.012	2.007	15.879	0.815	0.099
PSU 01	12.558	0.083	0.009	0.010	0.010	1.902	11.403	0.526	0.015
PSU 02	9.492	0.142	0.010	0.010	0.010	1.438	5.471	0.429	0.016
LUT 01	11.516	0.029	0.009	0.005	0.013	2.024	9.815	0.633	0.006
LUT 02	12.411	0.043	0.011	0.001	0.017	1.855	8.739	0.778	0.000
LUT 03	19.813	0.048	0.014	0.010	0.014	2.831	11.279	0.800	0.031
FLC 01	32.949	0.070	0.000	0.001	0.010	4.088	7.203	0.586	0.070
FLC 02	18.994	0.021	0.002	0.007	0.009	2.719	4.382	0.791	0.017
FLC 03	34.735	0.108	0.012	0.023	0.012	3.839	15.882	0.751	0.011
KUB 01	9.873	0.013	0.002	0.019	0.007	1.511	25.196	0.696	0.017
KUB 02	22.954	0.185	0.014	0.022	0.021	2.989	6.153	0.930	0.018
KUB 03	10.644	0.007	0.002	0.015	0.017	1.724	22.608	0.994	0.050

Partition Coefficient (Kd) for reducible fraction (POM season)									
Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr
BUN 01	5.095	0.022	0.014	0.012	0.007	0.327	20.814	0.694	0.061
BUN 02	3.817	0.026	0.014	0.016	0.006	0.257	30.683	0.765	0.066
BUN 03	4.527	0.020	0.014	0.016	0.001	0.323	23.251	0.636	0.025
BUN 04	6.138	0.038	0.010	0.008	0.006	0.292	26.705	0.528	0.038
KBR 01	2.688	0.031	0.012	0.014	0.007	0.185	24.465	0.963	0.048
KBR 02	2.520	0.030	0.012	0.005	0.003	0.185	20.223	0.660	0.070
KBR 03	3.738	0.045	0.014	0.000	0.010	0.293	19.624	0.786	0.041
HWB 01	2.840	0.023	0.014	0.000	0.006	0.250	16.122	0.585	0.041
ESP 01	1.580	0.035	0.013	0.012	0.015	0.122	14.426	0.446	0.014
ESP 02	1.073	0.037	0.014	0.004	0.014	0.077	17.466	0.456	0.048
ESP 03	3.874	0.055	0.004	0.010	0.000	0.311	23.653	0.554	0.045
ESP 04	1.480	0.041	0.005	0.008	0.000	0.126	20.752	0.405	0.031
ESP 05	1.182	0.038	0.009	0.015	0.002	0.093	14.051	0.259	0.021
TLB 01	2.199	0.040	0.009	0.002	0.004	0.205	16.877	0.233	0.046
TLB 02	0.982	0.024	0.009	0.005	0.001	0.054	9.681	0.173	0.098
PVR 01	1.514	0.030	0.002	0.021	0.014	0.183	83.877	1.468	0.203
MRE 01	1.187	0.036	0.005	0.003	0.020	0.120	35.640	0.369	0.118
MRE 02	0.683	0.038	0.005	0.006	0.011	0.087	29.835	0.686	0.186
MRE 03	1.435	0.039	0.009	0.013	0.008	0.156	27.587	0.586	0.166
MRE 04	1.203	0.029	0.007	0.000	0.006	0.138	20.242	0.360	0.139
PSU 01	1.311	0.032	0.009	0.008	0.006	0.125	10.063	0.207	0.027
PSU 02	3.177	0.040	0.009	0.006	0.005	0.349	8.632	0.231	0.044
LUT 01	1.382	0.017	0.011	0.003	0.010	0.146	10.140	0.380	0.059
LUT 02	1.104	0.029	0.011	0.005	0.013	0.103	14.783	0.746	0.130
LUT 03	1.611	0.028	0.013	0.010	0.011	0.159	18.803	0.516	0.111
FLC 01	1.505	0.036	0.000	0.000	0.012	0.139	16.342	0.138	0.089
FLC 02	1.308	0.025	0.000	0.002	0.000	0.127	22.278	0.438	0.036
FLC 03	3.804	0.052	0.010	0.013	0.000	0.411	17.197	0.317	0.024
KUB 01	1.109	0.016	0.002	0.009	0.006	0.135	19.383	0.364	0.042
KUB 02	1.867	0.079	0.012	0.016	0.012	0.162	26.127	0.737	0.081
KUB 03	1.897	0.028	0.000	0.022	0.017	0.209	51.044	0.623	0.085

Partition Coefficient (Kd) for oxidizable fraction (POM season)									
Sample ID	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr
BUN 01	0.805	0.007	0.028	0.012	0.023	0.093	1.240	0.556	0.338
BUN 02	0.557	0.006	0.028	0.032	0.023	0.066	1.735	0.550	0.279
BUN 03	0.600	0.009	0.026	0.024	0.024	0.091	1.677	0.449	0.231
BUN 04	0.894	0.005	0.023	0.024	0.022	0.109	1.690	0.335	0.270
KBR 01	0.465	0.011	0.030	0.032	0.025	0.055	1.492	0.718	0.246
KBR 02	0.425	0.005	0.027	0.018	0.026	0.058	1.160	0.428	0.234
KBR 03	0.607	0.009	0.027	0.003	0.028	0.071	1.416	0.605	0.256
HWB 01	0.577	0.008	0.027	0.011	0.032	0.074	1.194	0.363	0.273
ESP 01	0.322	0.007	0.025	0.021	0.037	0.077	1.548	0.405	0.221
ESP 02	1.310	0.005	0.023	0.006	0.036	0.075	1.787	0.401	0.281
ESP 03	0.823	0.004	0.014	0.016	0.013	0.108	2.116	0.451	0.261
ESP 04	0.436	0.006	0.018	0.022	0.022	0.081	2.058	0.250	0.231
ESP 05	0.294	0.006	0.020	0.024	0.020	0.054	1.624	0.227	0.204
TLB 01	0.613	0.008	0.020	0.020	0.026	0.086	1.910	0.276	0.352
TLB 02	1.696	0.007	0.020	0.015	0.025	0.042	1.213	0.245	0.328
PVR 01	0.105	0.006	0.013	0.009	0.029	0.048	3.110	0.151	0.513
MRE 01	0.188	0.013	0.018	0.013	0.046	0.073	2.173	0.156	0.289
MRE 02	0.351	0.012	0.018	0.015	0.022	0.095	1.899	0.223	0.292
MRE 03	0.310	0.005	0.023	0.022	0.026	0.083	1.798	0.289	0.290
MRE 04	0.373	0.001	0.020	0.012	0.028	0.099	1.563	0.244	0.279
PSU 01	0.032	0.001	0.022	0.022	0.031	0.054	1.183	0.269	0.199
PSU 02	0.804	0.005	0.022	0.022	0.036	0.095	0.921	0.252	0.172
LUT 01	0.493	0.001	0.022	0.012	0.036	0.086	0.878	0.209	0.188
LUT 02	0.315	0.000	0.024	0.014	0.035	0.067	1.109	0.304	0.173
LUT 03	0.633	0.005	0.025	0.025	0.033	0.112	1.294	0.239	0.213
FLC 01	0.250	0.009	0.010	0.000	0.025	0.055	1.721	0.131	0.389
FLC 02	0.162	0.004	0.011	0.004	0.024	0.060	1.986	0.106	0.124
FLC 03	0.865	0.008	0.022	0.023	0.020	0.117	1.641	0.329	0.157
KUB 01	0.175	0.002	0.015	0.010	0.025	0.074	2.151	0.182	0.246
KUB 02	0.356	0.004	0.027	0.034	0.035	0.095	1.360	0.373	0.179
KUB 03	0.426	0.001	0.010	0.003	0.026	0.240	3.790	0.237	0.293

