

**EVALUATION OF ECOLOGICAL RISK BASED ON THE
SEDIMENT AND WATER QUALITY IN KLANG STRAIT,
MALAYSIA**

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ABSTRACT

Sediment and water monitoring was performed from Nov. 2009 to Oct. 2010 to assess and evaluate the spatial and temporal distribution of physical and chemical parameters and biological variables such as PAHs, trace metals (Hg, Cd, Pb, Cu, Mn, Zn, Cr, Ni, V, and Fe), the structure of the benthic community in the sediment, nutrients and chlorophyll a in the water. Sediment and water samples were collected from 22 stations, which covered three coastal ports (North Port, West Port and South Port) and a control point. The primary objectives of this study were to evaluate the sources of pollutants and each pollutant's distribution, concentration and contamination degree, as well as to assess the biological response to these stressors based on the ecological risk.

Significant variations were found in the distribution and concentrations of all heavy metals and PAHs. The spatial and temporal scales of these variations were related to the several sources contributing to the contamination load in the Klang Strait and to seasonal fluctuations, respectively. The highest concentrations of all metals (except for Mn) were recorded at South Port at stations 16 and 17 parallel to the mouth of the Klang River and at station 13 around the container terminal in the West Port, whereas the lowest concentrations were recorded at the control point. Enrichment factor (EF) index also indicated that all metal concentrations except for Fe were influenced by anthropogenic effects. Similarly, the total organic carbon and fine particle size had significant correlations with most metals (Al, Cd, Cu, Fe, Ni, V and Zn). Thus, both natural processes and human activities contributed to the load of these pollutions in the Klang Strait. The PCA analysis is concordant with the pair isomer ratio of PAHs, which revealed that the anthropogenic sources of PAHs were a mixture of pyrogenic and petrogenic sources at all stations except for stations 4, 14 and 21, where combustion was the more frequent cause. Source analysis revealed that PAHs are primarily derived

from liquid fossil fuels related to the use of vehicles, crude oil and coal (petroleum combustion sources), and a minor amount of PAHs may be related to the direct discharge of petroleum and land-based runoff. Results revealed that most of the sediment samples are in a pristine state with respect to PAHs and metal contamination except for Cd, As, Hg and Pb. Surface sediment in the Klang Strait are moderately polluted by Hg, Pb and As, and only Cd was estimated to have a high level of contamination. Furthermore, risk analysis showed that living organisms in the strait have a high risk of Cd and Hg exposure and only a low risk of overexposure to the rest of the investigated metals and PAHs at all stations. Regarding the risk index classification, only sediments from stations 16 and 17 (mouth of the Klang River) can be considered to represent a high ecological risk. Other stations were categorized as representing slight to moderate risk, and adverse effects were rarely recorded at the control station, which usually showed normal responses. In addition, the level of response of benthic communities to pollutants in the sediment was completely homogeneous with the risk level in most of the stations. In the case of water-quality assessment, multi-metric indices and operational indicator have been proposed to classify trophic level at different sites. The trophic level of Klang Strait coastal water ranges from eutrophic to hypertrophic. Chl-a concentration was used to estimate the biological response of phytoplankton biomass and indicated eutrophic conditions in the Klang Strait and mesotrophic conditions at the control site. During the study period, no harmful algal bloom (secondary symptom) occurred, which may be related to hydrodynamic turbulence and water exchange, which prevent the development of eutrophic conditions in the Klang Strait.

Keywords: Ecological risk, Heavy metal, Polyaromatic hydrocarbons (PAHs), Nutrients, Benthic organisms, Chlorophyll a, Klang Strait, Malaysia

ABSTRAK

Dalam kajian ini, pemantauan mendapan dan air dilakukan dari Nov. 2009 ke Okt. 2010 bagi mengukur kualiti air dan kualiti mendapan dan menilai taburan ruang dan masa bagi pemboleh ubah fisikokimia dan biologi seperti PAH, logam berat (Hg, Cd, Pb, Cu, Mn, Zn, Cr, Ni, V, dan Fe), struktur komuniti benthik dalam mendapan, nutrien dan chlorophyll a dalam air. Sampel air dan mendapan dikumpul daripada 22 stesen, yang merangkumi tiga pelabuhan (Pelabuhan Selatan, Pelabuhan Utara dan Pelabuhan Barat) dan satu tapak kawalan. Tujuan utama penyelidikan ini adalah untuk menilai punca pelbagai jenis pencemaran dan taburan setiap pencemar, kepekannya dan tahap pencemarannya dan juga untuk mengukur respons biologi kepada tekanan-tekanan ini. Terdapat variasi signifikan dalam taburan dan kepekatan semua logam berat dan PAH. Skala spatial dan temporal variasi tersebut berkaitan dengan kepelbagaian punca yang menyumbang kepada beban pencemaran dalam Selat Kelang dan turun-naik bermusim, masing-masing.

Kepekatan tertinggi semua logam (melainkan Mn) dirakamkan di Pelabuhan Selatan di Stesen 16 dan 17 selari dengan muara Sungai Klang dan di stesen 13 di sekitar terminal kontena di Pelabuhan Barat, manakala kepekatan paling rendah dirakamkan di kawasan kawalan. Anggaran factor pengkayaan (EF) juga menunjukkan bahawa kepekatan semua logam melainkan Fe dipengaruhi oleh kesan antropogenik. Begitu juga, jumlah karbon organik dan saiz partikel halus mempunyai korelasi signifikan dengan kebanyakan logam (Al, Cd, Cu, Fe, Ni, V dan Zn). Oleh itu kedua-dua proses semula jadi atau mineralogi dan aktiviti manusia (kesan antropogenik) menyumbang kepada beban pencemar tersebut dalam Selat Kelang. Analisis PCA menyamai pair isomer ratio PAH, yang menunjukkan punca antropogenik PAH adalah gabungan punca pyrogenik dan petrogenik di semua stesen kecuali stesen 4, 14 dan 21,

di mana pembakaran menjadi punca yang paling kerap. Analisis punca menunjukkan bahawa PAH kebanyakannya berasal dari bahan api fosil cecair dan berkaitan dengan penggunaan kenderaan, minyak mentah dan batu arang (berpunca dari pembakaran petroliaam); ada sedikit amaun PAH yang mungkin berkaitan dengan pelepasan langsung petroliaam dan land-based runoff.

Dapatan kajian menunjukkan bahawa kebanyakan sampel mendapan adalah dalam keadaan asal dari segi PAH dan pencemaran logam melainkan Cd, As, Hg dan Pb. Mendapan permukaan dalam Selat Kelang dicemar secara sederhana oleh Hg, Pb dan As, dan hanya Cd dijangka menunjukkan pencemaran yang tinggi.

Tambahan pula, analisis risiko menunjukkan bahawa organisme hidup dalam selat itu mempunyai risiko tinggi untuk pendedahan kepada Cd and Hg dan hanya risiko rendah pendedahan lebih kepada logam lain yang dikaji dan PAH di semua stesen. Merujuk kepada klasifikasi indeks risiko, hanya mendapan dari stesen 16 dan 17 (muara Sungai Kelang) boleh dikira sebagai menghadapi risiko ekologiikal yang tinggi. Stesen yang terancam dan stesen lain dikategorikan sebagai berisiko rendah sehingga sederhana, dan kesan buruk amat jarang dirakamkan di stesen kawalan, yang mana kebiasaannya menunjukkan respons normal. Selain itu, tahap respons komuniti benthik kepada pencemar dalam mendapan adalah bersinkronisasi dengan tahap risiko di kebanyakan stesen.

Dalam penilaian kualiti air, indeks multi-metric dan operasional telah dicadangkan untuk mengklasifikasi status trophic di kawasan berlainan. Tahap trophic air Selat Kelang (Pelabuhan Selatan, Pelabuhan Utara dan Pelabuhan Barat) merangkumi keadaan eutrophic sehingga hypertrophic. Kepadatan Chl-a digunakan untuk menganggar respons biological biomass phytoplankton dan menunjukkan kondisi eutrophic dalam Selat Kelang dan kondisi mesotrophic di tapak kawalan.

Sewaktu kajian tiada kejadian eutrophication atau simptom sekunder kelihatan, dan ini mungkin berkaitan dengan gangguan hydrodinamik dan pergolakan air, yang menghindari perkembangan kondisi eutrophic dalam Selat Kelang.

Keywords: Risiko ekologi, logam berat, hidrokarbon poliaromatik (PAHs), nutrien, organisme bentik, klorofil a, Selat Klang, Malaysia

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LIST OF ABBREVIATIONS

AMBI	AZTI Marine Biotic Index
ASEAN	Association of Southeast Asian Nation
As	Arsenic
Al	Aluminum
Acy	Acenaphthylene
Ant	Anthracene
Ace	Acenaphthene
BaA	Benzo(a)anthracene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BaP	Benzo(a)pyrene
BghiP	Benzo(g,h,i)perylene
BMPs	Best Management Practices
Chy	Chrysene
Chl- <i>a</i>	Chlorophyll <i>a</i>
<i>CA</i>	Cluster analysis
Cd	Cadmium
Cu	Copper
Cr	Chromium
CF	Contamination Factor
Cd	Contamination Degree
Cm	Centimeter
DibA	Dibenzo(a,h)anthracene
DOE	Department of Environment
DIN	Dissolved Inorganic Nitrogen
Dw	Dry Weight
EI	Eutrophication Index
ERA	Ecological Risk Assessment
EHA	Ecosystem Health Assessment
EF	Enrichment Factor
Fla	Fluoranthene
Flr	Fluorene
FAO	Food and Agriculture Organization
Fe	Iron
g	Gram
GEF	Global Environmental Facility
H	Mercury
HAB	Harmful Algal Bloom
InP	Indeno[1,2,3,(c,d)]pyrene
IG	Ignition loss
ISQVs	Interim Sediment Quality Values
kg	Kilogram

Km	Kilometer
l	Liter
m	Meter
ML	Milion Liters
Mm	Milimeter
mg	Milligram
μg	Microgram
MEQ	Marine Environment Quality
MEH	Marine Ecosystem Health
Mn	Manganese
Ni	Nickel
NO_3^-	Nitrate
NO_2^-	Nitrite
NH_3	Ammonia
NH_4^+	Ammonium
ND	Below the method detection limit
Nap	Naphthalene
Phn	Phenanthrene
Pyr	Pyrene
ppm	Part per million
ppb	Part per billion
PO_4^{3-}	Phosphorous
PCA	principal components analysis
PAH	Poly Aromatic Hydrocarbon
Pb	Lead
SAV	Submerged Aquatic vegetation
SD	Standard Division
SIDS	Sudden Infant Death Syndrome
SiO_4^{4-}	Silicate
TPH	Total Petroleum Hydrocarbon
TOS	Total Organic Solid
TRIX	Trophic Index
UNEP	United Nations Environment Program
UNDP	United Nation Develop Program
USEPA	U.S. Environmental Protection Agency
V	Vanadium
WQI	Water Quality Indices
Zn	Zinc

CHAPTER I: STATEMENT OF PROBLEM

1.1 General Introduction

In the past century, estuary and coastal water pollution has become a worldwide crisis in the natural environment because anthropogenic and lithogenic sources discharge extensive amounts of pollutants. Most of these pollutants cause serious threats for marine organisms and human being's health and become environment crises in marine ecosystems including oil spills, red tides, contamination of fish and shellfish, mortalities of marine mammals and fish, eutrophication and hypoxia (Carl, 2006).

Ecological risk assessment is a process used and developed in environmental sciences to evaluate health status or ecological quality of an environment (Chapman, 2002; Wells, 2003; Xiao, Ouyang, Cheng, & Zhang, 2004). In fact, Ecological risk assessment evaluates the relationship between physical, chemical and biological stressors to their ecological effects and systematically quantifies and qualifies stressors and their adverse effects on environment (EPA, 1998). Therefore, assessing the ecological risk in a marine environment includes a combination of information to know the sources and different types of pollutants (as stressors) and their effects.

The marine environment is greatly influenced by industrialization and motorization. Thus in orders to assess the ecological risk, many researchers have focused on determining concentration and distribution of organic and inorganic contaminations (as stressors) such as: hydrocarbons, heavy metals and nutrients in sediment and water. These pollutants are discharged by several sources coming from land-based oil input, industrial and agricultural waste, and marine shipping oil spills.

