CHAPTER 2: LITERATURE REVIEW

Mangrove trees in Matang, Perak.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals in water

Trace elements of natural origin are transported by rivers and transferred to the coastal marine system through estuaries. There, trace elements are distributed between the dissolved and particulate phase, while their fate and bioavailability depend on the particle chemistry and competition between surface and dissolved forms in terms of complexation processes. Hence, the estuaries constitute a natural reactor in which heterogeneous processes at the interface between dissolved phase and suspended particulate matter and constitute an important part of the trace elements geochemical cycles. The distributions of trace metals and their rates of reactivity vary greatly between estuaries, depending on environmental factors, such as hydrodynamic residence times, mixing patterns and transport processes. Therefore, there is no universal pattern of trace metal behaviour in estuaries.

The ability of a water body to support aquatic life, as well as its suitability for other uses depends on many trace elements. Certain metals like Mn, Zn and Cu present in trace concentrations are important for the physiological functions of living tissue and regulate many biochemical processes. Water pollution by heavy metals resulting from anthropogenic impact has caused serious ecological problems in many parts of the world. This situation is provoked by the lack of natural elimination processes for metals. As a result, metals shift from one compartment within the aquatic environment to a great extent, including the biota, often with harmful effects.

The Department of Environment reported higher concentrations of heavy metals in the waters off the west coast of Peninsular Malaysia compared to other areas because of the extensive land use and industrialization. In 1990, Sg Perak, Sg Selangor, Sg Kelang, Sg Linggi and Sg Melaka recorded samples exceeding the standard values of 0.02mg/l of lead. Rivers that recorded values exceeding the proposed value of 0.4 mg zinc/litre included Sg Sepang Sg Langat and Sg Kelang. Sg Bernam which located in the west coast of Peninsular Malaysia, recorded copper values higher than the proposed value of 0.012mg/litre. Concentrations of cadmium were negligible in most of the rivers monitored.

Approximately all the samples collected from the coastal waters of Malaysia contained values of lead, copper and cadmium above the proposed standards of 0.05mg/l lead, 0.01mg/l copper and 0.005mg/l cadmium.The costal waters of Perak and Penang recorded high levels of cadmium, copper, lead, mercury and nickel. In 1990, around 50 percent of the 41 samples collected from Perak had value exceeding the proposed standard of 0.005mg mercury/litre. In 1989, more than 80 percent of the 42 samples collected from the coastal waters of Perak had values above the proposed standard of 0.01 mg nickel/litre.

A considerable amount of research has been conducted to determine concentrations of heavy metals in water. In northwestern part of Thailand Gulf, a geochemical survey was carried out in order to define concentrations and distribution patterns of selected heavy metals in the coastal system and estuarine area of the Mae Klong river. The results indicated the presence of two different sources of heavy metals in the studied environment and further identified a lithogenic component that might significantly influence the composition of coastal waters and suspended particulate matter (Censi. *et al*., 2006).

Perez *et al*., (1999) had studied on heavy metal concentrations in water and bottom sediments of a Mexican reservoir. The results showed that mercury, lead, chromium and iron were the main metal contamination problem. In the same study, spatial and temporal distributions of total metal levels had also been identified. No organised pattern was detected for any particular metal concentration. The temporal variations of metal concentrations showed evidence of the water self-cleaning capacity of the reservoir, despite high level metal contamination being determined (Perez et al., 1999).

In Port Jackson estuary, the concentrations of dissolved metals were determined for summer and winter under low-flow conditions. Dissolved Ni and Mn behaved mostly conservatively, whereas Cd, Cu and Zn showed mid-estuarine maxima. Peaks in Cd, Cu and Zn concentrations were located in the upper estuary, independent of the salinity and suspended particulate matter loading, and were consistent with anthropogenic inputs of metals in the estuary. Concentrations of dissolved Cu were highest in summer, whereas concentrations of Cd, Ni and Mn were significantly lower in summer than winter. The increase in temperature and biological activity during summer explained the seasonal variation (Hatje *et a*l., 2003).

2.2 Heavy Metals in sediments

Sediments represent an important sink for trace metals in aquatic systems. Concentrations of heavy metals in sediment can be greater than the overlying water. More than 90% of the heavy metal load in aquatic systems is bound to the suspended particulate matter and sediments (Calmano *et al.*, 1993). The distribution of heavy metals in sediment closest to populated areas can provide researchers with evidence of the anthropogenic impact on ecosystems and help to assess the risks associated with discharged human waste. Because of their large adsorption capabilities, fine-grained sediments represent a major repository for trace metal and a record of the temporal changes in contamination. Thus, sediments can be used for historical reconstruction. Sediment core studies have been used as pollution records over the last decades. The core studies has shown to be a great tool for establishing effects of anthropogenic and natural processes on depositional environments.