Correlation between Kd values and some water quality parameters Exchangeable fraction (monsoon season)

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Eh	PO4	SO4	NH$_3$N	CO$_3$	HCO$_3$	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.000																					
Pb	-.146	1.000																				
Cd	-.145	1.000	1.000																			
Co	-.145	1.000	1.000	1.000																		
Ni	-.143	1.000	1.000	1.000	1.000																	
Zn	.777	-.622	-.622	-.622	-.621	1.000																
Fe	.083	.858	.858	.857	.859	-.347	1.000															
Mn	.212	-.281	-.281	-.282	-.280	.350	-.197	1.000														
Eh	-.249	.125	.125	.126	.125	-.194	.185	-.310	1.000													
PO4	-.150	.927	.927	.927	.927	-.570	.858	-.378	.273	1.000												
SO4	.191	-.146	-.147	-.145	-.146	.347	-.294	.503	-.337	-.177	1.000											
NH$_3$N	-.379	.483	.483	.482	.483	-.384	.374	.032	.276	.516	.034	1.000										
CO$_3$	-.279	.112	.111	.112	.111	-.287	-.148	.058	-.156	-.028	.279	-.186	1.000									
HCO$_3$	.261	.041	.040	.042	.040	.181	-.175	.305	-.468	-.229	.496	-.206	.258	1.000								
Mg	.059	.126	.126	.126	.125	-.042	-.152	.325	-.536	-.181	.467	-.196	.534	.882	1.000							
Ca	.032	-.135	-.135	-.134	-.134	.107	.084	-.201	.421	.173	-.209	-.003	-.229	-.700	-.844	1.000						
Cl	.097	.101	.100	.102	.100	-.007	-.181	.365	-.506	-.108	.573	-.285	.652	.782	.856	-.461	1.000					
K	-.011	.071	.070	.070	.070	.125	-.167	.487	-.344	-.087	.752	.130	.478	.592	.652	-.409	.708	1.000				
pH	.187	-.218	-.218	-.216	-.218	.141	-.365	.319	-.498	-.362	.421	-.571	.493	.559	.610	-.264	.731	.448	1.000			
DO	-.195	.315	.314	.315	.314	-.385	.028	.166	-.226	.137	.300	.170	.390	.565	.629	-.514	.583	.274	.160	1.000		
TUR	-.180	.312	.312	.312	.313	-.146	.379	.033	.451	.465	-.039	.846	-.357	-.426	-.547	.424	-.484	-.063	-.650	-.090	1.000	
SAL	.126	.091	.091	.093	.091	.027	-.185	.352	-.522	-.138	.595	-.290	.653	.833	.899	-.528	.985	.719	.756	.579	-.507	1.000

Correlation between Kd values and some water quality parameters Reducible fraction (monsoon season)

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Eh	PO4	SO4	NH_3N	CO_3	HCO_3	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.000																					
Pb	-.058	1.000																				
Cd	-.419	-.371	1.000																			
Co	-.028	-.220	.120	1.000																		
Ni	-.179	-.114	.564	.131	1.000																	
Zn	.719	-.069	-.364	-.104	-.363	1.000																
Fe	-.273	.218	.327	-.161	.369	-.193	1.000															
Mn	-.043	-.105	.215	.138	.401	-.006	.672	1.000														
Eh	-.264	-.481	.221	.072	-.014	.045	.086	.055	1.000													
PO4	-.126	-.245	.140	.180	.169	-.032	.266	.543	.273	1.000												
SO4	.240	-.072	-.036	.173	.035	.153	-.064	.189	-.337	-.177	1.000											
NH_3N	-.154	-.210	-.034	.043	-.049	-.004	.410	.589	.276	.516	.034	1.000										
CO_3	-.213	.168	.070	.290	.120	-.055	-.107	.163	-.156	-.028	.279	-.186	1.000									
HCO_3	.571	.067	-.562	.254	-.252	.297	-.443	-.035	-.468	-.229	.496	-.206	.258	1.000								
Mg	.361	.281	-.543	.189	-.219	.190	-.334	.081	-.536	-.181	.467	-.196	.534	.882	1.000							
Ca	-.353	-.388	.781	-.007	.427	-.220	.355	.049	.421	.173	-.209	-.003	-.229	-.700	-.844	1.000						
Cl	.249	.077	-.163	.287	.047	.073	-.199	.215	-.506	-.108	.573	-.285	.652	.782	.856	-.461	1.000					
K	.165	.129	-.153	.101	-.042	.120	-.073	.216	-.344	-.087	.752	.130	.478	.592	.652	-.409	.708	1.000				
pH	.122	.290	-.033	.337	.043	-.101	-.178	-.106	-.498	-.362	.421	-.571	.493	.559	.610	-.264	.731	.448	1.000			
DO	.095	-.056	-.333	.260	-.017	.074	-.052	.458	-.226	.137	.300	.170	.390	.565	.629	-.514	.583	.274	.160	1.000		
TUR	-.123	-.432	.342	-.011	.204	-.021	.452	.521	.451	.465	-.039	.846	-.357	-.426	-.547	.424	-.484	-.063	-.650	-.090	1.000	
SAL	.285	.114	-.228	.331	.019	.103	-.256	.168	-.522	-.138	.595	-.290	.653	.833	.899	-.528	.985	.719	.756	.579	-.507	1.000

Correlation between Kd values and some water quality parameters Oxidizable fraction (monsoon season)

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Eh	PO4	SO4	NH_3N	CO_3	HCO_3	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.000																					
Pb	.010	1.000																				
Cd	-.105	-.073	1.000																			
Co	-.129	-.219	-.107	1.000																		
Ni	-.125	.082	.408	-.034	1.000																	
Zn	.304	.093	.237	-.083	.005	1.000																
Fe	-.046	.091	.365	-.065	.740	.247	1.000															
Mn	-.225	.081	.075	.381	.218	.122	.226	1.000														
Eh	.373	.117	-.246	-.093	-.127	.061	-.056	.285	1.000													
PO4	.230	.361	-.375	-.165	-.248	-.117	-.327	.080	.414	1.000												
SO4	-.370	-.108	-.143	-.036	-.032	-.292	-.144	-.416	-.333	-.111	1.000											
NH_3N	.111	.086	-.455	-.180	-.295	-.282	-.536	-.227	.228	.199	.121	1.000										
CO_3	.150	-.291	.254	.023	.000	.108	.200	-.396	-.168	-.348	.301	-.272	1.000									
HCO_3	-.510	-.297	.322	-.040	.370	-.047	.394	-.046	-.463	-.708	.514	-.242	.253	1.000								
Mg	-.340	-.514	.403	.091	.296	.031	.326	-.231	-.552	-.796	.499	-.284	.527	.883	1.000							
Ca	.334	.542	-.399	-.191	-.347	-.066	-.304	-.010	.439	.801	-.235	.061	-.215	-.699	-.840	1.000						
Cl	-.256	-.362	.266	-.051	.143	.006	.239	-.438	-.523	-.534	.599	-.377	.647	.783	.855	-.451	1.000					
K	-.186	-.342	-.001	.042	.041	-.234	-.072	-.484	-.357	-.403	.774	.116	.474	.593	.651	-.403	.706	1.000				
pH	-.123	-.270	.348	-.082	.203	.091	.169	-.292	-.468	-.429	.412	-.533	.535	.572	.652	-.294	.778	.478	1.000			
DO	-.217	-.294	.259	-.013	-.009	.098	.180	-.222	-.313	-.446	.370	.005	.385	.611	.650	-.518	.598	.273	.275	1.000		
TUR	.125	.334	-.632	-.226	-.432	-.218	-.553	-.110	.419	.489	.006	.831	-.414	-.449	-.615	.489	-.542	-.085	-.616	-.233	1.000	
SAL	-.271	-.376	.290	-.035	.180	-.009	.267	-.389	-.531	-.591	.623	-.373	.649	.831	.897	-.518	.986	.719	.796	.605	-.558	1.000