In the marine environment (water and sediment), these organic and inorganic compounds may cause serious problems because excess concentrations can alter the characteristics of marine ecosystems resulting from several kinds of hazardous and toxic contents which can accumulate in a biological community (Loska & Wiechula, 2003; Neff, 2002). Also, studies show that heavy metals and hydrocarbon compounds have high carcinogenic and mutagenic activities (Neff, 2002). Thus, determining concentration of hydrocarbons and heavy metals concentration and their distribution in water and sediment is a key part of the evaluation and assessment programs in coastal areas because they help to indicate the contamination degree, potential threat of pollutants and pollution sources (Morillo, Usero, & Rojas, 2008).

Bio-assessing and surveillance are practical methods of monitoring the health status of ecological receptors in a marine environment (Burger & Gochfeld, 2001). In recent decades, biological indicator organisms have been widely used to assess the effects of pollutants. Bio-indicators can obviously show the ability of stressors to cause adverse effects in a marine environment. As a matter of fact, they act as receptors which respond to stressors by their alternation in population or histological structures. According to the National Academy of Science, use of bio-indicators are practical in promoting the knowledge of environmental issues, supporting environmental characteristics, standard enforcement and improving existing methods to assess ecological risk to the environment (Frontalini & Coccioni, 2011; Tullos, Penrose, & Jennings, 2006). Phytoplankton structure is one of the important bio indicators, which is widely used in studies of aquatic ecosystem function. It is used for monitoring response to environmental stressors, due to their fast population changes in the aquatic ecosystem (Bianchi et al., 2003; Lu, Xu, & Yang, 2010; OSPAR, 1998).

Alternation of abundance and diversity of phytoplankton reflects the nutrient potential and disturbance into the aquatic ecosystems and has direct relationship with

the nutrient concentration. Nutrient enrichment causes increase phytoplankton growth as primary producers create extra biomass accumulation which can develop harmful algae bloom. Bloom makes negative effects on aquatic ecosystem such as hypoxia condition, oxygen depletion and elevated turbidity and ultimately causes high mortality of the aquatic organism due to oxygen defect or the attendance of the toxic phytoplankton species (USEPA, 2008; Wan, Zhu, & Zhao, 2007).

In sediment, macro benthic organisms are important bi-indicators for assessing environmental change and chemical contaminate effects due to their close relation to sediment, high sensibility to chemicals contaminates and their ability to take up and accumulate different kinds of compounds specially heavy metals (Caçador et al., 2011; Coccioni, 2000; Foster, Arminot, & Rogerson, 2012; USEPA, 2008). Factors which influence on accumulation by benthic organisms are: concentration of chemicals contaminates, season, size, hydrodynamics activities of the aquatic environment (Beltman, Clements, Lipton, & Cacela, 1999; Boyden & Phillips, 1981; Stevenson, 1984). Benthic organisms are considered the main connection in transferring of compounds to higher trophic levels (Mucha, Vasconcelos, & Bordalo, 2005).

Klang Strait is a main gateway with the busiest shipping route on the west coast of Peninsular Malaysia and it is extremely affected by port activities. Important activities of this area are: fishing, ecological habitats, international commerce and industrial sites. Klang Strait coastal waters have been much degraded in recent decades (Yap & Kahoru, 2001).

Land runoff, industrial waste, navigation and transportation release chemical pollutants into the strait such as petrogenics like poly aromatic hydrocarbons (PAH), persistent toxicants like heavy metals, nutrient and total suspended solid (TOS). Ecological and biological conditions are influenced by these pollutants (Yap, 2005). Although many efforts have been made to improve aquatic ecosystems in this area, the

increase in the chemical discharges has caused great concern among environmental managers. Thus, the constant release of pollutants requires comprehensive assessment of organic and inorganic pollutants and their ecological effects in order to establish management policies for protecting ecological condition and biological communities in Klang Strait coastal waters.

1.1.1 Problem statement

The essential issues are to understand the fundamental characteristics of a natural ecosystem in terms of ecological and biological condition, main habitat types and the pollutants that influence the ecosystem stability and to be familiar with the main concepts of ecological risk assessment.

The problems addressed in this research are as follows:

Which sources (anthropogenic or lithogenic) are discharging heavy metals, petroleum hydrocarbons and nutrients as stressors into Klang Strait?

What are the main stressors and their effects on biological community structure (due to exposure)?

Which methods and indexes must be used to analyse the effects and characteristics of exposure?

How do biological systems respond to the stressors?

1.1.2 Scope and objectives

This research was started in March 2009 and continued until March 2012 (see ‘milestones’, appendix1) and was sponsored by University Malaya grants (IPPP and UMRG). The main purpose of this study is to provide comprehensive and practical data

for the environmental management of Klang coastal waters in the context of the rapid industrial and economical development in this area.

Selected physical, chemical and biological parameters were determined to assess water and sediment quality including the polyaromatic hydrocarbons (PAHs) and heavy metals (Al, As, Hg, Cd, Pb, Cu, Mn, Zn, Cr, Ni, V, and Fe) in sediments, nutrients (NO_3^- , NO_2^- , DIN, PO_4^{3-} , NH_4^+ , NH_3 , SiO_4^{4-} and Chl-a) in water and benthic community and Chl-a as biological indicators.

An ecological risk assessment was conducted based on the major components of ecological risk, including problem formulation, selection of endpoints, characterisation of risks and risk quantification using an aquatic ecological risk-assessment model (Suter, 1993; Xiao et al., 2004).

Assessment of pollution in the Klang Strait coastal water is a difficult task due to the great variability in environment conditions. This area is affected extensively by nonpoint sources, different depth, tidal condition and strong marine current, due to the northeast monsoon. These limitations have an effect on pollutants concentration, although the sediment situation in this area is independent of tidal influence. Several concepts have been used to reduce the impacts of these limitations, such as increasing number of stations, temporal assessment, and multiple sediment samplings during the north and south monsoon.

This dissertation is divided into five chapters. Chapter 1 includes a description of the general introduction, background study, problem statement, scope and objectives, and the organisation of thesis. Chapter 2 contains a theoretical review of the related literature that provides information about the characteristics of water and sediment composition and PAHs, heavy metals, nutrient, bio-indices and bio-indicators. Also, this section is widely focused on the essential issues of ecological risk frameworks in the marine environment.

Chapter 3 covers the methodology for laboratory experiments with their procedures for assessing ecologic risks, bio-indices and data analysis. Chapter 4 contains the results of the analysis with discussion of the graphs and tables.

Chapter 5 discusses the conclusion of this thesis with a description of a new ecological approach based on the obtained results. Additionally, this chapter contains recommendations for future studies.

There are two main purposes for this PhD study. The first aim is to comprehensively determine the sediment and water quality as well as benthic infaunal biodiversity in coastal environment of Klang Strait November 2009 and 2010. Using these newly collected data, the second aim of this study is to assess and evaluate the ecological risks of various common environmental stressors in the area. The results will be highly essential to the environment management of Klang coastal waters since these areas are undergone a rapid industrialisation and economic growths.

1.1.3 Hypothesis

Many researchers from 1980 to 1997, mentioned in the literature review, high concentrations of chemicals and petrogenic pollutants in Klang Strait that are due to anthropogenic sources, such as navigation and transportation, industrial activities and sewage pollution (Yap & Kahoru, 2001). These pollutants can directly or indirectly cause many serious problems and inflict damage upon the ecological and biological condition of Klang Strait coastal water. In this research, I aim to determine whether these types of pollutants (heavy metals, nutrients and PAHs), which are from different anthropogenic sources, influence the health status and biological communities of Klang Strait. Thus, the first hypothesis is that these pollutants can influence the ecological health status of Klang Strait (H1), and the second hypothesis is that they do not influence the health status of Klang Strait (H0).

1.2 Background of this study

There are many studies which describe general observation about ecological and biological conditions in the marine environment (Speers & Whitehead, 1969; Suter, 1993). Most of these studies focused on identifying pollution sources and determining marine pollutants concentration and their ecological critical level for biological communities in enclosed or semi enclosed seas (Black Sea, Mediterranean Sea, Aral Sea, Baltic Sea, and others), estuaries and coastal waters. The results of these observations are considered as standard guidelines to assess the marine environment in the 21th century described in several publications such as: The Black Sea (Mee, 1992), the Baltic Sea (Hansson & Rudstam, 1990; Wulff & Niemi., 1992), The Mediterranean Sea (Pearce, 1995), a Summary article on Seven Enclosed and Coastal Seas (Platt, 1995) and the coastal waters and estuary (Boesch & Rosenberg, 1981; Hakanson, Kvarnas, & Karlsson, 1986).

In the 20th century, many researchers emphasized Best Management Practices (BMPs) in aquatic areas to control and manage different types of water pollution due to municipal and industrial wastewater (Neary, 2008). The following publications described how anthropogenic activities affect the marine environment such as: McClelland (1992), Lucas (1991), California Department of Toxic Substances Control, and Puget Sound keeper Alliance (1993)., Buller et al (1995) and American Boat and Yacht Council (1995), Amaral et al (1996). Terms of BMPs issues have been specified for petroleum hydrocarbon, hazardous materials and vessel discharge concentrations. In fact, the issues of BMPs were applied by the industrial designers to provide the engineering systems (different types of filter, reactors and clarifiers) which can prepare principal components to control pollution systems (Neary, 2008).

Most of the research in the 21th century determine degradation degree and their effects in estuary and coastal water by evaluating the density of human population, the degree of industrial development and drainage area in coastal and estuary waters. Most of the evaluation research have been specified to describe health status of the marine environment such as: Harteet al.,(2007); Xiao (2004); Pedersen et al.,(2005); Hill(2006); Freestone (2007); Smith (2006).

In recent decades, the scientific knowledge has been developed into models, indexes and assessment to generate information practical for a specific purpose in marine environment like Ecological Risk Assessment (ERA) and Ecosystem Health Assessment (EHA). In 1998, The U.S. Environmental Protection Agency (EPA) published guidelines for Ecological Risk Assessment which described specific structures as a framework for ecological risk assessment. The guideline was replaced with the previous edition of EPA report (EPA/630/R-92/001, February 1992) which involved principles and terminology to assess the ecologic risk process (EPA, 1998). In this guideline, there was confusion due to distinctions, because it focused on risks of past actions without considering predictive methods or formula to assess the future consequences of past events.

Glenn and Sutell (2006) prepared a new handbook on ecological risk assessments which eliminated distinctions instead of the decision-practical function of ecological risk. They performed ecologic risk assessment combined with future consequences of past events. They assessed effects of continuous toxic, distribution of toxicity degree of contaminants to other areas and destruction of habitats due to wrong restoration and the analysis of such information can be used as a method or formula for assessment problem, clarifying effects that may have influence in the future, explaining the casual relationship between stressors and exposures and creating a scientific rule for restoration and remediation (Suter & Glenn, 2008).

The issues to apply for Ecosystem Health Assessment (EHA) in the marine environment emerged in the late 1980s and their characteristics were very obvious (ecological indicator book). The EHA study has been applied to assess health status in water and sediment because it was able to quantify the environmental problems according to observation and environment indexes and indicators.

The first international conference on the use of indicators for assessment of health status was held at In Fort Lauderdale Florida in October 1990. Since then several national and international conferences have been held on EHA. In 1992, *Ecosystem Health* was the first book that was published by Island Press. In mid-1990, a second book with the same title was published by Blackwell and also started publication of *Ecosystem Health* journal with Rapport as editor in chief. In the 21th century, the following comprehensive handbooks were published on EAH issues which are used as a general reference for ecosystem health and environmental indicators: *Integrated Assessment of Ecosystem Health* by Kate et al (2000); a handbook entitled, *Ecological Indicators for Assessment of Ecosystem Health* published by Taylor and Francis groups in 2005 and 2010; *Water Quality for Ecosystem and Human Health* by (GEMS)/Water Programme in 2009 and (Raffaelli & Frid, 2010; Suter & Glenn, 2008).

During the last three decades, many books were published on water quality assessment since water quality assessment is a method to monitor ecosystem health. Ecological indexes and indicators are two main tools to assess hazards, eutrophication formation, trophic status and to define frameworks in marine water (Neary, 2008; Neff, 2002).

The marine water index was first recommended to assess the status of consequential variables by Brown *et al* (1970) and was later extended by the National Sanitation Foundation (1974).

This index entitled the National Sanitation Foundation Water Quality Index (NSFWQI) to evaluate water quality in different aquatic areas. Vollenweider *et al* (1998) applied oxygen saturation, nitrogen, phosphorus and chlorophyll concentration to determine trophic index (TRIX). Recently, a new TRIX version was developed by using the dominated phytoplankton in order to complete the European Water Framework Directive (WFD) (Ferreira et al., 2011).