The accumulation of heavy metals in mangrove sediments has been reported for a number of countries including Hong Kong, Brazil and Nigeria (Machado *et al.*, 2002; Liang et al., 2003; Essien *et al.*, 2009). Although there have been investigations on the levels of heavy metals in marine sediments of Malaysia (Yap *et al.*, 2002), heavy metal data for local mangrove habitants are lacking.

The metal contents in sediments are often used to describe the contamination of metals in different environment. For instance Li *et al*. (2007) studied on heavy metals in coastal wetland sediments of the Pearl River Estuary, China. The total concentrations of heavy metals such as Zn, Ni, Cr, Cu, Pb and Cd, and their chemical speciation were investigated. The results showed that the sediments were significantly contaminated by Cd, Zn and Ni. Pb, Cd and Zn that was strongly associated to with exchangeable fractions, while Cu, Ni and Cr were predominantly associated with organic fractions. The results found Cd and Zn would be the main potential risk and the sediment quality is no longer meeting the demand of the current wetland utilization strategies (Li *et al.*, 2007).

Zheng *et al*. (2008) have investigated the distribution and sources of Hg, Pb, Cd, Zn and Cu in the surface sediments of Wuli River, Cishan River and Lianshan River. They also assessed heavy metal toxicity risk with the application of two different sets of Sediment Quality Guideline (SQG) indices. The results showed that Hg contamination in the sediments of Wuli River was originated from the previous sediment contamination of the chlor-alkali producing industry, whereas Pb, Cd, Zn and Cu contaminations were mainly derived from atmospheric deposition and unknown small pollution sources. The heavy metal contamination to Cishan River sediments was mainly derived from zinc plant while sewage wastewater was the main primary source for Lianshan River. Hg is the major toxicity contributor to Wuli River and Lianshan River followed by cadmium. In Cishan River, Cd is the major sediment toxicity (Zheng *et al*., 2008).

Analyses of heavy metals from sediment samples from 59 stations spread throughout the Yangtze River intertidal zone indicated that the metal concentrations showed significant spatial variation. The results from statistical analyses have suggested that the concentrations of Cd were closely related to total organic carbon content whereas Cu, Cr, Ni, Pb and Zn had a close association with Mn. This study also suggests that the metal contamination cannot be simply evaluated by examining metal concentrations alone. A complementary approach that integrates sediment standard criteria, enrichment factor and geoaccumulation index should be considered in order to provide a more accurate appraisal of the fate and transport of metals from anthropogenic sources and the resultant environmental impact of these materials on intertidal sediments (Zhang *et al*., 2009).

Fractionation of heavy metals in sediments can help in understanding potential hazards of heavy metals. Study done by Li R. Y. *et al.*, 2007 analyzed total concentrations and fractions of selected heavy metals (Cd, Cr, Cu, Pb, and Zn) in surface sediments from Dianchi Lake, Yunnan Province, China, in addition to factors that may affect distributions of the various heavy metal fractions. Total concentrations of the heavy metals decreased in the order Zn > Cu > Pb > Cr > Cd. These heavy metals, except Cr were much higher than their background levels, showing that the Dianchi Lake was polluted with Cd, Zn, Pb, and Cu. Cadmium and Zn occurred mainly as the non-residual fraction. In contrast most of the Cr, Pb and Cu occurred in the residual fraction. Correlation analysis showed that total heavy metal concentrations, organic matter and reducible Fe were the main factors affecting the distributions of the various heavy metal fractions. In the Waihai section of Dianchi Lake, the concentrations of Cd, Zn, Pb, and Cu in the non-residual fraction were significantly lower than those of the Caohai section. This indicated that potential heavy metal hazards in the Caohai section were greater than the Waihai section.

Morillo *et al*. (2002) analyzed seventeen sediment samples from the Odiel and its main tributaries. The chemical partitioning of metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Co) in each sample was determined in four fractions (acid-soluble, reducible, oxidizable and residual). The total content of each of the metals was also determined. The results revealed high concentrations of Fe, Cu, Zn, Pb and Cd, as a result of contamination from the mining and industrial activity. Based on the chemical distribution of metals, Cd, Zn and Cu were the most mobile metals. Cd is the metal that showed the highest percentages in the acid-soluble fraction and the lowest in the residual fraction. However, Pb, Fe, Cr and Ni are present in the greatest percentages in the residual fraction, which implies that these metals are strongly bound to the sediments.