Correlation between Kd values and some water quality parameters Exchangeable fraction (POM season)

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr	Eh	PO4	SO4	CO_3	HCO_3	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.00																					
Pb	.470	1.00																				
Cd	.326	.527	1.00																			
Co	.252	.228	.060	1.00																		
Ni	-.042	-.002	.310	-.126	1.00																	
Zn	.880	.419	.166	.228	.025	1.00																
Fe	.246	-.117	-.183	.333	-.192	.026	1.00															
Mn	.222	.142	.094	.272	-.145	-.030	.452	1.00														
Cr	-.247	-.342	-.250	-.222	.110	-.320	.160	.100	1.00													
Eh	-.165	-.140	-.240	.247	.221	-.200	.067	-.131	.108	1.00												
PO4	.079	-.185	-.202	-.228	-.004	.066	-.028	-.283	.180	.171	1.00											
SO4	.144	.028	.155	-.171	-.417	-.059	.265	.308	.317	-.572	-.216	1.00										
CO_3	.183	.185	.304	-.153	-.182	-.045	.287	.293	.287	-.237	-.186	.726	1.00									
HCO_3	-.116	-.261	-.138	-.220	-.195	.007	-.318	-.186	.019	-.506	.056	.364	-.179	1.00								
Mg	.079	-.077	.081	-.293	-.366	.042	-.033	.072	.092	-.696	-.162	.783	.513	.622	1.00							
Ca	-.053	.185	-.072	.217	.352	-.022	-.032	-.077	.101	.495	.109	-.497	-.352	-.405	-.830	1.00						
Cl	.132	.005	.109	-.166	-.259	.004	.049	.380	.280	-.522	-.086	.806	.537	.544	.839	-.564	1.00					
K	-.261	-.143	-.209	-.094	-.331	-.142	-.173	-.125	.092	-.513	-.194	.558	.203	.733	.754	-.452	.633	1.00				
pH	.120	.106	.230	-.321	-.216	.124	-.079	.169	-.071	-.978	-.165	.575	.262	.493	.682	-.473	.524	.475	1.00			
DO	.288	-.118	-.153	-.042	-.240	.337	-.100	-.134	-.322	-.109	.233	.130	-.147	.381	.227	-.307	.169	.208	.069	1.00		
TUR	.062	.030	-.194	.149	-.172	.208	-.458	.008	-.327	-.024	-.037	-.234	-.385	.199	-.077	.068	-.074	.077	.019	.477	1.00	
SAL	.133	.018	.118	-.254	-.353	.101	-.090	.108	.091	-.730	-.195	.814	.515	.657	.967	-.686	.878	.781	.719	.221	.014	1.00

Correlation between Kd values and some water quality parameters Reducible fraction (POM season)

	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr	Eh	PO4	SO4	CO$_3$	HCO$_3$	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.00																					
Pb	.088	1.00																				
Cd	.390	.025	1.00																			
Co	.184	.122	-.017	1.00																		
Ni	-.325	.019	-.056	.078	1.00																	
Zn	.870	.169	.256	.213	-.323	1.00																
Fe	-.008	.010	-.407	.558	.397	.041	1.00															
Mn	.193	.011	.117	.488	.286	.156	.734	1.00														
Cr	-.406	-.037	-.290	.074	.458	-.343	.561	.429	1.00													
Eh	.042	-.072	-.309	.392	.279	.176	.460	.214	.080	1.00												
PO4	.071	-.277	-.199	-.167	.038	.174	.196	.222	.258	.171	1.00											
SO4	.220	-.221	.178	-.149	-.265	.062	.015	.042	.185	-.572	-.216	1.00										
CO$_3$	.354	-.189	.282	-.119	-.101	.157	.044	.127	.162	-.237	-.186	.726	1.00									
HCO$_3$	-.239	-.173	-.111	-.237	-.059	-.206	-.134	-.085	.174	-.506	.056	.364	-.179	1.00								
Mg	.044	-.314	.138	-.401	-.265	-.019	-.282	-.164	.029	-.696	-.162	.783	.513	.622	1.00							
Ca	-.050	.465	-.123	.407	.272	-.013	.369	.227	.243	.495	.109	-.497	-.352	-.405	-.830	1.00						
Cl	.148	-.193	.151	-.134	-.142	.089	.152	.264	.209	-.522	-.086	.806	.537	.544	.839	-.564	1.00					
K	-.275	-.043	-.210	-.239	-.188	-.197	-.145	-.248	.198	-.513	-.194	.558	.203	.733	.754	-.452	.633	1.00				
pH	-.084	.013	.312	-.423	-.220	-.267	-.446	-.174	-.035	-.978	-.165	.575	.262	.493	.682	-.473	.524	.475	1.00			
DO	.241	-.313	-.172	-.227	-.367	.155	-.084	-.096	-.278	-.109	.233	.130	-.147	.381	.227	-.307	.169	.208	.069	1.00		
TUR	-.072	.154	-.226	-.152	-.373	-.052	-.148	-.100	-.273	-.024	-.037	-.234	-.385	.199	-.077	.068	-.074	.077	.019	.477	1.00	
SAL	.080	-.202	.167	-.350	-.298	-.005	-.248	-.117	.060	-.730	-.195	.814	.515	.657	.967	-.686	.878	.781	.719	.221	.014	1.00