In 1989, Magurran divided diversity indexes into three categories based on abundance and enrichment such as Margalof, Simposon, Pielou Evenness and Shannon-wiener indices which are used in some studies to assess biodiversity in marine ecosystems.

In marine waters, defining indicators to assess water quality is difficult because these areas are extremely dynamic and heterogeneous with different conditions in different types of ecosystems (Ferreira et al., 2011). Thus, the existing specific indexes and indicators for coastal waters are under new developments or their use is limited to specific ecosystems where they have been developed. Much research regarding EHA and selection of indicators showed that it is impossible to arrange a set of ecologic indicators to be applied for specific problem or specific ecosystem (Jørgensen, Constanza, & Xu, 2005; McLusky & Elliott, 2007). Many different types of Water Quality Indexes (WQI) have been defined but it is still argued to develop new WQIs according to many general indicators which can be used to compare same problems in the same types of aquatic ecosystems. Thus different frameworks are defined for different types of marine ecosystem in different areas.

Sediment quality is widely assessed in the world because apart from water, sediment also acts as possible media of contaminate transportation. The best approach in assessing sediment quality is based on determining concentration of chemicals

contamination and individual bioassay (bioaccumulation and toxicity) (Chapman, 2002; Donahue, 2010; Förstner, Ahlf, & Calmano, 1993).

Since the beginning of the 20th century, heavy metals and petroleum compounds have been recognized as potential contaminants the marine environment that are increased due to the growth of the petroleum industry and the marketing of petroleum products (Patin, 1999). In the first decades of the 20th century, many reports appeared in scientific news about changes of marine biological communities due to fuel oil and crude oil released from ship wrecks (Elias et al., 2009).

After World War II, the scientific literature about the effects of oil pollution greatly increased and in 1967 the wreck of the Torrey Canyon in coast of England was used as the first comprehensive study based on assessing effects of oil and metal pollution and their cleanup methods on environmental resources. From 1970s until early 1980s, researchers focused on the harmful effects of petroleum hydrocarbon and metals in marine ecosystem and human health; thus these researches increased (NOAA, 1991).

After 1980, there is abundant literature on these contaminants which cover vast topics such as contamination of marine organism, bioaccumulation and chemical fate, sediment toxicity, remediation and clean up, and biological effects on all types of animals and plant life in environments. In recent studies, the potential threat of heavy metals and petroleum hydrocarbon to aquatic organisms has been widely assessed by using various methods (McClelland, 1992; NOAA, 1991).

In 1993, the Land-Ocean Interactions in the Coastal Zone (LOICZ) was initiated with biogeochemical programs to evaluate biogeochemical processes and accumulation and fate of contaminants in coastal and estuaries zones. The United States National Oceanic and Atmospheric Administration (NOAA) and United States Environmental Protection Agency (USEPA) published comprehensive reports and guidelines on the concentration of metals and PAHs in aquatic sediment (McClelland, 1992; NOAA,

1991). NOAA and EPA programs have been developed to classify toxicity level in aquatic sediment by evaluating concentrations of contaminants and distribution of benthic fauna as indicators. Also, many organizations and sites started to assess and classify marine sediment information such as the Canada Ministry of Environment Ontario Provincial SQGs, Interim Sediment Quality Values (ISQVs) and Department of Environment Research of New York Sediment Screening Criteria (O'Connor, 1994; O'Connor, 1992).

1.2.1 Research background in the Klang Strait

Klang Strait is widely influenced by chemicals and petrogenic pollutants, silt and sedimentation and sewage pollution which cause many problems and inflict damage on coastal areas. From 1981 until 1997, some studies began to assess environmental conditions in different coastal zones of the strait in association with many research institutions such as DOE–Selangor (Department of Environment), ASEAN (Association of Southeast Asian Nations) and GEF/UNDP/IMO (Regional Programmers on Building Partnerships in Environmental Management for the Seas of East Asia) (Yap, 2005).

From 1989 until 1993, DOE recorded high concentrations of oil and grease in marine water from 1.3 to 2.8 mg/L. In 1995, its concentration decreased significantly (0.3 to 0.6 mg/L). Concentration of petroleum hydrocarbon (crude oil) was determined from 0.0063 mg/l to 0.063 mg/l in marine water and ranged in sediment from 83.3 mg/kg to 703.9 mg/kg (Yap, 2005). According to the standard classification of the FAO (the Food and Agriculture Organization) and Marched in 1982, the Klang Strait coastal area was categorized as moderately polluted with petroleum hydrocarbons. Studies show that the petrogenic pollutants in Klang Strait originate from oil spill events and ship ballasting or pumping bilges due to tanker and non-tanker operations.

In 1997, 25.000 tons of heavy fuels oil were released into the Straits of Singapore because of a collision between two tankers; thus, 700 tons of oil poured into Malacca Strait and roughly affected the coastal area of Klang Strait (Yap & Kahoru, 2001).

The studies of Law and Singh, (1986-1988); Ho et al, 1993; Yap 1998; Everaarts & Swennen,1987, have recorded high concentrations of common chemical pollutant such as heavy metals in marine water, sediment and biota in Klang Strait (Yap, 2005).

The level of iron and lead was higher than the standard of coastal water as a result of navigation and transportation, land-based pollutants and industrial activities. In 1997, the Malaysia government have decreased the impact of chemicals, petrogenic and others stressor by applying regulations, guidelines and international agreement and law(Yap, 2005). Also, Malaysia ratified two international conventions (MARPOL 73/78 and OPRC, 1990) in 1997, to prevent and control tanker and non-tanker based discharges and oil spill incidents; moreover, a national offshore limit was considered for pollutant discharges such as platform draining and industrial outlets (Selangor Waters Management Authority, 2005).

During 1991 until 1998,the Association of Southeast Asian Nation (ASEAN) and the ASEAN–Canada Cooperative Program on Marine Science-Phase II (CPMS-II) assessed regional marine ecosystems and water quality based on the concentration of 10 specific parameters (oil and grease, bacteria, phenol, total suspended solid, Cd, Hg, As, Pb, Cu, Cr, , NO₃, NO₂⁻, DO and temperature).

Klang and Malacca Strait were considered as focal areas to optimize marine ecosystems based on advantages of environmental collaborative programs. All of these programs were performed based on these approaches: to improve the quality standard of the tropical marine environment and their framework, monitoring the basic studies of pollution range and toxic red tides (Selangor Waters Management Authority, 2005).

Although the marine standards or guidelines have been developed for the Malaysia marine environment, their ability to protect living resources has not been thoroughly evaluated. It requires ecological risk assessment to estimate quantities, impact of anthropogenic pollutants and tolerance levels of biota. The main goals of ecological risk assessment remain the early stage of detection and appropriate action to protect vulnerable environment in Klang Strait (Selangor Waters Management Authority, 2005).

The first study on phytoplankton structure was by Anton in 1991 which reported 76 species of diatoms and noted a high patchy distribution of phytoplankton in this strait. Also she determined the biomass level that ranged from 0.045 to 11.3 $\mu\text{g/L}$. In 2005, the diversity and abundance of phytoplankton structures were reported in *Ecology of Klang Strait*; classified into three divisions (Bacillariophyta, pyrrophyta and cyanophyta) with 52 taxa and Bacillariophyta shows high density (853 cell per milliliter, or 98.7%) (Ibrahim, 1988).

From 1974 until 1994, there were many studies on benthic community in mangrove forests in the vicinity of Klang Strait by Chang, Sarpedonti, Sasekumar and Alongi which divided macro fauna into few invertebrate groups including a few species of polychaete, 30 species of gastropods and 45 species of crustaceans also bivalves and sipuncula were dominated (Yap & Kahoru, 2001).

The first technical report of Port Klang was published in 2005. That report was initially prepared during the Regional Training Course on Environmental Risk Assessment held between 23 to 28 July 2001. The training course was organized in collaboration with Regional Programmer on Building Partnerships in Environmental Management for the Seas of East Asia (PEMSEA). Also a book '*Ecology of Klang Strait*' was published in 2005 describes its physical environment, intertidal habitats, open water and estuaries in Klang Strait.

CHAPTER II: LITERATURE REVIEW

The literature contains assessment theories of the marine environment which explains the following scientific topics of this research: 1) strategies to monitor marine environment quality 2) strategies for monitoring water quality 3) strategies for monitoring sediment quality, and 4) ecological risk assessment.

2.1 Strategic of marine environment assessment

The quality of the marine and coastal environments is mainly influenced by lithogenic and anthropogenic sources. Lithogenic sources are natural and result from the weathering of bedrock, volcanic processes, atmospheric circulation, runoff via hydrological processes, and biological activities that lead to changes in the physical and chemical balance of the aquatic area. Anthropogenic effects on the marine environment are due to human activities such as agriculture, industry, consumption and energy harvesting, and mining, all of which can load an extensive amounts of pollutants into marine and coastal waters by rivers and industrial outlets (Mohsen, Majid, & Maryam, 2010). When pollutants exceed from the standard range, they have harmful and toxic effects on survival and growth rate of marine organisms and species diversity in the marine environment also suffer (Jørgensen et al., 2005). Thus, since 1980, many studies, including those from Buckley (1995); NOAA's (1998); IOC (1996); Percy and Wells (1997); Cobb and Vandermeulen (2001) and Westhead and Reynoldson (2004), have focused on assessing and managing the Marine Environment Quality (MEQ) and Marine Ecosystem Health (MEH).

According to the definition put forth by the Canadian Environmental Group from 1988 to 1996, MEQ is “the condition of a particular marine environment measured in relation to each of its intended uses and functions”(Suter & Glenn, 2008).

As matter of fact, MEQ is a quantitative assessment of the biological, physical, and chemical nature of marine water and sediment in relation to lithogenic and anthropogenic effects, and intended uses on spatial and temporal patterns. Although MEQ and MEH are sometimes used synonymy in the literature, they do have different meanings.

MEQ refers to original and natural trends without any undisturbed conditions in the long-term, whereas MEH is a description of present status or conditions in the short-term. The Canadian Environmental Group described a framework to assess MEQ and MEH that includes four concepts: characteristics and uses, stressor factors, ecosystem responses (using indicators), and health or status of the environment. Harding (1992) incorporated parts of ecological risk assessments (sources, effects and exposure) with the MEQ concept from 1999 until 2000, developed a useful framework of MEQ by describing the connection between research, monitoring of chemical and biological variables (indicator), assessment, objectives, and guidelines. As described above, the assessment of MEH and MEQ require monitoring, research approaches, objectives, guidelines and indicators (Jørgensen et al., 2005; Suter & Glenn, 2008).

2.1.1 Monitoring and research approach

An important aspect of marine assessment is the monitoring process, which includes research and data collection of physical, chemical, and biological variables in the short-and long term, in order to compare with standard measurements and the natural background which may describe the current condition of the marine environment (Neary, 2008). The monitoring process is essential for any environmental quality and ecosystem health assessment; the data collected through sampling work designed for monitoring process should clarify the following objectives: (a) to assess the status and trends of marine environmental health; (b) to clarify how marine

environmental quality is influenced by pollutants; (c) to define the interrelationship between different variables; (d) to discriminate between lithogenic and anthropogenic sources; (e) to condense information in large-volume data; (f) to apply both historical data and current data as valuable scales for assessing temporal trends; (g) to provide comprehensive monitoring results to make recommendations for management decisions and policies in the future (Jørgensen et al., 2005).

2.1.2 Objective of marine quality assessment

The monitoring programme depends on assessment objectives that have been described in a comprehensive survey. The objective may set up key information about the ecosystem that can describe the needs of various programme assessments (Neary, 2008). The main objectives of monitoring assessments have been focused on:

- Estimation of the spatial and temporal distribution of marine environmental quality in order to choose sampling stations and sampling frequencies.
- Estimation of the concentration of specific descriptors in order to evaluate pollution.
- Estimation of the feasibility and costs of monitoring operations.

Thus, the process of implementing objectives must focus on many ecological and biological factors and activities that affect the quality of the marine environment, such as geographical conditions, water uses, and pollution sources.

2.1.3 Guidelines and standards

Guidelines and standards are vital tools that can help establish quality standards that protect aquatic environmental health. Guidelines are able to interpret trends of physical and chemical variables which are based on experimental and scientific

assessments, and have high abilities to define the acceptable range of toxicity and their adverse effects on human life and marine organisms (**Table 2.1** and **Table 2.2**). These guidelines arrange limits for the biological, physical, and chemical variables in marine water and sediment, which are essential for the safe undertaking of different activities such as agriculture, industrial, and recreational activities (EPA, October 2001).