Another study done by Yap *et al*., (2002) had focused on concentrations of Cu and Pb in the offshore and intertidal sediments of the west coast of Peninsular Malaysia. It was found that total Cu and Pb from the west coast of Peninsular Malaysia were generally low and similar to those already reported in other Malaysian localities. For the offshore sediment, the higher metal levels indicated that the offshore area of the Straits of Malacca had started to receive impact from the sea-based activities. The elevated levels of metals found in the intertidal sediments could be due to land-based activities in general (Yap *et al*., 2002).

2.3 Heavy Metals in aquatic organisms

Fish and marine products contain many elements which are essential for human life at low concentration. Nevertheless, they can become toxic at high concentrations. However, certain heavy metals such as mercury, cadmium and lead do no show essential functions in life and are toxic even at low concentration when ingested over long period. These metals were present in the aquatic environment long before human being existed. The proportion between the natural background concentration of heavy metals and anthropogenic heavy metals in fish varies from element to element. In unpolluted areas, fish normally carry natural burden of heavy metal concentration. In heavily polluted areas, the heavy metal concentrations actually found are exceeding the natural concentration (Kalay *et al*., 1999).

Fish and other aquatic animals take up heavy metals from their food and water that passes through their gills. The uptake of metals is often dependent on the amount of food ingested and on the heavy metal content of the food. Accumulation takes a long time and may result in high concentrations in aged organisms. Some species, which are relatively long lived, are known for storing higher amounts of heavy metals in different organs. The main organs which are used in fish for storage and detoxification of heavy metals are liver, kidney and bones. These organs are normally not used for human consumption in Europe and America. In Asia, however, smaller fish are consumed wholely and other gut contents often are used in fermented sauce or salted. There is a vast literature on the content of heavy metals in fish, mollusc and crustaceans. Majority of these papers have reported high concentrations of heavy metals which are due to anthropogenic activities. The parts that are mostly investigated for heavy metal concentration are organs and tissues which normally accumulate and store heavy metals. Less information is available about the heavy metal content in the edible part consumed by humans.

Abdullah. *et al*., (2007) found that mollusk has a potential to be used as bioindicator for the contamination of Cd and Zn in water and sediment of an estuarine environment, as indicated by its high concentration factors (BCFs) values. The species seemed to accumulate certain metals in its tissue and resisted the entry of others from its surrounding environment.

Study done by Mohammad and co-workers (2002) on heavy metal concentrations in water and tiger prawn (*Penaeus monodon*) from Sabah, East Malaysia had shown that there was no general correlation between metal levels in water and in the prawn tissue. The data suggested complexities in uptake and retention of metals in tiger prawns. The animal seemed to resist the build-up of certain metals whereas it allowed the entry of others to the extent of exceeding the proportion that occurred in the environment. Some of the controlling factors include the nature of the metals, environmental factors, the body's reaction, physiological tolerance, tissue thresholds and regulatory mechanisms (Mohammad *et al*., 2002).

Ahmad Ismail et al. (1995) had studied the level of heavy metals in ten species of marine prawns along the coastal areas of Peninsular Malaysia. It was found that the levels of trace metals in most of the samples studied were below the maximum permissible limit of the Food Regulations in Malaysia, with the exception of a few samples collected from the coasts of Melaka and Matang, which contained higher levels of Pb and Cd. However, there was no clear evidence on the relationships of heavy metals in sediments and prawns (Ahmad Ismail *et al.*, 1995).

In the southern part of the Korean Peninsula, concentrations of trace elements in the tissue of *Mytillus galloprovincaialis* varied with size of mussels, season, depending on many factors like sexual development, and seawater temperature. The levels of some trace metals in seawater were correlated significantly with those in soft tissue and byssal threads. There were spatial variations in metal concentrations in the soft tissue and byssus attributed to different sources of trace elements located near the sampling sites. Significant relationships were found between heavy metals in mussel soft tissues and byssal threads and suspended matter.

2.4 Distribution pattern of heavy metals in tissues and organs

The difference in the accumulation of trace metals in various organs of fishes may be attributed to the proximity to the tissues to the availability of the metals. The age, size and feeding habits of fish or aquatic animals as well as their retention time in polluted waters may affect the heavy metals accumulation in these organisms. For fish, the gills, skin and digestion tract are potential sites of absorption of water borne chemicals. There may be variations in the bioaccumulation of different metals in fish. Kidneys and liver tend to accumulate maximum heavy metals concentrations due to their capacity to accumulate trace metals brought by blood from other parts including gills and muscles. This will induce the binding protein, metallothionein that is believed to play a crucial role against the trace metals by binding them. (Adhikari *et al.* 2009).