Correlation between Kd values and some water quality parameters Oxidizable fraction (POM season)																						
	Cu	Pb	Cd	Co	Ni	Zn	Fe	Mn	Cr	Eh	PO4	SO4	CO_3	HCO_3	Mg	Ca	Cl	K	pH	DO	TUR	SAL
Cu	1.00																					
Pb	.114	1.00																				
Cd	.244	.166	1.00																			
Co	.038	.098	.588	1.00																		
Ni	-.152	-.032	.208	-.077	1.00																	
Zn	.074	-.254	-.230	-.099	-.099	1.00																
Fe	-.246	.004	-.669	-.331	-.220	.497	1.00															
Mn	.291	.244	.739	.370	-.189	-.046	-.278	1.00														
Cr	.050	.298	-.280	-.333	-.108	-.085	.464	-.075	1.00													
Eh	-.028	-.193	-.301	-.238	.088	.633	.540	-.161	.128	1.00												
PO4	-.237	-.152	-.140	-.314	.007	.006	-.011	-.160	.213	.171	1.00											
SO4	.096	.379	.195	.177	-.208	-.411	-.174	.114	.291	-.572	-.216	1.00										
CO_3	.410	.474	.310	.166	-.081	-.271	-.170	.275	.410	-.237	-.186	.726	1.00									
HCO_3	-.277	-.059	-.116	-.055	.050	-.370	-.257	-.274	-.155	-.506	.056	.364	-.179	1.00								
Mg	.116	.239	.101	-.026	-.092	-.583	-.394	.012	.076	-.696	-.162	.783	.513	.622	1.00							
Ca	-.124	-.158	-.066	.198	.145	.406	.297	-.067	.021	.495	.109	-.497	-.352	-.405	-.830	1.00						
Cl	-.022	.329	.136	.051	-.052	-.593	-.188	.075	.306	-.522	-.086	.806	.537	.544	.839	-.564	1.00					
K	-.065	-.010	-.225	.037	.006	-.437	-.209	-.375	-.018	-.513	-.194	.558	.203	.733	.754	-.452	.633	1.00				
pH	-.004	.178	.310	.209	-.035	-.669	-.546	.170	-.079	-.978	-.165	.575	.262	.493	.682	-.473	.524	.475	1.00			
DO	-.151	-.198	-.183	-.181	-.253	-.100	-.052	-.199	-.216	-.109	.233	.130	-.147	.381	.227	-.307	.169	.208	.069	1.00		
TUR	-.109	-.085	-.180	-.002	-.124	-.139	-.073	-.169	-.417	-.024	-.037	-.234	-.385	.199	-.077	.068	-.074	.077	.019	.477	1.00	
SAL	.093	.263	.152	.108	-.086	-.626	-.434	.028	.041	-.730	-.195	.814	.515	.657	.967	-.686	.878	.781	.719	.221	.014	1.00

Correction for all fractions during monsoon season for stations 1-9

	F1Cu	F2Cu	F3Cu	F4Cu	F1Pb	F2Pb	F3Pb	F4Pb	F1Cd	F2Cd	F3Cd	F4Cd	F1Co	F2Co	F3Co	F4Co	F1Ni	F2Ni	F3Ni	F4Ni	F1Zn	F2Zn	F3Zn	F4Zn	F1Fe	F2Fe	F3Fe	F4Fe	F1Mn	F2Mn	F3Mn	F4Mn	F1Cr	F2Cr	F3Cr	F4Cr	PO_4	Fine	Silt	OC	$CaCO_3$
F1Cu	1.00																																								
F2Cu	-.264	1.00																																							
F3Cu	-.126	.770	1.00																																						
F4Cu	.817	-.235	-.195	1.00																																					
F1Pb	.007	.352	.520	-.005	1.00																																				
F2Pb	.489	.313	.470	.659	.333	1.00																																			
F3Pb	.360	.454	.536	.528	.193	.647	1.00																																		
F4Pb	.272	-.320	-.546	.383	-.003	-.305	-.017	1.00																																	
F1Cd	.020	-.456	-.489	-.095	-.793	-.549	-.364	.308	1.00																																
F2Cd	.072	-.910	-.621	.111	-.497	-.363	-.374	.248	.649	1.00																															
F3Cd	.457	-.913	-.863	.400	-.300	-.314	-.371	.603	.434	.735	1.00																														
F4Cd	.204	.044	-.181	.189	.451	-.228	.090	.820	-.152	-.214	.285	1.00																													
F1Co	-.340	-.235	-.359	.083	-.109	.146	-.363	-.036	-.035	.251	.100	-.308	1.00																												
F2Co	-.529	-.161	-.145	-.129	.203	.020	-.378	.007	-.144	.230	-.018	-.135	.883	1.00																											
F3Co	-.473	-.418	-.421	-.223	.089	-.273	-.670	.168	.087	.425	.276	-.026	.808	.911	1.00																										
F4Co	-.546	.628	.145	-.556	-.251	-.233	-.216	-.307	.042	-.558	-.580	-.191	.093	-.023	-.066	1.00																									
F1Ni	.351	-.538	-.491	.377	-.811	-.065	-.038	.226	.826	.683	.505	-.323	.127	-.140	-.017	-.204	1.00																								
F2Ni	.419	-.678	-.518	.569	-.551	.116	-.005	.324	.618	.772	.623	-.225	.335	.132	.216	-.500	.904	1.00																							
F3Ni	-.096	-.617	-.348	.004	-.640	-.098	-.280	-.220	.596	.810	.326	-.701	.439	.302	.368	-.229	.741	.751	1.00																						
F4Ni	.114	.449	.257	.172	-.489	.342	.580	-.341	.088	-.320	-.419	-.414	-.194	-.490	-.663	.419	.323	.068	.079	1.00																					