Table 2.1, List of Sediment Quality Guidelines (SQGs)

Institution Sediment quality Guideline (SQGs)	Effects ranges	Application
National Ocean and atmospheric Administration (NOAA). (Buchman, 2008)	<ER-L: Adverse effects are rarely observed. ≥ ER-L and < ER-M: Adverse effects are occasionally observed. ≥ ER-M: Adverse effects are frequently observed.	Suitable both from fresh and salt water
Canada Ministry of Environmental Ontario Provincial SQGs for Metals and Nutrient . (Persaud, Jaagumagi, & Hayton, 1992) New York Sediment Screening Criteria. (Long & Morgan, 1990)	< LEL (Lowest Effect level): the effect in the sediment is Considered to be acceptable. ≥LEL and <SEL (Sever Effect Level): contaminated, moderate impact To benthic life. ≥ SEL: contaminated and significant harm to benthic aquatic life.	Suitable freshwater sediment metal guidelines
Hong Kong Special Administrative Region Interim Sediment Quality Values (ISQVs) (Chapman, Allard, & Vigers, 1999).	ISQVs-Low: adverse biological effects are unlikely. ISQVs-high: sever adverse biological effects are very likely.	Seabed dredged sediment
Development and evaluation of sediment quality guidelines for Florida coastal waters. (Macdonald, Carr, Calder, Long, & Ingersoll, 1996)	TEL (Threshold effect levels): Adverse effects are rarely observed. ≥ TEL and < PEL: Adverse effects are occasionally observed. ≥ PEL(probable effects level): Adverse effects are frequently Observed.	Coastal and marine water
Sediment Quality Criterion (SQC). (Lyman, Glazer, Ong, & Coons, 1987; Pavlou, 1987)	SQC-chronic: Adverse effects are rarely observed. SQC- acute: Adverse effects are frequently observed.	Coastal and marine water

Table 2.2. Summary of four set of SQGs for selected chemicals in sediment of coastal and marine area (Macdonald et al., 1996; Macdonald et al., 1992)

Sediment Quality Guidelines (SQGs)	MacDonald		NOAA090		NOAA08		SQC (USEPA)	
	TEL	PEL	ER-L	ER-M	ER-L	ER-M	Chronic	Acute
Metal, (mg/kg)								
Arsenic	7.24	41.6	33	85	8.2	70	8.2	16
Cadmium	0.68	4.21	5	9	1.2	9.6	7.7	24
Chromium	52.3	160	80	145	81	370	NG	NG
Copper	18.7	108	70	380	34	270	14	54
Lead	30.2	112	35	110	46.2	218	33	840
Mercury	0.13	0.7	0.15	1.3	0.15	0.71	0.01	0.15
Nickel	15.9	142.8	30	50	20.9	51.6	NG	NG
Silver	0.73	1.77	1	2.2	1	3.7	NG	NG
Zinc	124	271	120	270	156	410	190	560
Total PCBs (µg/kg)	21.6	189	50	400	22.7	180	NG	NG
Pesticides (µg/kg)								
Chlordane	2.26	4.79			0.5	6	0.3	NG
Dieldrin	0.72	4.3	0.5	6	0.02	8	200	NG
p,p'-DDD	1.22	7.81	0.02	8	2	20	NG	NG
p,p'-DDE	2.07	374	2	20	2.2	27	NG	NG
p,p'-DDT	1.19	4.77	2	15	1	7	1.6	NG
Total DDT	3.89	51.7	1	7	1.58	46.1	1.6	210
Lindane (gamma-BHC)	0.32	0.99	3	350	NG	NG	3.1	NG
PAHs (µg/kg)								
Acenaphthene	6.71	88.9	150	650	16	500	2400	NG
Acenaphthylene	5.87	128	NG	NG	44	640	NG	NG
Anthracene	46.9	245	85	260	85.3	1100	190	NG
Fluorene	21.2	144	35	640	19	540	59	NG
Naphthalene	34.6	391	340	2100	160	2100	500	10500
2-Methylnaphthalene	20.2	201	65	670	70	670	NG	NG
Phenanthrene	86.7	544	225	1360	240	1500	2400	14000
Total low molecular weight PAHs	312	1442	NG	NG	552	3160	NG	NG
Benz(a)anthracene	74.5	693	230	1600	261	1600	1600	55000
Benzo(a)pyrene	88.8	763	400	2500	430	1600	18000	450000
Chrysene	108	846	400	2600	384	2800	1200	115000
Dibenz(a,h)anthracene	6.22	135	50	260	63.4	260	12000	NG
Fluoranthene	113	1494	500	3600	600	5100	1600	9000
Pyrene,	153	1398	350	2200	665	2600	850	49500
Total high molecular weight PAHs	655	6676	NG	NG	1700	9600	NG	NG
Total PAH	1684	16770	4000	35000	4022	44792	NG	NG

2.1.4 Indicators, methods, and statistical measures

Indicators are often applied to define health status, to assess sediment and water quality, and to prepare useful information for managing and protecting the marine environment. According to the definition by Ferris and Humphery (1999) “an indicator may be defined as a characteristics which, when measured repeatedly, demonstrates ecological trends and a measure of current state or quality of an area”. Walls (2000) gives a more simple definition, “an indicator is a variable that describes the state of the system”. Burger (2006a) proposed a comprehensive definition of indicator: “Indicator: Index or measurement end point to evaluate health of a system; physical, biological, economic and human” (Kitsiou & Karydis, 2011).

Indicators are the main tools that have been used to monitor ecosystems, because indicators act as signals or signs that can reflect physical, chemical, and biological disturbances; they have the ability to identify significant stressors and their effects on the marine environment. Over the past few years, much research has been done to select practical indices that can be implemented in the monitoring process, and are able to provide practical information related to the specific question of environmental assessment, which are applied to making strategic decisions of management (Hakanson & Blenckner, 2008). Generally, practical indicators should have the following characteristics: 1) easy to handle and inexpensive to measure; 2) sensitive to small variations in stressors and relevant to environmental threat; 3) independent of reference point; 4) have high international applicability in vast geographical regions with a great abundance of communities; 5) clearly predictable by logical quantitative and qualitative models (Hakanson & Blenckner, 2008; Jørgensen et al., 2005). **Table 2.3** describes specific Indicators and indices in the marine environment based on physicochemical parameters, quantities of plankton and benthic communities, species identification and density of species.

Although, there is extensive information about ecological and biological indicators in the literature, it has been difficult to fulfill all five of these characteristics because most indicators are more or less specific for certain kinds of stressors, and applicable to only specific types of ecosystems.

Table 2.3. Conventional index for assessment of marine environment base on water and sediment quality and example of physic-chemical and biological indicators (Ferreira et al., 2011; Pinto et al., 2009)

Type of method	Index Name	Biological indicators	Physicochemical indicator	Sample timeframe
*Integrate multi-parameter	EPA NCA	Chl a	Water clarity, DO, DIP, DIN	June- Oct
	TRIX	Chl a	DO, DIN, TP or PO4	Annual
	TWQL/LWQI	CHL a, macroalgae, Seagrass	DO, DIN, DIP	
	ASSETS	CHL a, macroalgae, seagrass, HAB	DO	
	WFD	CHL a, microphytoplankton, macroalgae, seagrass, HAB	DO, DIP, DIN,TP,TN, Water clarity	Summer
	WFD	CHL a, macroalgae, seagrass, macrobenthos	At least 5 year data available with monthly sampling in surface layer	
	HEAT	CHL a, Primary production macroalgae, seagrass,HAB, macrobenthos	DO, DIP, DIN,TP,TN, Water clarity	Annual
	IFREME	CHL a, HAB, seagrass, macro benthos	DO, DIP, DIN,TP,TN,SRP Water clarity, sediment organic matter, sediment TN,TP,DIN,DIP	
	EI	Chl a	PO4, DIN	
	Benthic index of Environment	Benthic community	-----	
Benthic Quality Index	Benthic community			
AMBI	Benthic community			
Multivariate AMBI (M-AMBI)	Benthic community			
APBI	Benthic community			
Present/absent of species	Benthic opportunistic amphipoda index (BOPA)	Benthic community	-----	
	Diversity	Shannon-wiener		Benthic and plankton community
		Margalaf		Benthic and plankton community
		K-dominance		Benthic and plankton community

Currently, the ecological and biological indicators applied in different circumstances, for different stressors and different aquatic areas are classified on seven levels: (1) The presence or absence of a particular species is applied to assess the degree of pollution, which is classified as: unpolluted, slightly polluted, polluted, or very polluted; (2) The ratio between classes of specific species such as the Nyggrad algae index; (3) concentrations of particular chemical compounds; (4) trophic levels; (5) rate process; (6) composite indicators, and (7) holistic indicators (Jørgensen et al., 2005).

Ecological indicators usually provide information about the structure of an ecosystem and the accounting function of specific components; for example, the concentration of nutrients and chlorophyll a, water flow and diversity, and abundance of vertebrates, invertebrates, and plants. This synoptic information is not more effective in assessing the health status of an ecosystem, so the effective attribute of an indicator is to mix several ecological factors in a single formation as indices that can be practical for providing general ecological issues and environmental assessments.

The absence or presence of a specific species is one of the common indicators for determining degree of pollution; for example, the Bellan indices, based on characterizing the dominant species, is known as a sign of pollution in environments with species such as polychaetes and amphipods (Bellan, 1967, 1980). Most authors do not recommend these indicators because the density of some indicator species may change naturally, and there is no credible method to determine if the significant change in the indicator species of a population was due to pollutants or occurred naturally (Warwick & Clarke, 1998). In spite of these criticisms, AMBI index (Borja, Franco, & Pérez, 2000; Borja, Muxika, & Franco, 2003), Benthic index (Simboura & Zenetos, 2002), ISD index (Reizopoulou & Nikolaidou, 2006) and Ecological Evaluation Index (EEI) (Orfanidis, Panayotidis, & Stamatis, 2003) were updated based on the account

between the presence of a species stating a kind of pollution, and of species stating a non-polluted condition in aquatic area. In fact, in these indices, benthic organisms are classified into several ecological groups based on their responses to types of pollutants, particularly organic materials.

It has been successfully applied as a practical tool for detecting the type of anthropogenic pollutant (especially organic matter and heavy metals inputs) in the framework of European Water for estuary and marine coastal water (Kitsiou & Karydis, 2011; Zaldívar et al., 2008).

Biodiversity indices, such as Shannon-Wiener index, Margalef, Simpson, and K-dominance, have been frequently applied to describe the biological variety in marine environments. Statistical multivariate methods have been used to calculate these indices based on simple formulas, so these indices provide a widely logical concept base of diversity measure which can quantify and clarify the relationship between diversity of biological organisms and disturbances which may act as stressors (Kitsiou & Karydis, 2011).

Recent studies have been done by testing the monotonicity and linearity of 22 indices based upon phytoplankton richness and diversity. The results showed that monotonic increased only in Menhinick, Margalef, and Evenness indices. The indices of Simpson, Shannon-Wiener, Hill N_1 and N_2 , McIntosh and Hulbert, showed a curve with a hump-shape instead of one characteristic of monotonicity. These indices have inverse relationships to abundance value of species. In addition, this research shows that Menhinick and Evenness indices can be applied for both issues: monotonicity and linearity (Kitsiou & Karydis, 2011; Spatharis, Roelke, Dimitrakopoulos, & Kokkoris, 2010).

In 1998, Wollenweider suggested the use of the Multi-metric trophic index (TRIX) to monitor the trophic status and eutrophication trend in coastal water. It

integrates Dissolved Inorganic Nitrogen (DIN), total phosphorus (TP) or inorganic phosphorus ($p\text{-po}_4\mu\text{mol/l}$) (as a biotic component or measure of the potential of biomass), Chl-a (as a proxy for biomass of phytoplankton), and Oxygen saturation percentage as a biotic component to determine productivity. TRIX has been widely applied to assess trophic status in different marine areas such as the Black sea, Caspian sea, Persian sea, Montego Estuary, southeast Mexico, and Helsinki sea (Kitsiou & Karydis, 2011; Vollenweider, Giovanardi, Montanari, & Rinaldi, 1998). Although, some reports have shown that there are drawbacks to the suitability of TRIX because this index cannot provide some requirements of the European water framework (WFD, 2000/60/EC) also TRIX does not conform to the natural reference condition to normalize the scale. Many researchers are attempting to rescale TRIX base on reference condition of oligotrophic water.