Adhikari *et al.* (2009) found that muscle of various fish species from Kolleru Lake, India contained the lowest concentrations of trace metals among all the tissues investigated. Muscle does not come into direct contact with the metals as it is totally covered externally by the skin that in many ways help the fish to ward off the penetration of the trace metals (Adhikari et al., 2009). Since it is not an active site for detoxification and therefore transport of trace metals from other tissues to muscle does not seem to arise.

Liver tissues in fish are more often recommended as environmental indicator organisms of water pollution compared to any other fish organs. This is possibly because liver tend to accumulate pollutants of various kinds at higher levels from their environment as reported by Galindo *et al*. (1986). The accumulation of the tested metals in liver could be based on the greater tendency of the elements to react with the oxygen carboxylate, amino group, nitrogen or sulphur of the mercapto group in the metalothionein protein (Kendrick et al., 1992).

Papagiannis and co-workers (2004) have evaluated the level of contamination of two heavy metals appearing at high concentrations in lake water in four fish species (*Cyprinus carpio, Silurus aristotelis, Rutilus ylikiensis, and Carassius gibelio*) caught in the lake. The metal concentrations were determined in three different tissues, namely muscle, liver and gonad in order to assess the metal contamination in these tissues. The study showed that *Cyprinus carpio* and *Rutilus ylikiensis* were contaminated with the highest metal content. Tissue analysis revealed that liver and gonads have accumulated the highest levels of Cu and Zn. Metal concentrations in the edible part of the examined fish such as muscle were at the safety permissible levels for human consumption (Papagiannis *et al*., 2004).

Concentrations of cadmium and lead in five species of fish from River Neretva, Croatia were determined. The results showed that concentrations of cadmium were very high in kidneys of carp and mullet. Kidneys tend to accumulate cadmium, whereas the concentration of cadmium in muscle was lower. The lead concentration in all fish species is similar except carp. The carp had shown to accumulate this heavy metal in all tissue aparts from gonads (Has-Shon *et al*., 2006).

Al-Yousuf *et al*., (2000) had determined the influence of sex and body length on metal accumulation in fish. The results showed that the average metal concentration in liver, skin and muscle of the female fish were found to be higher than those found in the male fish. The accumulation of zinc, copper, manganese and cadmium in the liver tissues of *Lithrinus lentjan* was found high compared to skin and muscle tissues.

2.5 Distribution pattern of heavy metals in difference depth of sediment cores

Coastal and estuarine regions are the important sinks for many persistent pollutants and they accumulate in organisms and bottom sediments (Szefer *et al*., 1995). Geochemical characteristics of the sediments can be used to understand the trends and the sources of the pollution. Due to the large adsorption capabilities, fine grained sediments represent a major repository or trace metal and a record of the temporal changes in contamination. Thus, it can be used for historical trends.

Over the last few decades, the study of sediment cores has been reported to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. A number of recent works have used sediment profiles to describe the contamination history. For example, Pereira *et al.*, (1998) studied on the contamination of mercury in sediments from Aveiro lagoon, Portugal. From a set of four cores, they had observed that at least one core was presented with enriched mercury layer at the surface and background concentration at the bottom.

Metal contamination of soil can occur by a variety of processes. It can be stated that in areas of active aerial contamination the metal profile in soil tends to show highest concentrations in the upper layers of the soil profile. Areas with contamination resulting from past mining contamination tend to show disturbed profiles according to the past historical record of contamination and disturbance, while mineralized areas often show higher metal concentrations in both upper and lower levels of the soil profile.

Several authors have concluded that some metals show a distinct enrichment in surface layers and horizons of many soils. Ong Chee, (1999) studied on the concentration of seven heavy metals in sediments and mangrove root samples from Mai Po, Hong Kong. The study revealed that the metal concentrations in the upper 0-10 cm of the sediment cores from the mudflat were 4-25% higher than those found in the bottom 21-30 cm. The Relative Topsoil Enrichment Index was approximately 1.0 for all the metals. The mean metal concentrations in the sediments decreased in the order of Fe > Zn > Pb > Ni > Cu > Cr > Cd (Ong Chee, 1999).

Higher concentrations of heavy metals were found in the fine-grained than the sand-sized fractions of the sediment from Hong Kong mangrove swamps. However, the differences between these two fractions became less significant when the swamp was more contaminated. The heavy metal concentrations in sediments varied significantly within each mangrove swamp. Mangrove swamps at different geographical locations had different heavy metal concentrations, reflecting the degree of anthropogenic pollution. Although more metals were retained in the fine-grained sediments in most samples, metals would be accumulated in the sand-sized fraction if the swamp received heavy metals from anthropogenic sources. The elevated heavy metal content was mainly due to anthropogenic inputs, including domestic, industrial and agricultural discharges from either the tidal water or the inland fresh water (Tam *et al*., 2000).