F1Zn	.978	-.127	-.003	.764	.171	.547	.383	.198	-.155	-.106	.337	.250	-.386	-.544	-.512	-.485	.158	.234	-.260	.089	1.00																				
F2Zn	-.024	.576	.272	.077	.304	-.041	.419	.562	-.093	-.511	-.294	.728	-.336	-.169	-.267	.207	-.276	-.323	-.697	.062	.023	1.00																			
F3Zn	.094	.168	.279	-.021	.719	.304	-.259	-.173	-.575	-.373	-.153	.154	.143	.302	.262	-.063	-.628	-.430	-.434	-.586	.239	-.031	1.00																		
F4Zn	.122	.752	.391	.220	.020	.567	.512	-.267	-.374	-.786	-.592	-.101	-.021	-.263	-.488	.571	-.156	-.288	-.411	.743	.210	.307	-.013	1.00																	
F1Fe	.672	-.714	-.495	.521	-.512	-.016	.002	.328	.634	.704	.738	-.074	-.152	-.346	-.139	-.577	.843	.839	.549	.073	.518	-.328	-.420	-.341	1.00																
F2Fe	-.060	-.567	-.310	-.410	-.421	-.657	-.528	.025	.725	.667	.429	-.186	-.260	-.197	.122	-.180	.469	.325	.544	-.229	-.165	-.399	-.328	-.679	.552	1.00															
F3Fe	.031	.304	.453	-.141	.735	.391	-.097	-.500	-.779	-.530	-.344	-.044	-.001	.112	.035	.024	-.753	-.612	-.447	-.316	.214	-.207	.865	.172	-.506	-.341	1.00														
F4Fe	-.600	.588	.073	-.528	-.216	-.253	-.263	-.172	.074	-.503	-.529	-.110	.240	.145	.108	.972	-.175	-.415	-.197	.325	-.553	.270	-.062	.527	-.579	-.200	-.040	1.00													
F1Mn	.629	.202	.227	.542	-.208	.389	.690	.200	.249	-.112	-.036	.087	-.498	-.647	-.700	-.160	.483	.365	-.042	.625	.576	.346	-.446	.417	.519	-.016	-.400	-.191	1.00												
F2Mn	-.025	-.734	-.585	-.008	-.584	-.400	-.540	.250	.826	.881	.590	-.263	.373	.316	.531	-.253	.767	.780	.817	-.267	-.203	-.399	-.308	-.626	.634	.689	-.563	-.158	-.069	1.00											
F3Mn	.609	.180	.036	.534	.496	.568	.203	.106	-.600	-.527	.073	.369	-.046	-.188	-.212	-.101	-.345	-.204	-.592	-.035	.732	.113	.564	.482	-.059	-.564	.593	-.117	.152	-.544	1.00										
F4Mn	-.737	.378	-.038	-.626	.188	-.342	-.431	-.142	-.320	-.449	-.358	.091	.361	.404	.409	.711	-.582	-.632	-.331	-.127	-.635	.108	.207	.230	-.774	-.252	.296	.763	-.646	-.304	.029	1.00									
F1Cr	-.763	.420	.235	-.572	.465	-.232	-.270	-.106	-.447	-.399	-.471	.178	.307	.571	.450	.430	-.756	-.687	-.404	-.401	-.653	.288	.444	-.019	-.909	-.370	.376	.485	-.737	-.335	-.113	.772	1.00								
F2Cr	-.445	.418	.330	-.425	.769	.039	-.225	-.237	-.755	-.579	-.421	.221	.186	.406	.334	.269	-.920	-.777	-.567	-.440	-.265	.105	.711	.117	-.827	-.409	.789	.297	-.642	-.560	.359	.735	.796	1.00							
F3Cr	-.476	.811	.650	-.377	.656	.257	.132	-.381	-.745	-.832	-.806	.073	.094	.268	.037	.508	-.855	-.818	-.617	-.009	-.296	.338	.531	.493	-.942	-.623	.651	.511	-.331	-.728	.274	.668	.767	.852	1.00						
F4Cr	.580	.259	.137	.710	-.209	.524	.636	.294	.160	-.178	-.066	.118	-.150	-.328	-.498	-.053	.413	.366	-.122	.510	.528	.475	-.189	.495	.300	-.406	-.363	-.055	.767	-.076	.235	-.549	-.433	-.550	-.188	1.00					
PO_4	-.152	-.021	-.189	-.233	-.283	-.219	-.639	-.044	.405	.064	.002	-.203	.342	.281	.365	.431	.165	.057	.154	-.224	-.176	-.076	.362	-.064	-.080	.134	.035	.454	-.317	.415	-.110	.186	.233	.015	.012	.068	1.00				
Fine	-.565	-.081	-.085	-.471	.525	-.467	-.454	.234	-.281	.025	.043	.438	.214	.567	.623	-.049	-.623	-.441	-.283	-.813	-.501	.174	.432	-.529	-.540	-.013	.277	.041	-.785	-.042	-.140	.534	.804	.677	.381	-.624	.088	1.00			
Silt	.566	.078	.082	.471	-.527	.466	.452	-.233	.283	-.024	-.040	-.437	-.213	-.567	-.622	.049	.625	.443	.284	.812	.502	-.176	-.432	.528	.542	.014	-.278	-.041	.784	.043	.141	-.534	-.805	-.678	-.383	.623	-.086	-.999	1.00		
OC	-.381	-.314	-.156	-.413	.485	-.335	-.654	-.021	-.287	.177	.189	.151	.310	.578	.692	-.181	-.527	-.310	-.060	-.894	-.316	-.269	.632	-.619	-.353	.134	.516	-.130	-.882	.098	-.007	.409	.613	.665	.249	-.757	.217	.867	-.866	1.00	
$CaCO_3$	-.037	.247	.484	.179	.408	.516	.266	-.278	-.454	-.175	-.380	-.166	.220	.386	.082	-.179	-.348	-.155	-.106	-.189	.017	.067	.541	.019	-.396	-.527	.392	-.196	-.231	-.235	.056	-.150	.410	.263	.397	.230	.198	.222	-.223	.248	1.00