Thus, recent research studies do not recommend this index for shallow aquatic areas that are dominated by macroalgal and seagrass, and instead apply benthic indices which is more effective because the biomass of phytoplankton is not appropriate for defining the nutrient effect (Giordani, Zaldivar, & Viaroli, 2009; Primpas & Karydis, 2010).

In 2010, Primpas proposed another multimetric index to assess trophic status on a five-point scale; namely, the Euthrophic Index (EI). This index tests three standard sets of water types (oligotrophic, mesotrophic, eutrophic) and historical data of Rhodes costal water. Results showed that EI is effective and valid (Primpas & Karydis, 2010). There are some indices that try to assess the effect of environmental stressors, based on ecological strategies of different organisms, variation in abundance, biomass of marine organisms, and environmental information such as: infaunal index, polychaetes feeding guilds, r/K strategies, and ABC Curves of Pearson and Rosenberg.

The use of these indices is usually not recommended because the variation pattern of most marine organisms is unpredictable and dependent upon many physicochemical parameters.

Statistical analysis methods are practical for the quantitative monitoring of the marine environment and can be divided into two main groups: one-dimensional statistical analysis and multi-dimensional analysis (**Table 2.4**). The results of these statistical methods can provide the following outcomes: 1) condense large data of individual variables; 2) provide information about health status and trends if the scales of the health of the environment are available; 3) classify the sampling point base on quality levels; and 4) clarify the interrelation between variables. These outcomes can be used not only as final results or “end products”, but also can contribute to multiple criteria methods such as remote sensing, spatial analysis, mapping, and modeling. The advantages and shortcomings of statistical methods are explained in Table 3. Multiple criteria analysis methods are complex assessment methods that are used to optimize data of sampling programs.

These methods are able to use various criteria to classify sampling points based on spatial structure (health statuses and trend), degree of homogeneity, and anisotropies. These methods are also able to predict health status and trends in the future based on the estimated relationship between cause and effect of pollution by dynamic and empirical analyses. Although statistical methods and indicators are easily applied to assessing marine and coastal water quality, to some extent, the researchers face problems in processing laboratory data, especially in regards to the concentration of physicochemical variables and the phytoplankton community. These problems include: 1) extremely inter-correlated variables; thus, the total effects due to these variables are not additive because it is essential to obtain uncorrelated variables in some cases; 2) in most cases, the distribution of variables does not conform to normality.

Thus if the parametric method is applied to these variables, data transformation will occur and a great deal of raw data will be lost. So non-parametric methods are useful for these distributions; 3) seasonal changes in variables cause high variations in mean values, which lead to overlapping groups of data characterizing the type of trophic states; 4) it is difficult to discriminate between lithogenic and anthropogenic causes of nutrients and select control sites, as unpolluted references are not always practical for this problem. Thus, the concentration of nutrients must compare with the reference or background values of specific marine areas (Kitsiou & Karydis, 2011).

Table 2.4. Statistical analysis methods applied to quantitative assessment for marine environment quality (Kitsiou & Karydis, 2011)

Type of the method	Name of method	Advantage	Disadvantage
One-dimensional statistical analysis	Descriptive statistic	Provide a statistic summary of central tendency and variability. It can be used to any type of data which define the quality of environment.	a statistic summary cannot provide any final evidence about health status.
	Frequency Distribution (FD)	FD describes the profile of physic-chemical values and forms the basic scale for health status of environment.	Normality pre-requisite for probabilistic application is not usually fulfilled.
	Outliers	Outlying values describe the extreme condition of environment, (pollution problem and eutrophic trend)	Limitation of methodology due to the non-normally distributed variables: limited use does not allow method validation in environmental study.
	ANOVA	It statistically detects the differences between significant level and compare means of more than two groups/level	ANOVA assumes normality not commonly met in different variables: fairly often the data are pseudo-replicates.it is suitable just for parametric data.
	Correlation and regression	It is easily applied to understand the interaction among variables	It required normality; the natural information are distorted by data transformation.
Multi-dimensional statistical analysis	Principal Component Analysis (PCA)	It detects the main variables which influence on health status/ trends. It is easy to apply and understand outcome.	PCA in most of case is preliminary method to assess marine environment quality
	Cluster Analysis (CA)	It is easily applied to Classify of sampling points based on different variable. Non-parametric	Limited access to significant test. There is different outcome (dendrogram) because of several similarity estimate and clustering algorithms.

2.2 Strategies for monitoring water quality

In the marine environment, a comprehensive assessment of water quality should include the monitoring of hydrological, physicochemical, and biological variables.

2.2.1 Hydrology and hydrodynamic features

All coastal water bodies are influenced by other water sources, from atmosphere to marine, via the hydrological cycle, hydrodynamic activities, river discharge, and underground; these are directly and mutually connected to each other. Thus complete interpretations of water quality assessment are generously dependent upon the knowledge of hydrology and hydrodynamic properties such as variation of rainfall and river discharge (stream flow), suspended load, climatic condition, size of water bodies, tidal flow, and circulation. This information about these properties can provide meaningful and practical conclusions to monitoring water quality because of their direct effect on chemical components and biological communities (EPA, October 2001). A common example of their effect is to control resident time in estuarine and coastal waters. Residence time directly effects the growth rate of phytoplankton and the composition of communities via controlling the cycle of nutrients and their reactions (Noble, Tymowski, Fletcher, Morris, & Lewitus, 2003; Richardson, Pinckney, & Paerl, 2001). Nutrient cycling is the practical linkage to converting the inorganic form of nutrients to their organic forms. In addition, the spiraling of nutrients can provide downstream net nutrients in each successive cycle of nutrients. In general, there is a connection between resident time, nutrient supply, and biomass of phytoplankton.

A long resident time is a cause to decrease the transport of downstream nutrients so the regeneration cycles of sediments are increased; therefore nitrogen compounds can stay in the system for a long time and serve as a nutrient supply to increase phytoplankton growth.

In this case, the tidal system, freshwater flow, and different circulation makes for a short resident time that commonly increases the sensitivity of the system to nitrogen discharge (Gallo, 2007).

2.2.2 Physical and chemical variables

Most physical and chemical characteristics in coastal area depend on geomorphology, climatic, and geochemical conditions in the study area. It is necessary to determine these characteristics during specific period to understand the health status of the coastal environment, especially in regards to general characteristics such as salinity, total dissolved solid, conductivity, redox potential, temperature, and nutrient concentration which can make general classifications of marine water with different natures (**Table 2.5**).

2.2.2.1 Temperature

Temperature is a main variable that is influenced by marine currents, climatic and geographic conditions. The temperature of surface waters is usually within the range of 0 °C to 30 °C (EPA, October 2001; Neary, 2008), although in the dry season, it may reach more than 30 °C. Many studies have shown that temperature has a direct impact on most of the physical, chemical, and biological processes in water bodies; for example, increasing the water temperature can lead to an increased rate of chemical reactions and metabolic decomposition, and low temperatures can cause decreased rates of dissolved gases. One of the fundamental impacts of temperature in aquatic areas is that temperature directly correlates with growth rate; the growth rate of bacteria and phytoplankton are greatly doubled by increasing temperature in a very short period, causing increased turbidity, so if nutrient concentrations are suitable, it can lead to algal blooms and cause eutrophic conditions in water bodies (EPA, October 2001; Neary, 2008).

Table 2.5. General classification from different countries based on the quality standard of estuary and coastal water (Selangor Water Management Authority, 2005; USEPA, 1991)

Class	I Excellent	II Good	III Satisfactory	IV Passable	V Poor
<u>Malaysia</u>					
DO (mg/l)	7	5-7	3-5	3	1
NH3-N	0.1	0.3	0.9	2.7	2.7<--
NO2	----	0.4	0.03	5	----
NO3	-----	7	----	----	----
TP	----	0.2	0.1	----	----
TSS	25	50	150	300	300<
TDS	25	50	150	300	300<
PH	5-7	3-5	3	1	-----
EC(umhos/cm)	1000	1000	----	6000	----
<u>Finland</u>					
Chl-a(µg/l)	<4	<10	<20	20-50	>50
Secchi(m)	>2.5	1-2.5	<1	----	----
TP (µg/l)	<12	12-20	20-40	40-80	>80
<u>Sweden</u>					
Chl(µg/l)	<1.5	1.5-2.2	2.2-3.2	3.2-5	>5
Secchi (m)	>5.4	4-5.4	3.4-4	2.5-3	>2.6
TN(mg/l)	<266	266-350	350-490	490-756	>756
TP(mg/l)	<22.6	22.6-28	28-34	34-40	>40
<u>Class Thailand</u>	I Natural resource preservation	II Coral reef conservation	III Aquaculture	IV Recreation	V Industrial, ports and Residential districts area
DO (mg/l)	not exceed than 4	not exceed than 6	not exceed than 4		
NO3 (µg /l)	not exceed than 20	not exceed than 60			
PO4 (µg- /l)	not exceed than15		not exceed than45	not exceed than15	not exceed than45
Unionized Ammonia (µg /l)	not exceed than 70		not exceed than100	not exceed than70	
Salinity	any change shall not exceed 10% of the minimum salinity				
Suspended solid	an increase shall not exceed the average value within 1 day, 1 month or 1 year [4] added by its corresponding deviation value				
PH	7-8.5				

2.2.2.2 Dissolved Oxygen

Dissolved Oxygen (DO) content and oxygen saturation percentage are other fundamental characteristics of coastal water, and its concentration is used as operational indicators of pollution in aquatic areas. The percentage of oxygen saturation is typically measured in the surface and bottom of water as an index representing the ratio of production and respiration. It largely affects all chemical and biological reactions, and is vital for all types of aquatic life. For example, in bottom water, a shortage of oxygen causes dissolved nutrients, such as ammonia, orthophosphorus, and hydrogen sulfide, to increase. In unpolluted water, the oxygen concentration is usually less than 10 mg/L at 25 °C, and can vary with salinity, temperature, turbulence, and atmospheric deposition.

In addition, biological processes such as photosynthesis of algae and rates of respiration can alter the DO concentration even less over 24 hour periods. Nutrients and waste discharge with high concentrations of organic compounds can lead to anaerobic conditions as a result of the decreased DO concentration, because the degrading organic compound causes increased microbial activity (Neary, 2008). The concentration of oxygen saturation in deep water has been extensively applied as an operation bio-indicator for water quality index, because its concentration directly reflects the condition of benthic organisms and organic matter.

For example, several studies have shown that key species of benthic organisms will die if the percentage of oxygen saturation decreases to 20%, or the concentration of dissolved oxygen is lower than 2 mg/L (Hakanson & Blenckner, 2008).

2.2.2.3 pH

pH is the main variable for assessment of water quality; it shows the acid balance in marine water and how it affects all chemical and biological processes. The pH in most unpolluted water is recorded to be between 6.0 and 8.5.

Some natural substances, such as fulvic and humic acids, as well as the balance between carbonate, bicarbonate, and carbon dioxide ions, control the natural value of pH. The balance in pH values can be changed by industrial discharge, which are acid-forming compounds caused by atmospheric deposition, and the photosynthesis and respiration process of algae in eutrophic conditions. For example, most research shows that organic content due to effluents can decrease pH values, and higher values of pH occur under eutrophic conditions, and salt lake and groundwater discharge.

2.2.2.4 Turbidity and suspended solid

Turbidity and suspended solid are main factors that reflect the clarity and transparency of water quality. The main sources of turbidity in marine and coastal water include high phytoplankton growth, organic detritus, soil erosion due to runoff, industrial waste, agriculture, forestry, and reconstruction. The Secchi disk is direct reflection of water clarity and turbidity because it reflects depth of light penetration and amount of light scattered by suspended matter, so it is commonly applied as an operational bio-indicator for assessing the water quality index in aquatic areas. Many studies have focused on variations in Secchi depth and its relationship to other variables in aquatic areas, using multiple regressions. Their results showed a significant relationship between Secchi depth and concentration of chlorophyll a (chl a), Total Nitrogen (TN), Suspended Particulate Matter (SPM), and salinity. Therefore, empirical models were defined based on these significant relationships, which are important in

understanding and predicting variable concentration changes in estuary and coastal water (Hakanson & Blenckner, 2008).

2.2.2.5 Salinity

Salinity describes the concentration of dissolved salts and ions in aquatic areas. The range of salinity is very important for growth rate and reproduction of aquatic species and plants (EPA, October 2001). It also effects the flocculate of suspended particles, which is known as the operational bio-indicator for understanding variations in water clarity in estuary and coastal waters (Hakanson & Blenckner, 2008). Conductivity shows the water property that conducts electrical currents; this property is relative to the ion concentration in aquatic areas. Salinity and conductivity are often applied as a surrogate of measurement for each other (EPA, October 2001).

2.2.2.6 Nutrients

Nutrients are vital elements for biological characteristics because macronutrients have direct effects on metabolism, organism growth, and biomass of primary producers (phytoplankton and marine plants), including carbon, oxygen, hydrogen, phosphorus, nitrogen, sulphur, and calcium. Many micronutrients, such as iron, silica, manganese, and molybdenum, are essential in low concentrations for metabolism, growth rate of organisms, and cellular tissue, which most often act as cofactors in enzymes. Nitrogen (N) and phosphorus (P) are the major macronutrients that are required to control the growth of phytoplankton, and the productivity of the marine system is directly or indirectly influenced by N and P inputs, which can either increase or reduce primary production. Successful strategies of management in the atrophic estuary and coastal water depend on the precise understanding of limiting nutrients. Early studies indicated that N is limiting in marine water, while in freshwater, P was detected as the limiting

nutrient in the Chesapeake Bay (Fisher, Peele, Ammerman, & Harding, 1992), the Black Sea (Cociasu, Petranu, & Mihnea, 1999) and the Delaware Bay (Pennock & Sharp, 1994), but in recent decades many researchers have stated that, P can be limiting as well as N in marine water. This is commonly true along the estuarine and coastal water because these regions are frequently influenced by freshwater input such as rivers and farmland runoff, which are rich in nitrogen as a result of anthropogenic activities and fertilizer. Thus, it is so common which P to be limiting during the high discharges period of the freshwater and N act as limiting factor in low discharges of freshwater (Sylvan, 2008).

For example phosphorus was limited in Eastern Mediterranean System (EMS) specially in winter phytoplankton bloom and ratio of N:P was unusually high (28:1) (Kitsiou & Karydis, 2011; Krom, Emeis, & Van Cappellen, 2010).

The bio-available forms of nitrogen that are measured include nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3) and ammonium (NH_4^+). The high concentrations of nitrogen can significantly increase the growth rate of algae, especially if total nitrogen is above 1000 $\mu\text{g/l}$.

Nitrogen compounds, including the organic and inorganic forms, are known as indicators for monitoring water quality. Although many studies have shown that inorganic nitrogen has a major role in stimulating the biomass of algae, dissolved organic nitrogen, which is more than 70% of dissolved nitrogen, is discharged by the river into the estuary and coastal water (Stepanaukas, Leonardson, & Tranvik, 1999).

Some experimental research has shown that due to the re-mineralizing process, Dissolved Organic Nitrogen (DON) may increase the growth of algae, as DON in rainwater can incite the growth of phytoplankton and bacterio-plankton. However, further experiments must be done in order to know if these results are applicable (Hakanson & Blenckner, 2008).

In the environment, Dissolved Inorganic Nitrogen (DIN) consists of nitrate, nitrite, and the ammonium ion. Ammonia naturally originates from decomposition of organic and inorganic matter, nitrogen reduction by micro-organisms, and biota excretion. It is also loaded into aquatic areas by industrial outlets, fertilizer runoff, and urban waste. Thus, it is good indicator of organic material. In water solution, total ammonia includes the sum of un-ionized ammonia and ionized ammonium/ammonia, and there is equilibrium between these two forms. Approximately 97% of total ammonia is composed of ionized ammonia, and this substantial equilibrium is controlled by pH, temperature, salinity, and concentration of total ammonia (Hakanson & Blenckner, 2008; Neary, 2008). The increase in pH and temperature causes an increase in the concentration of unionized ammonia, which in the range of 1.0 μM , has toxic effects on marine organisms, especially larva, incites algal growth, and damages the ecological balance (Cociasu et al., 1999).

Ammonia also has the ability to form complexes with heavy metals, and can be adsorbed onto suspended solids, bed sediments, and particles of colloidal size (Neary, 2008). In estuary systems, the concentration of ionized ammonia commonly increases with the mixing of fresh and marine water. In general, the interface between marine and fresh water increases the electrolytes of salt solutions, which has significant effects on primary production and nitrification, so high amounts of ionized ammonia are released into the water (Risgaard-Petersen et al., 2004).

Nitrate is an essential form of nitrogen for aquatic plants. It may be decreased to nitrite (NO_2^-) by biochemical reactions such as the de-nitrification, and the nitrite is rapidly converted to nitrate by oxidation. In unpolluted water, the concentration of nitrate rarely exceeds 0.1 mg/l, but when it is influenced by anthropogenic activities

(especially waste and fertilizer run-off), its concentration increases up to 5 mg/l which indicates pollution.

The concentration of nitrate and nitrite are general indicators which can clarify the state of nutrients and organic pollution in water bodies (Hakanson & Blenckner, 2008). Silica (SiO_4^{4-}) is another limiting nutrient for diatom production, and commonly originates from natural sources (lithogenic) such as weathering, so the ratio of N:Si or P:Si is a practical benchmark for estimating the relationship between anthropogenic and lithogenic nutrients (Suthers & Rissik, 2009). In 1999, Eyre and Balls indicated that the concentration of Si has the tendency to be much higher in tropical estuaries and coastal water (Hakanson & Blenckner, 2008).

Since the 19th century, the results of many studies have shown that plants require a specific ratio of nutrients for efficient and maximum growth. In 1855, Liebig presented the Law of Minimum, which indicates that limiting concentrations of nutrients can lead to extra growth of phytoplankton and plants. In 1958, Alfred Redfield described the relationship between the biomass of phytoplankton and the specific elemental stoichiometry for C, N, and P at a ratio of 106:16:1. The optimal ratio for N, SiO_2 , and P is 16:16:1, which is called the Redfield ratio. This ratio implies that primary production is limited if the concentration of N or P (C is ignored because carbon is fixed by phytoplankton, and CO_2 has high saturation in surface marine water) are lower than the elemental ratio (16:1) (17 and 24). Many studies have demonstrated that the risk of harmful algal bloom is increased when the ratio of TN/TP is below 15 (Hakanson & Blenckner, 2008).

In 1992, oceanographers described the effects of the variation of nutrient supply in marine environment. Biomass limitation (Liebig, also known as biomass limitation), which indicates that the nutrient supply can limit the biomass of phytoplankton. In addition, limiting nutrients are able to stimulate increases in the concentration of

phytoplankton biomass. For instance, if the ratio of N: P is 10, then the addition of nitrogen can lead to an increase phytoplankton biomass.

Measuring the nutrient concentrations is a simple and rapid method to describe limitations, as nutrient concentrations are practical indicators of ecosystem status when nutrient data is mixed with biological data or nutrient ratios (Sylvan, 2008).

2.2.2.7 Other components

Heavy metals and petrogenic compounds are other parameters that are analyzed to assess water quality; however, many researchers have indicated that these parameters cannot logically assess water quality since water bodies, especially estuary and coastal waters, are extremely dynamic and heterogeneous. In addition, some of these chemical analyses and their quality control can be too costly, and must be performed over long periods of time with a high degree of replication. Thus researchers need to focus on monitoring these parameters in sediment instead of water.

2.2.3 Biological characteristics

Biological communities are composed of different organisms with individual species. Biological communities are widely affected by biogeochemical reactions that also play vital roles in regulating the biogeochemical balance in the environment, because they have the ability to clean and detoxify water. As a matter of fact, biological communities not only respond to physicochemical variations in their environment, but they are also able to drive such variations (Ostroumov, 2005).

They respond to physicochemical variations in different ways, with a common example being the biological response to changes in the abundance and diversity of

specific species, such as decreases of sensitive species or duplications of tolerant species.

Bio-monitoring is a useful tool for assessing the quality of the aquatic environment, because biological communities are able to integrate the effects of certain types of stressor over time in order to provide extensive measurements of the variation in environmental conditions. Bio-monitoring can be performed at different trophic levels include the single cell (bacteria, fungi, protists and viruses), primary producers (algae, phytoplankton and vascular plants), primary and secondary consumers, such as invertebrates and fishes.

2.2.3.1 Phytoplankton

Phytoplanktons (tiny drifting plants) are major biological communities which have vital roles in the aquatic food chain and are known as indicators of coastal and estuary conditions. Thus, it is necessary to be knowledgeable about changes in phytoplankton communities and their interactions with aquatic areas. This can reflect the physicochemical quality of the aquatic area because phytoplanktons are able to significantly respond to variations in nutrient concentration, light, sediment load, and zooplankton grazing.

The response time of phytoplankton to these variations is known as a practical scale for comparing the quality of the aquatic area on temporal and spatial scales. The abundance and diversity of phytoplankton species can clarify the health status and trophic condition in aquatic systems. In addition, some types of phytoplankton and their photopigment concentration (chlorophyll a, carotenoid) are known as specific bio-indicators for environmental assessments (Suthers & Rissik, 2009).

2.2.3.2 Types of phytoplankton

The major group of phytoplankton that are found in temperate and tropical coastal water include bacillariophyceae (diatoms), Dinophyceae (dinoflagellates), Cyanophyceae (blue-green algae) Euglenophyceae, Chlorophyceae, chrysophyceae, Prymnesiophyceae, and Chryptophyceae. Most of these groups are classified into three groups based on size, such as the picoplankton (0.2–2 µm), nanoplankton (2–20 µm), and microplankton (20–200 µm). In temperate areas, more than 80% of phytoplankton biomass is attributed to nanoplanktons, while in tropical coastal waters, the picoplankton composes 80% of total phytoplankton (Suthers & Rissik, 2009).

2.2.3.3 Chlorophyll *a*

Chlorophyll *a* is the green pigment in most photosynthetic plants. Measuring chlorophyll *a* levels are a good reflection of the biomass of phytoplankton and trophic status in aquatic areas. Photo-adaptation is the main factor that widely changes the amount of chlorophyll per cell. Chlorophyll *a* concentrations are commonly influenced by nutrient supply, stability of water column, depth of euphotic zone, zooplankton grazing, sinking and mixing, although several studies have shown that chlorophyll *a* concentration range from 20 to 40 µg/l in enriched estuary during the summer. However, under optimal conditions, chlorophyll *a* concentrations may increase from 50 to 80 µg/l, in presence of high nutrient concentration. During the winter, the chlorophyll concentration decreases to between 1 and 5 µg/l near the coastal areas due to low loading of nutrients (Hakanson & Blenckner, 2008).

2.2.3.4 Eutrophication

Eutrophication has been known as a problem underlying the disturbance of coastal water bodies for the past 50 years (Kitsiou & Karydis, 2011). Many researchers have found several definitions for eutrophication, and have tried to make operational methods, models, and indicators to assess eutrophication. The main point is that assessment of eutrophication in marine coastal water is difficult because of the complexity of the process, and effect and cause which influences eutrophication formation. According to the first definition by Naumannin (1919), Hutchinson (1967), Halser and Steelein (1947): “eutrophication is the high growth rate of algae which follow rate of nutrient in aquatic area”. Vollenweider (1992) defined the eutrophication issue in comprehensive detail by stating, “eutrophication-in its more generic definition that implies to both fresh and marine waters, is the process of enrichment of waters with plant nutrients, primarily nitrogen and phosphorus that stimulates aquatic primary production and its more serious manifestations lead to visible algal blooms, enhanced benthic algal growth of submerged and floating macrophytes”. A simple definition was also given by Nixon (1995) “Eutrophication is an increase in the rate of supply of organic matter to an ecosystem”.

This definition was accepted by research and scientific organizations such as the Europe Environmental Agency (EEA), United Nations environment programme (UNEP), and European Commission Directive (Kitsiou & Karydis, 2011). UNEP considered eutrophication as a disturbance in the marine environment; it also emphasizes excessive levels of organic matter as the cause of eutrophication. In the 21th century, the logical and scientific definition of eutrophication was given based on the European Water Framework Directives (WFD-2000/60/EC and MSFD-2008/60/EC), decision of Justice European Court in 2004 and definition of OSPAR (1998): “Eutrophication is a process driven by enrichment of water by nutrients, especially

compounds of nitrogen and/or phosphorus, leading to: increased growth, primary production and biomass of algae; changes in the balance of organisms; and water quality degradation". The consequences of eutrophication are undesirable if they appreciably degrade ecosystem health and/or the sustainable provision of goods and services (Ferreira et al., 2011). Although all definitions emphasized nutrient enrichment as causes of eutrophication, some effects are not always due to nutrient enrichment. Rather, some effects can originate from other factors such as changes in climate condition, and changes in the population of common predators due to overfishing and disease. It is essential in eutrophication assessment, to consider on one hand, the variation of relevant symptoms, and on other hand, that specific eutrophication symptoms may be irrelevant. For example, a decrease of seagrass is a eutrophication symptom in only shallow marine coastal water such as the Strait of Danish and some parts of the German and Mediterranean coast, and is not relevant to eutrophication in deep marine environments.