Correction for all fractions during monsoon season for stations 10-28

	F1Cu	F2Cu	F3Cu	F4Cu	F1Pb	F2Pb	F3Pb	F4Pb	F1Cd	F2Cd	F3Cd	F4Cd	F1Co	F2Co	F3Co	F4Co	F1Ni	F2Ni	F3Ni	F4Ni	F1Zn	F2Zn	F3Zn	F4Zn	F1Fe	F2Fe	F3Fe	F4Fe	F1Mn	F2Mn	F3Mn	F4Mn	F1Cr	F2Cr	F3Cr	F4Cr	PO_4	Fine	Silt	OC	$CaCO_3$
F1Cu	1.00																																								
F2Cu	.241	1.00																																							
F3Cu	.402	.469	1.00																																						
F4Cu	-.601	-.235	-.196	1.00																																					
F1Pb	-.400	-.084	-.014	.300	1.00																																				
F2Pb	-.397	-.200	.192	.584	.703	1.00																																			
F3Pb	-.293	-.387	-.268	.280	.122	.161	1.00																																		
F4Pb	.290	.217	.098	-.182	-.332	.063	-.496	1.00																																	
F1Cd	.350	-.112	-.220	-.257	-.251	-.294	-.211	.162	1.00																																
F2Cd	.124	-.056	-.026	-.175	-.141	-.035	-.071	.295	.523	1.00																															
F3Cd	.500	.159	.060	-.443	-.371	-.222	-.139	.346	.558	.545	1.00																														
F4Cd	-.015	-.136	-.192	-.058	.197	-.100	-.227	.146	-.218	-.074	-.526	1.00																													
F1Co	-.009	.152	.099	-.300	-.144	-.393	-.090	-.149	-.287	-.340	-.520	.335	1.00																												
F2Co	-.147	.068	.024	-.196	.009	-.291	.069	-.298	-.339	-.284	-.624	.308	.933	1.00																											
F3Co	-.003	.123	.109	-.209	-.134	-.373	-.134	-.167	-.226	-.269	-.539	.304	.918	.933	1.00																										
F4Co	.272	-.033	.128	-.114	.003	-.045	-.162	.349	-.153	-.161	-.409	.808	.400	.272	.316	1.00																									
F1Ni	.457	-.205	-.074	-.268	-.141	-.124	-.320	.437	.601	.355	.180	.344	-.041	-.146	-.076	.503	1.00																								
F2Ni	.308	-.218	.006	-.183	-.064	-.090	-.332	.329	.398	.278	-.020	.478	.037	-.044	-.003	.588	.924	1.00																							
F3Ni	.395	-.365	-.067	-.226	-.137	-.107	-.228	.339	.466	.251	.129	.414	-.065	-.192	-.146	.578	.928	.945	1.00																						
F4Ni	-.189	-.114	.013	.533	.011	.451	.005	.372	-.514	-.239	-.137	.149	-.403	-.428	-.401	.173	-.252	-.168	-.099	1.00																					
F1Zn	.906	.429	.450	-.660	-.462	-.438	-.365	.386	.352	.172	.586	-.115	.013	-.173	-.053	.212	.500	.394	.430	-.260	1.00																				
F2Zn	.047	.925	.335	-.064	.051	-.089	-.489	.201	-.238	-.133	.076	-.033	.044	-.038	.034	-.087	-.298	-.275	-.427	.074	.228	1.00																			
F3Zn	.414	.637	.401	-.154	.212	.104	-.253	.089	.011	-.015	.270	-.176	-.083	-.139	-.084	-.069	.039	-.116	-.149	-.158	.448	.614	1.00																		
F4Zn	-.142	-.232	-.032	.583	-.015	.467	-.208	.443	.027	.233	.026	.043	-.363	-.422	-.373	.137	.325	.388	.381	.566	-.087	-.111	-.104	1.00																	
F1Fe	.467	.188	.278	-.140	-.344	-.002	-.422	.533	.388	.203	.616	-.358	-.358	-.549	-.404	-.044	.502	.441	.479	.081	.674	.148	.257	.503	1.00																
F2Fe	.047	-.157	.061	.376	-.021	.443	-.231	.446	.459	.288	.175	-.276	-.342	-.374	-.287	-.032	.529	.432	.410	.113	.105	-.187	.055	.739	.619	1.00															
F3Fe	.403	-.077	.220	.070	-.226	.309	-.192	.574	.513	.397	.569	-.434	-.510	-.595	-.477	-.090	.500	.321	.402	.153	.432	-.173	.179	.587	.775	.856	1.00														
F4Fe	-.024	-.026	.063	.337	-.225	.338	-.120	.375	.185	.226	.506	-.648	-.535	-.594	-.538	-.473	.027	-.056	.006	.361	.103	.019	.094	.689	.696	.700	.760	1.00													
F1Mn	.333	-.071	.115	-.091	-.128	.068	-.079	.464	.535	.443	.102	.140	.027	-.004	.034	.472	.796	.727	.689	-.227	.376	-.299	-.010	.348	.380	.646	.587	.100	1.00												
F2Mn	.075	-.152	-.114	.171	-.041	.118	-.205	.371	.664	.613	.126	.120	-.153	-.165	-.096	.232	.736	.679	.609	-.205	.126	-.239	-.083	.546	.368	.757	.573	.249	.847	1.00											
F3Mn	.032	.003	-.194	.025	.108	-.076	-.246	.149	.532	.642	.062	.331	-.070	.006	.021	.191	.434	.459	.352	-.255	-.001	-.054	-.116	.255	-.027	.282	.121	-.100	.551	.751	1.00										
F4Mn	-.265	-.087	-.043	.354	-.107	.174	-.132	.041	-.179	-.106	.215	-.347	-.354	-.429	-.423	-.369	-.197	-.058	-.015	.462	-.093	.096	-.127	.588	.494	.242	.214	.716	-.321	-.119	-.224	1.00									
F1Cr	.353	.310	.368	-.487	-.253	-.338	.040	-.208	.026	-.163	.094	-.365	.497	.431	.465	-.182	-.123	-.285	-.289	-.593	.369	.125	.379	-.621	-.048	-.218	-.074	-.201	-.093	-.300	-.444	-.426	1.00								
F2Cr	.408	.569	.294	-.658	-.343	-.567	-.163	.108	-.187	-.109	-.016	.165	.658	.558	.556	.257	.003	-.056	-.128	-.400	.489	.409	.388	-.569	-.118	-.476	-.332	-.458	-.023	-.307	-.214	-.477	.703	1.00							
F3Cr	.247	.319	.196	-.438	-.423	-.449	.106	-.089	-.266	-.375	.096	-.245	.383	.269	.287	-.118	-.257	-.364	-.312	-.210	.327	.244	.312	-.564	-.016	-.457	-.241	-.160	-.375	-.616	-.750	-.143	.786	.738	1.00						
F4Cr	.020	.095	.062	.151	-.227	.203	-.105	.292	-.130	-.065	.496	-.638	-.422	-.491	-.454	-.531	-.260	-.319	-.236	.445	.142	.190	.144	.413	.591	.311	.481	.855	-.295	-.229	-.437	.768	-.066	-.243	.149	1.00					
PO_4	.236	.222	.113	-.134	-.423	-.139	-.462	.454	-.154	-.103	.387	-.265	-.028	-.198	-.021	-.213	-.162	-.233	-.191	.334	.304	.339	.124	.218	.495	.087	.275	.502	-.334	-.266	-.394	.471	.153	.133	.335	.748	1.00				
Fine	.005	.256	-.029	-.377	.064	-.463	.248	-.478	-.368	-.219	-.234	.292	.348	.449	.336	.054	-.447	-.345	-.388	-.235	-.059	.218	-.007	-.787	-.661	-.941	-.844	-.780	-.478	-.619	-.096	-.403	.219	.514	.357	-.459	-.280	1.00			
Silt	-.005	-.255	.029	.377	-.063	.464	-.248	.478	.367	.218	.234	-.292	-.349	-.449	-.336	-.054	.446	.344	.388	.235	.059	-.217	.008	.786	.661	.940	.844	.780	.477	.618	.095	.403	-.218	-.514	-.356	.460	.281	-.999	1.00		
OC	.035	-.296	-.401	-.610	-.245	-.553	.193	-.186	-.053	-.043	.147	.097	.262	.269	.190	-.113	-.068	-.082	.011	-.310	.044	-.290	-.324	-.565	-.241	-.619	-.447	-.372	-.361	-.458	-.302	-.103	.261	.347	.473	-.060	.127	.504	-.504	1.00	
$CaCO_3$	-.176	-.256	-.051	-.205	-.099	.084	.002	.163	.224	.163	.461	-.410	-.185	-.244	-.181	-.342	-.126	-.193	-.033	-.033	-.103	-.234	-.196	-.033	.190	.067	.215	.338	-.093	-.085	-.192	.299	-.006	-.252	.049	.344	.213	-.258	.258	.287	1.00