Harmful Algal Bloom (HAB) is the main symptom of eutrophication, so it is important to distinguish between shifts (regime shift is a sudden change in the state or condition of marine by altering the balance and persistence, which can be due to external perturbations and internal dynamics) due to land discharge (fertilizer) which is practical in making management decisions, and those that originated from natural events such as upwelling (Ferreira et al., 2011; Kitsiou & Karydis, 2011; Siokou-Frangou, Christaki, Mazzocchi, Montresor, & Ribera, 2010). The last definition of eutrophication referred to water quality degradation including decreases in biodiversity, transparency, oxygen compounds, and harmful algal bloom (HAB). HAB is known as a marine phenomenon which is important for knowing what species increase blooming, and what conditions make blooming occur.

There are several factors (nutrient, temperature, marine current, resident time, and grazing) that can individually effect algal bloom formation, but often there are combination effects that cause blooming to occur.

Moreover, various species of algae communities are different in several aspects such as their tolerance and requirements, so one compound of water quality parameters may be effective for the growth rate of one species, while a different compound may be effective for another species. For example, high concentrations of nutrient and temperature with low alkalinity may enhance cyanobacteria bloom, while chrysophytes may increase in soft, cold, and oligotrophic conditions with slight acidity. The effect of bloom is directly dependent on phytoplankton species that causes bloom so there are two types of harmful bloom: 1) high-biomass (*Noctiluca*, *Phaeocystis*, *Lepidodinium*) that are harmless because they are non-toxic, and just cause discoloration. This may be harmful to aquatic organisms by reducing dissolved oxygen and shading (Ferreira et al., 2011); 2) toxic or potentially toxic algae.

These species have powerful toxins that are dangerous to aquatic fish, mammals, and humans because their toxins are able to accumulate in shellfish and transfer high levels along the food chain; it is known as Harmful Algal Blooms (HABs) and include dinoflagellate (*Alexandrium spp.*, *Gymnodinium spp.*, *Karenia spp.*, *Dinophysis spp.*, *Pseudonitzschia spp.*, *Gamberdiscus*, and *Gonyaulax*) and some diatoms (Ferreira et al., 2011; Suthers & Rissik, 2009). Therefore managing and controlling bloom requires enough information about the causes of bloom, and sources of nutrient discharge and toxicity. There are several options to prevent bloom conditions and control biomass of phytoplanktons in estuary and coastal water. For example, although zooplankton grazes, during warm seasons with high temperatures and intense light, grazing is unable to consistently control the biomass of phytoplankton.

Researchers have shown that the grazing of zooplankton is likely to be effective in decreasing biomass if the production rate of phytoplanktons is low. The practical option for decreasing bloom is to reduce the concentration of nutrient discharge by treating sewage and applying a nutrient reduction device.

Several assessment methods have been integrated with indicators that evaluate and classify marine system based on eutrophication conditions or trophic status, which is commonly described according to productivity such as a state of low productivity (oligotrophic), intermediate productivity (mesotrophic), and high productivity (eutrophic) (Suthers & Rissik, 2009). These methods use water column variables such as DO, chlorophyll, nutrients (TRIX and EI) macroalgal, SAV, HAB and macrobenthos indicators (AMBI, BI, and ISD) to assess trophic status (Borja et al., 2012; Devlin, Bricker, & Painting, 2011; Ferreira et al., 2011).

2.3 Strategies for monitoring sediment quality

Water quality assessment alone is not enough to protect marine environments; assessment of sediment quality is essential for this purpose because sediment acts as repositories for inorganic and organic contaminants in the marine ecosystem. Biological communities are directly or indirectly affected by sediment contaminants, especially through leaching and re-suspension processes, which lead to bioavailability of contaminants in aquatic areas (Nascimento, 2007). These contaminants are able to form chemical complexes, and adsorb into particular substances or dissolve into the pore water of sediment. Thus, despite sediment contaminants, dynamics extensively vary by the consecutive fluxes of physicochemical and biological variables in or out of the sediment, although these contaminants can be stable in sediment over the long term. This dynamic may change the quality of pore water and the distribution of biological communities (Nascimento, 2007; Prospero, 2002).

In general, for the comprehensive assessment of sediment quality, the following tenets should be followed:

The concentration and effect of contaminants depend on the condition of water bodies, specific chemical compounds (PAH, Metals), the natural properties of the sediment, and the indigenous biological communities (flora and fauna). It is clear that these combinations are different in different areas. Thus, it is essential to consider the combination of biological, physical, and chemical variables to monitor the sediment quality. The reliable assessment of sediment quality includes hazard identification, exposure evaluation, determination of the biological effects of pollutants, and risk estimation; these information can address associated uncertainties (GIPME, 2003; Lehr & Keeley, 2005).

The assessment of sediment quality should be able to discriminate between a portion of naturally-occurring contaminants (metal and hydrocarbons) and anthropogenic sources. The natural concentration of chemical compounds is characterized as a base and background for identifying the source of anthropogenic additions (GIPME, 2003; Lehr & Keeley, 2005). In general, sediment quality assessments have included the use of sampling strategies in different spatial and temporal scales, analysis of the physico-chemical and biological variables by laboratory testing (for estimation of toxicity and bioaccumulation), and evaluation of ecological indicators such as the structure of benthic communities (GIPME, 2003; U.S.EPA, 2004).

2.3.1 Physical assessment

The analysis of physical characteristics is the first step in assessing sediment quality, and this information is essential for understanding the effect of contaminants on benthic communities, fate, bioavailability, and transportation of contaminants in

sediment. Physical characteristics are analyzed based on measurement of parameters such as total solid, distribution of particular size, specific gravity, and acidity (pH) by analytical techniques which were originally devoted to soil (U.S.EPA, 2004).

The analysis of particle size estimates the frequency of size fraction of mineral particles in sediment, and defined in percentage of sand, silt and clay. Particle size widely influences the concentration of chemical and organic compounds and the structure of biological communities. It has also been applied to account for some variation in biological communities, and to test toxicity in environmental research (U.S.EPA, 2004).

Fine- particles of sediments adsorb organic and inorganic matter more than coarse-particles; thus, there is a concern about particles with dimensions greater than 2 mm, because these particles cannot retain high quantities of contaminants.

The retention of sand ($2\text{mm} > \text{particles} > 63\mu\text{m}$) is low because of the minimal surface area for absorbing contaminants. In comparison, silt and clay (particles $< 63\mu\text{m}$) are extremely prone to retention of high contaminants (especially anthropogenic sources) because when the dimensions of particles decrease, the ratio between particle surface area and mass increases, leading to enhanced surface exchange of sediments to accumulate hydrophobic and ionic compounds. Thus, in environmental research, the finer particles (silt and clay) are more evaluated for comparison with other grains of other sizes (GIPME, 2003; Horowitz, 1991).

In previous research, particle size was frequently used as normalization for standardizing concentrations of chemical compounds in sediment (Covelli & Fontolan, 1997; Frenz et al., 2003; Horowitz, 1991; Kersten & Smedes, 2002), but recent research does not consider this method (Granulometric normalization method) for normalizing chemical compounds.

This method alone is not able to estimate the precise concentration of contaminants because of the extensive grain size separation (Ling, 2007; Ravichandran, Baskaran, Santschi, & Bianchi, 1995).

Total solids are a type of gravimetric method based on the concentration of organic and inorganic materials that remains in a sample after the drying process. The values of total solid are able to convert the wet weight of contaminate concentration to dry weight; thus, it provides useful and practical information for assessing sediment quality. Specific gravity is a ratio between the mass of a given chemical compound concentration and an equal concentration of distilled water.

This method can be applied to predict variations in sediment (U.S.EPA, 2004). Acidity is a main physical parameter that directly effects the chemical reaction of contaminants. For example, in low acidity (pH <5), the majority of contaminants, especially heavy metals (Al, Fe, Mn), can be converted to soluble forms, although some elements like Pb, may stay in an insoluble form in redox or low pH conditions. Thus in acidic conditions, contaminants become more available to marine organisms and cause an increase in the rate of bioaccumulation (Ling, 2007).

2.3.2 Chemical assessment

Chemical assessments can be applied to estimate the particular level of contaminants in sediment relative to natural conditions. In natural conditions, the sediment does not completely contain synthetic organo-metallic materials, and also contains elements that constitute natural mineral components.

These constituents are evaluated based on geochemical normalization methods (GIPME, 2003). Chemical analyses may provide information about specific levels of contaminants that, if bio-available, can lead to toxicity and bioaccumulation (U.S.EPA,

2004). PAH and PCB compounds, metals, and pesticides are usually considered for chemistry assessment.

2.3.2.1 Heavy metals

In recent decades, many researchers have focused on the potential threat of heavy metals in the environment (BOGP, 2009; Fang et al., 2004; Liu et al., 2010; Shulkin & Presley, 2003; Tarique, 2008; WorldBank, 2007) because of their toxicity and ability to accumulate into the food chain (Pan & Wang, 2011; Wang, Yan, Fan, & Xu, 2002).

Despite attempts to control anthropogenic sources, metal concentrations are increasing in the marine environment and are a serious threat for living organisms and human health (Bellos & Sawidis, 2005; Islam & Tanaka, 2004; Tarique, 2008; Wang, 2009). In order to archive the significant assessment of heavy metals, the following variables should be noted: metal concentration (in water, sediment and organism), sources, pathways, transport mechanism, and effect on organisms. In monitoring the marine environment, the estimation of heavy metal concentration is important for understanding the criteria of expected concentrations which occur naturally in different media (sediment, water and organisms) (Lehr & Keeley, 2005; Tarique, 2008). The majority of trace elements originate from igneous rock. **Table 2.6** shows the natural concentration of selected metals in different media. These concentrations can be used as background concentrations or concentrations that are unaffected by anthropogenic sources. This information can help to discriminate between the portion of metals due to anthropogenic sources or natural sources in environmental studies.

Table 2.6, Natural concentrations of heavy metals in different media, values in $\mu\text{g/g}$ dry weight (Hakanson, 1979)

	Sedimentary rocks	Igneous rocks	Soil	Land plants	Land animals	Mean values From 10 lakes	Seawater (bowen 1966)	Fresh water
Ag	0.05	0.07	0.1	0.06	0.006	≤ 1		0.00013
Al	4000-80.000	82000	71.000	500	4-100	26.000		0.24
As	1-13	1.8	6.0	0.2	≤ 0.2	8.6	0.0026	0.0004
Cd	0.035-0.3	0.2	0.06	0.6	≤ 0.5	0.58	0.0001	<0.08
Co	0.1-20	25	8.0	0.5	0.03	18.5		0.0009
Cr	10-100	100	100	0.23	0.075	48.7	0.00005	0.00018
Cu	4-50	55	20	14	2.4	28.7	0.003	0.01
Fe	4000-50.000	56300	38000	140	160	26.7		0.67
Hg	0.03-0.4	0.08	0.03-0.8	0.015	0.046	0.12	0.00003	0.00008
Mn	50-1000	950	850	630	0.2	860		0.012
Mo	0.2-2.5	1.5	2	0.9	<0.2	≤ 10		0.00035
Ni	2-70	75	40	3	0.8	49.7	0.0054	0.01
Pb	7-20	12.5	10	2.7	2	34.9	0.00003	0.005
Sn	0.5-6	2	10	0.3	< 0.15	< 10		0.00004
V	20-130	135	100	1.6	0.15	≤ 150	0.0019	0.001
Zn	15-100	70	50	100	160	110.6		0.01

The natural concentration of heavy metals in soil and sediment are greatly influenced by igneous rock origin. For example, some fraction of trace metals in igneous rock originate from dissolved processes in lakes, rivers, and oceans. However, the majority of trace metals show large fractions in soil, which originate from weathering processes. Most trace metals have similar interactions during weathering, deposition, and erosion. For example, the fine particle sizes of clay minerals have the high capacity to retain trace elements, unlike sand and quartz minerals. Therefore, to evaluate heavy metals value, it is essential to have information about particle size and soil/sediment mineralogy.