Correction for all fractions during POM season for stations 01-11

	F1Cu	F2Cu	F3Cu	F4Cu	F1Pb	F2Pb	F3Pb	F4Pb	F1Cd	F2Cd	F3Cd	F4Cd	F1Co	F2Co	F3Co	F4Co	F1Ni	F2Ni	F3Ni	F4Ni	F1Zn	F2Zn	F3Zn	F4Zn	F1Fe	F2Fe	F3Fe	F4Fe	F1Mn	F2Mn	F3Mn	F4Mn	F1Cr	F2Cr	F3Cr	F4Cr	PO_4	Fine	Silt	OC	$CaCO_3$
F1Cu	1.00																																								
F2Cu	.852	1.00																																							
F3Cu	-.079	-.024	1.00																																						
F4Cu	.302	.448	.659	1.00																																					
F1Pb	.329	.630	.204	.631	1.00																																				
F2Pb	.011	.103	.368	.603	.611	1.00																																			
F3Pb	-.095	-.085	-.425	-.623	-.383	-.336	1.00																																		
F4Pb	-.090	-.044	.084	.371	.152	.492	-.009	1.00																																	
F1Cd	-.520	-.377	-.157	-.535	-.310	-.572	.569	-.071	1.00																																
F2Cd	-.410	-.456	-.061	-.561	-.492	-.670	.390	-.075	.892	1.00																															
F3Cd	-.435	-.406	-.486	-.793	-.403	-.669	.615	-.271	.892	.809	1.00																														
F4Cd	-.556	-.407	-.426	-.583	-.179	-.091	.477	-.266	.447	.174	.542	1.00																													
F1Co	.501	.304	-.059	.221	-.127	-.147	.254	.161	-.084	-.089	-.082	-.298	1.00																												
F2Co	.474	.174	-.341	-.020	-.286	-.359	.106	-.094	-.171	-.095	.025	-.292	.846	1.00																											
F3Co	.278	.167	-.507	-.141	-.138	-.314	.174	-.146	-.122	-.171	.159	-.199	.507	.779	1.00																										
F4Co	.310	.227	-.082	.236	-.057	-.377	-.072	-.036	.009	.024	.053	-.474	.700	.816	.769	1.00																									
F1Ni	-.695	-.779	.068	-.330	-.405	-.015	.232	.443	.569	.650	.442	.208	-.230	-.289	-.341	-.243	1.00																								
F2Ni	-.712	-.621	.183	-.070	-.131	.031	.134	.429	.656	.597	.421	.258	-.144	-.295	-.367	-.081	.880	1.00																							
F3Ni	-.834	-.746	.098	-.318	-.441	-.227	.211	.317	.717	.723	.523	.282	-.344	-.397	-.341	-.188	.883	.862	1.00																						
F4Ni	.567	.382	-.524	-.269	-.195	-.566	.353	-.103	.099	.175	.310	-.322	.631	.774	.769	.683	-.284	-.367	-.330	1.00																					
F1Zn	.975	.804	-.017	.389	.371	.135	-.140	.097	-.542	-.407	-.487	-.640	.538	.468	.247	.315	-.576	-.604	-.774	.540	1.00																				
F2Zn	.889	.878	-.181	.136	.384	.011	.062	-.218	-.399	-.400	-.330	-.214	.238	.172	.044	-.027	-.728	-.720	-.790	.364	.807	1.00																			
F3Zn	.559	.657	.392	.795	.430	.361	-.407	.288	-.564	-.570	-.801	-.492	.297	.067	-.192	.130	-.491	-.299	-.444	-.115	.573	.525	1.00																		
F4Zn	.231	.226	.101	.585	.122	.305	-.183	.820	-.316	-.289	-.478	-.556	.504	.333	.214	.421	.028	.086	-.011	.195	.372	-.028	.568	1.00																	
F1Fe	.839	.586	.018	.360	.324	.357	-.331	.072	-.803	-.602	-.661	-.633	.269	.334	.208	.112	-.508	-.665	-.785	.308	.877	.663	.467	.278	1.00																
F2Fe	.553	.416	-.308	-.155	.271	-.110	-.002	-.412	-.223	-.152	.095	-.275	.119	.357	.572	.295	-.464	-.573	-.621	.606	.518	.429	-.262	-.270	.551	1.00															
F3Fe	.164	-.089	.329	.337	.069	.629	-.242	.513	-.563	-.354	-.573	-.543	.035	-.004	-.047	-.111	.233	-.011	-.103	-.139	.315	-.067	.175	.418	.604	.087	1.00														
F4Fe	.530	.349	-.282	-.157	.288	-.110	-.178	-.324	-.194	-.021	.088	-.347	-.035	.240	.362	.186	-.289	-.422	-.492	.509	.523	.403	-.238	-.267	.584	.922	.156	1.00													
F1Mn	.148	.131	-.130	.254	.333	.804	.055	.536	-.539	-.670	-.489	.131	.115	-.054	-.067	-.346	-.063	-.128	-.325	-.230	.245	.189	.265	.375	.404	-.072	.519	-.135	1.00												
F2Mn	.339	.292	-.338	-.311	.287	.079	.410	-.335	-.002	-.110	.266	.199	.109	.131	.322	-.058	-.291	-.373	-.498	.376	.309	.393	-.398	-.432	.296	.787	-.004	.630	.228	1.00											
F3Mn	.217	.051	-.186	-.211	.199	.279	.391	-.114	-.006	-.084	.184	.258	.272	.188	.127	-.107	.002	-.063	-.352	.180	.253	.212	-.340	-.299	.267	.507	.199	.413	.428	.849	1.00										
F4Mn	.667	.542	-.272	.015	.367	-.200	-.248	-.423	-.240	-.132	.012	-.380	.180	.439	.488	.434	-.534	-.520	-.649	.603	.625	.523	-.017	-.176	.576	.890	-.055	.918	-.216	.543	.312	1.00									
F1Cr	-.355	-.495	-.514	-.691	-.427	-.411	.253	-.451	.380	.349	.634	.723	-.036	.166	.077	-.122	.163	.109	.148	.067	-.423	-.246	-.663	-.559	-.419	.049	-.517	.043	-.145	.246	.321	.028	1.00								
F2Cr	.043	-.023	.023	-.162	.221	.000	-.315	-.717	-.164	-.104	.092	.105	-.357	-.094	.082	-.120	-.318	-.361	-.375	-.061	-.028	.063	-.415	-.715	.164	.654	-.099	.636	-.212	.553	.377	.580	.372	1.00							
F3Cr	.319	.341	.461	.211	.404	.262	-.031	-.163	-.077	-.027	-.224	-.243	-.221	-.376	-.439	-.296	-.043	-.025	-.192	-.230	.308	.414	.243	-.307	.335	.189	.296	.287	-.034	.244	.266	.205	-.470	.197	1.00						
F4Cr	.930	.827	-.089	.218	.300	-.126	-.090	-.032	-.315	-.165	-.292	-.522	.377	.313	.076	.191	-.565	-.581	-.647	.540	.910	.873	.527	.203	.698	.436	.019	.502	.000	.223	.078	.610	-.306	-.034	.305	1.00					
PO_4	.228	.325	-.143	-.247	-.013	-.277	.009	-.759	-.195	-.240	-.047	.236	-.345	-.180	-.016	-.277	-.659	-.703	-.444	-.026	.030	.500	.043	-.605	.084	.251	-.439	.144	-.228	.213	-.144	.217	.145	.454	.145	.213	1.00				
Fine	.341	.497	-.369	-.318	.030	-.670	.330	-.397	.383	.327	.464	-.004	.089	.137	.310	.252	-.424	-.373	-.185	.625	.221	.441	-.123	-.235	-.092	.435	-.656	.348	-.522	.328	-.100	.454	.100	.126	-.067	.487	.468	1.00			
Silt	-.368	-.503	.366	.318	.000	.696	-.343	.425	-.386	-.331	-.462	-.020	-.151	-.185	-.296	-.267	.442	.378	.208	-.633	-.241	-.469	.091	.242	.095	-.405	.692	-.315	.526	-.314	.082	-.446	-.144	-.109	.074	-.512	-.476	-.994	1.00		
OC	.098	.214	-.419	-.505	-.123	-.784	.416	-.488	.598	.533	.719	.141	.056	.178	.386	.317	-.198	-.151	.021	.620	-.019	.170	-.419	-.386	-.304	.443	-.707	.356	-.656	.364	-.008	.429	.307	.223	-.129	.227	.349	.930	-.922	1.00	
$CaCO_3$	.714	.811	-.511	.154	.445	.010	.013	.074	-.358	-.458	-.237	-.239	.233	.316	.431	.278	-.621	-.551	-.620	.517	.667	.745	.453	.310	.540	.418	-.077	.386	.248	.239	-.009	.538	-.317	-.152	.043	.667	.235	.429	-.419	.213	1.00

Correction for all fractions during POM season for stations 12-31

	F1Cu	F2Cu	F3Cu	F4Cu	F1Pb	F2Pb	F3Pb	F4Pb	F1Cd	F2Cd	F3Cd	F4Cd	F1Co	F2Co	F3Co	F4Co	F1Ni	F2Ni	F3Ni	F4Ni	F1Zn	F2Zn	F3Zn	F4Zn	F1Fe	F2Fe	F3Fe	F4Fe	F1Mn	F2Mn	F3Mn	F4Mn	F1Cr	F2Cr	F3Cr	F4Cr	PO_4	Fine	Silt	OC	$CaCO_3$
F1Cu	1.00																																								
F2Cu	.507	1.00																																							
F3Cu	.121	.322	1.00																																						
F4Cu	.021	.324	-.036	1.00																																					
F1Pb	.335	.520	.221	-.224	1.00																																				
F2Pb	.371	.372	-.024	-.033	.825	1.00																																			
F3Pb	.163	.012	.134	-.041	.131	.288	1.00																																		
F4Pb	.297	.013	-.316	.172	.326	.482	.014	1.00																																	
F1Cd	.000	.221	.463	-.469	.533	.333	-.106	-.387	1.00																																
F2Cd	-.037	.137	.371	-.605	.488	.259	-.137	-.379	.964	1.00																															
F3Cd	-.131	.087	.264	-.614	.496	.298	-.158	-.357	.944	.975	1.00																														
F4Cd	-.157	.036	.008	-.451	.229	.170	.257	-.260	.454	.571	.583	1.00																													
F1Co	.219	.471	-.041	.361	.320	.414	-.252	.271	.040	-.020	-.014	-.241	1.00																												
F2Co	-.060	.213	-.084	.585	.064	.280	-.216	.306	-.001	-.088	-.104	-.207	.642	1.00																											
F3Co	.077	.270	.202	-.399	.734	.644	-.003	-.009	.809	.791	.809	.444	.441	.222	1.00																										
F4Co	.124	-.064	-.320	.527	-.224	-.073	-.102	.493	-.737	-.703	-.724	-.501	.360	.293	-.419	1.00																									
F1Ni	.145	.055	-.085	.122	-.030	.176	-.058	.233	.167	.121	.139	.034	-.120	.166	.002	-.243	1.00																								
F2Ni	-.200	-.235	-.370	.124	-.257	-.015	.098	.161	-.150	-.130	-.103	.096	-.335	.178	-.263	-.082	.717	1.00																							
F3Ni	-.205	-.080	-.158	-.232	-.001	-.035	-.031	.008	.226	.287	.353	.314	-.378	-.255	.050	-.409	.713	.618	1.00																						
F4Ni	.579	.158	-.344	.216	-.083	.061	-.081	.521	-.504	-.480	-.515	-.275	-.044	.105	-.446	.399	.306	.372	.019	1.00																					
F1Zn	.976	.418	.184	-.064	.299	.299	.110	.260	.070	.052	-.064	-.146	.156	-.122	.093	.087	.172	-.206	-.144	.519	1.00																				
F2Zn	.371	.974	.235	.372	.412	.280	-.001	-.094	.171	.094	.060	.052	.471	.254	.211	-.066	.018	-.169	-.077	.114	.263	1.00																			
F3Zn	-.013	.351	.081	.435	-.130	.056	-.213	-.012	-.054	-.131	-.192	-.129	.302	.467	-.086	.091	.254	.287	-.092	.160	-.033	.390	1.00																		
F4Zn	.132	-.124	-.476	.129	.091	.317	.042	.272	-.219	-.258	-.222	.047	-.060	.047	-.106	.196	.145	.374	-.115	.373	.071	-.128	.248	1.00																	
F1Fe	-.170	-.001	-.175	.319	-.485	-.287	-.121	-.005	-.389	-.379	-.393	-.200	.471	.450	-.221	.331	-.046	.141	-.275	.054	-.222	.115	.475	-.011	1.00																
F2Fe	-.097	.011	-.361	.837	-.339	.034	-.028	.256	-.490	-.597	-.562	-.433	.307	.664	-.369	.479	.343	.474	-.024	.332	-.177	.089	.420	.270	.408	1.00															
F3Fe	.092	.085	-.301	.745	-.440	-.107	-.128	.360	-.690	-.769	-.776	-.542	.382	.515	-.503	.664	.133	.190	-.265	.469	.024	.119	.587	.236	.593	.794	1.00														
F4Fe	.346	.065	-.358	.457	-.162	.188	-.089	.580	-.496	-.542	-.537	-.399	.115	.393	-.390	.506	.470	.520	.007	.797	.276	.042	.413	.479	.261	.624	.698	1.00													
F1Mn	-.299	-.166	-.313	.441	-.071	.132	.217	.047	-.229	-.233	-.202	-.129	.300	.422	.025	.455	-.265	.010	-.240	-.281	-.336	-.078	-.111	.021	.157	.486	.197	.005	1.00												
F2Mn	-.284	-.084	-.307	.632	-.171	.043	-.072	.003	-.141	-.230	-.164	-.257	.183	.592	-.114	.260	.256	.414	.073	.044	-.353	.020	.050	.163	.108	.800	.327	.298	.639	1.00											
F3Mn	.035	.450	.428	-.094	.718	.515	-.230	.050	.729	.670	.645	.350	.370	.320	.765	-.343	.046	-.226	-.046	-.342	.051	.376	.198	.035	-.192	-.292	-.363	-.239	-.129	-.123	1.00										
F4Mn	.508	.001	-.217	.037	.104	.208	-.074	.529	-.280	-.277	-.281	-.316	-.183	-.031	-.288	.338	.342	.356	.089	.822	.477	-.085	-.062	.422	-.227	.159	.186	.769	-.209	.080	-.188	1.00									
F1Cr	-.230	-.269	-.255	.253	-.355	-.061	.299	-.109	-.317	-.394	-.326	-.119	-.286	.019	-.435	-.201	.162	.442	.075	.106	-.295	-.174	.081	.229	.140	.472	.228	.187	.161	.353	-.448	-.020	1.00								
F2Cr	-.327	-.381	-.258	.123	-.365	-.065	.097	-.260	-.072	-.147	-.057	-.052	-.397	.058	-.308	-.261	.332	.581	.209	.106	-.379	-.280	.092	.309	-.008	.455	.111	.267	.090	.533	-.366	.159	.802	1.00							
F3Cr	-.115	-.279	-.428	.540	-.539	-.250	.127	.116	-.725	-.775	-.743	-.444	-.141	.175	-.737	.351	.074	.445	-.120	.435	-.193	-.180	.135	.340	.325	.723	.588	.474	.282	.517	-.662	.232	.798	.631	1.00						
F4Cr	.486	.065	-.114	-.169	.346	.484	-.088	.503	.081	.080	.097	-.056	-.100	.015	.078	.054	.500	.337	.211	.648	.461	-.044	-.012	.385	-.337	.014	-.016	.635	-.348	-.001	.097	.869	-.107	.184	-.048	1.00					
PO_4	.130	-.035	-.280	.130	-.283	-.322	-.217	-.004	-.305	-.288	-.284	-.269	-.128	-.089	-.451	.124	.338	.416	.261	.532	.105	.017	-.033	.204	.127	.301	.186	.269	-.279	.297	-.421	.366	.205	.312	.494	.239	1.00				
Fine	.040	-.095	.244	-.401	.209	-.205	.055	-.318	.271	.335	.303	.091	-.292	-.420	.139	-.167	-.452	-.388	-.093	-.238	.086	-.114	-.744	-.286	-.504	-.564	-.717	-.584	.033	-.091	.046	-.027	-.307	-.238	-.291	-.127	.066	1.00			
Silt	-.040	.096	-.243	.394	-.207	.204	-.056	.316	-.267	-.331	-.298	-.086	.291	.416	-.136	.163	.450	.384	.094	.236	-.085	.114	.744	.284	.503	.557	.713	.580	-.039	.083	-.043	.024	.302	.234	.285	.126	-.069	-.999	1.00		
OC	-.163	-.042	.219	-.585	.325	-.060	.101	-.393	.532	.589	.625	.360	-.270	-.446	.392	-.479	-.204	-.258	.240	-.447	-.136	-.034	-.722	-.375	-.458	-.627	-.850	-.699	-.098	-.108	.178	-.209	-.280	-.115	-.478	-.097	.052	.803	-.800	1.00	
$CaCO_3$	-.117	-.015	.246	-.020	.181	-.019	.272	-.207	.111	.133	.059	.312	-.075	-.202	.112	.117	-.393	-.244	-.197	-.331	-.061	-.039	-.153	.151	-.150	-.202	-.232	-.411	.216	-.080	.224	-.265	-.209	-.277	-.160	-.332	-.116	.325	-.325	.264	1.00