Providing reliable data for dissolved metals in aquatic areas is more difficult than comparing metals in organisms and sediments because of the low concentration of elements in water (around thousand or more times).

The matrix effect of seawater interferences, the high potential of contamination of sampling and laboratory activities in seawater, and the accurate estimation of dissolved metals is essential to providing ultrapure chemical standards, expensive per-concentration measurements, and clean laborious methods based on quality assurance program (Lehr & Keeley, 2005; Pan & Wang, 2011; Tarique, 2008). Furthermore, sediment assessment gives the historical view of contaminate input in different sediment layers, which reflects specific values in specific times. For example, the value in sediment layers from preindustrial times is considered a background value, which is comparable to values in near-surface layers in estimating anthropogenic enrichment factors (Lehr & Keeley, 2005; Pan & Wang, 2011; Trefry & Presley, 1976).

In general, the concentrations of heavy metals in marine organisms act as intermediates among those in water and those in sediment. The measurement of reliable data for metal concentration in organisms is difficult because metal concentrations widely depend on organisms, specific organs and tissues, seasons, food supply, and life stage. Moreover, there is no clear data for the background levels of heavy metals in marine organisms. The concentrations of metals are influenced by two major sources, lithogenic and anthropogenic, which introduce metals to the marine environment by several routes such as river discharge, deposition in the atmosphere, and industrial waste input. It is not easy to determine which source is most effective for specific metals at specific locations, but the heavy metal effect in the environment depends on sources, concentration, and their potential reactivity.

These potentials include mobility, biological uptake, and toxicity of heavy metals, which are closely related to the chemical form of heavy metals that usually react with other components of the sediment. For example, in sediment media, desorption and bioavailability of metals, which associate with the exchangeable phase, are easier to compare with metals that associate in the reducible phase (Lehr & Keeley, 2005; Pan & Wang, 2011).

The different forms of heavy metals have different physicochemical and biological interactions, which lead to various responses to the marine environmental condition. Most trace elements act as “particle-reactive” and are quickly able to associate with other particles; thus, the concentration of trace elements are higher in particles than in the dissolved form. The biological interaction of metals and accumulation directly relates to its form that influences biological uptakes, transfer, and the resulting effects. In several cases, the soluble form of metals is able to transfer beyond cell membranes and some organs in organism. The physical condition of the environment (pH and temperature), type of organism, and situation, also have an effect on controlling these transfers (Lehr & Keeley, 2005).

There is much research on the toxic effects of essential and nonessential (toxin) heavy metals, which are successful in the case of human toxicity. As and Pb have toxic effects, but other metals are not well recognized. In general, the optimal concentration of heavy metals in the environment causes optimal function (reproduction, growth, etc) of organisms and humans, and the variation of optimal concentration leads to a decrease in optimal function and maybe even death.

At least twenty heavy metals have been introduced as essential elements to the health of both humans and organisms at low quantities, and are toxic at slightly higher quantities.

These include iron, chromium, nickel, manganese, copper and zinc. Lead, cadmium, mercury, and arsenic are known as toxic metals and are considered the top twenty hazardous substances in the priority list which was prepared by the ATSDR and U.S.EPA in 2001 (USEPA). There are controversial discussions about the classification of aluminum as a toxic metal because aluminum has no biological role. Its accumulation and toxic effects have been reported in renal patients. Therefore, the normal capacity of aluminum elimination is not toxic to organisms and humans. There has been much research on the toxic effects of essential and nonessential (toxin) heavy metals, which has been successful in the case of human toxicity in regards to As and Pb; however, the toxic effects of other metals are not well recognized. In general, the optimal concentration of heavy metals in the environment causes optimal function (reproduction, growth, etc) of organisms and humans, and the variation of optimal concentrations leads to a decrease in optimal functioning and maybe even death (Lehr & Keeley, 2005; Ling, 2007; Tarique, 2008).

2.3.2.2 Petroleum hydrocarbons

Petroleum contamination is a major hazardous compound that causes the greatest concern for aquatic life in marine sediments, particularly in areas close to anthropogenic sources (Baumard, Budzinski, & Garrigues, 1998; Beyera et al., 2010; Khairy, Kolb, Mostafa, EL-Fiky, & Bahadir, 2009; Nahla, 2009; Neff, 2002). In recent years, many research organizations and scientists such as the Massachusetts Department of Environmental Protection (MADEP), Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), Hansen et al. (2003), and Ditoro et al. (1991), have tried to formulate an accurate benchmark for determining total petroleum hydrocarbon (TPH) concentrations in marine sediment.

According to these researchers, TPH is generally defined as “a term used to define the sum of hydrocarbon concentrations occurring in crude and refined petroleum that yield a positive hydrocarbon signal when analyzed by a specific analytical method” (MADEP, 2007). Petroleum hydrocarbons are very dangerous for aquatic life and humans because of their toxicity and accumulation abilities which are dependent upon hydrocarbon composition, fraction properties, sources, and natural processes (Nahla, 2009; Neff, 2002).

2.3.2.2.1 Composition of petroleum hydrocarbons

Petroleum hydrocarbons contain various mixtures of thousands of organic, and few inorganic compounds, which solely contain hydrogen and carbon with variable concentrations of chemical materials such as nitrogen, sulfur, and oxygen. They are composed of light volatile hydrocarbons with short chains to heavy long chains and branched compositions (MADEP, 2007; Speers & Whitehead, 1969). Hydrocarbons are divided into two major groups: aliphatic and aromatic; there is also a smaller compound of both. The solubility and toxicity of aromatic hydrocarbons are more than aliphatic hydrocarbons, and equal to carbon. Aliphatic compounds are saturated and are known as alkenes or paraffin materials. They contain carbon chains with single chemical bonds that are occupied with hydrogen (covalent), and their composition may include linear (normal composition), cyclic, and branched chains.

Aromatic petroleum hydrocarbons are unsaturated and contain benzene rings which can be bonded with alkyl groups. Their composition includes alkyl benzenes. Benzene is a major part of aromatic hydrocarbon in refined and crude oil.

Benzene rings are able to frequently bond to one or more benzenes by fuse connection to form polyaromatic hydrocarbon (PAHs) (MADEP, 2007).

The smallest PAH is Naphthalene, which has two benzene rings and a low molecular weight (128.2 g/mol). Coronene is the heaviest PAH (300.3 g/mol) with six condensed benzene rings, and is potentially toxic because of its mobility in sediment.

In lower toxic levels, some PAHs composed of anthracene and pyrene, are able to be easily oxidized and associate with other toxic compounds, because these PAHs are only active in the liquid phase; thus, they can always stay in water columns (MADEP, 2007; Patin, 1999). Their hydrocarbon composition widely depends on the refining process of crude oil, which is applied to manufacture products such as gasoline and middle distillate fuels (kerosene, jet fuel, diesel fuel and heating oil of home). Refining includes the distillation process to separate fractions of petroleum hydrocarbon based on different boiling points, and stimulating chemical interactions to convert fraction forms of hydrocarbon to specific forms (MADEP, 2007).

2.3.2.2.2 Fraction of petroleum hydrocarbon

Petroleum pollutants contain complexes of hydrocarbon and organic materials, which change extensively in composition after being released into the marine environment. Thus, ecological risk assessments of petroleum pollutants solely based on TPH concentration, are not accurate and have large errors for several reasons including the fact that estimation of risk according to the concentration of hundreds and thousands of particular hydrocarbons in oil pollutants is very complex and ultra-expensive, and lacks enough information beyond the mobility and toxicity of hydrocarbon compounds in sediment (MADEP, 2007).

The sediment clean-up approach defines the specific method used to classify hydrocarbon compounds into different classes and groups based on the limited criteria of the number of carbons with the same properties in physicochemical and toxicities. This classification is called fraction, and provides an accurate and reliable assessment of petroleum hydrocarbon in comparison to previous methods.

There is a common rule that increasing the number of carbons (molecular weight), decreases the solubility of hydrocarbons, and increases their toxicity in aquatic areas **Table 2.6**.

Table 2.6, Comparison of different hydrocarbon fractions to characterize risk (MADEP, 2007)

Aliphatic Hydrocarbons		Aromatic Hydrocarbon	
Recommended Fractions	Current MADEP Fractions	Recommended Fractions	Current MADEP Fractions
C5-C8	C5-C8	C6-C8 (Benzene, Toluene, Ethylbenzene, Xylene)a	
C9-C12	C9-C18	C9-C12	C9-C10
C13-C18		C13-C15	C11-C22
C19-C36		C16-C24	

The present four fractions for aromatic and aliphatic hydrocarbons were applied to develop a sediment benchmark for protecting aquatic organisms using the current MADEP method for human risk assessment. In the aromatic fraction, the classification C6-C8 contain BETEX compound (Benzene, Toluene, Ethylbenzene, Xylene) are entirely mobile with high volatility, and cannot contribute to accumulation and toxicity in aquatic areas. Thus their concentrations are not practical for assessing ecological risk of sediment and are sometimes just recommended for pollutant characterization.

Based on several observations, the C9-C12 and C13-C15 fractions are sufficiently solubility in aquatic solutions to be toxic and to accumulate in marine organisms.

The fraction of C16-C24 is composed of four or five fused rings of PAH, and their molecular weight is very high (Di Toro, McGrath, & Stubblefield, 2007; MADEP, 2007). Thus this fraction has low mobility and solubility in aquatic areas. Despite the fact that all PAHs are not acutely toxin/carcinogenic but commonly PAHs with four to six rings have carcinogenic effect for example 7,12-Dimethylbenzene [a] anthracene, Benzo[a]pyrene and 3-Methylcholanthrene are strongly toxin (Neff, 2002); because they have enough mobility in sediment to be toxin. The light aliphatic fractions C5-C8 and C9-C12 are adequately soluble which likely cause toxicity in contaminated sediment. Although, they are depleted by natural environmental processes, such as biodegradation, which greatly decrease their presence in sediment. These fractions mostly originate from middle distillate and light fuels, that almost all include very high amounts of aliphatic in comparison to aromatics. The fractions, C13-C18 and C19-C36, have high weight in aliphatic hydrocarbons with low solubility, and their tendency is very high to associate with organic carbons and oil compounds in sediment, and they have little bound into water phase where they can be bio-concentrated by benthic organisms. Therefore, these fractions of aliphatic hydrocarbons cannot cause significant toxic effects in sediment which is contaminated by petroleum pollutants (Neff, Ostazeski, Gardiner, & Stejskal, 2000).

2.3.2.2.3 Natural process of environment

Unlike heavy metals, petroleum hydrocarbons are not persistent in the marine environment. Different natural processes degrade TPH to polar organic compounds, which are eventually converted to carbon dioxide and water.

Following discharge of hydrocarbons into the marine environment, petroleum hydrocarbons are influenced by natural processes such as dispersion, evaporation, dissolution, and biodegradation. These natural processes directly and indirectly affect petroleum hydrocarbon composition, accumulation, and toxicity in sediment (Nahla, 2009). After being released into the marine environment, petroleum hydrocarbon products have a high tendency to be retained in separate oil phases. Thus, dispersion into the sediment occurs and depends upon hydrocarbon density, viscosity, porosity, and permeability of intermediate (Sale, McWhorter, & Piontek, 1992). Volatile fractions of aromatic and aliphatic hydrocarbons (lowest molecular weight) have a high evaporation rate, and are thus removed rapidly from surface sediment and water bodies.

Their evaporation rate is slow in deep layers of sediment, especially if the sediment contains silt and clay (fine particle size). Dissolution and dispersion are the two main processes that cause depletion of hydrocarbons in marine sediment by water, which is percolated into oily sediment and biological degradation. Dissolution of hydrocarbon occurs between the oil and water phases, and when the sub-surface oil contacts the infiltrating water and surface water. In fact, the dissolution process directly depends upon the rate of solubility in the two phases (MADEP, 2007).

Generally speaking, the solubility of petroleum hydrocarbon in the environment is widely varied and based on several parameters such as salinity, temperature, pressure, TPH molecular weight, and distribution. In marine aquatic areas, petroleum hydrocarbon solubility and bioavailability (especially PAHs) are directly controlled by salinity (Schlautman, Yim, Carraway, Lee, & Herbert, 2004) and research shows that there is an inverse relationship between solubility and salinity; the solubility of TPH in fresh water can be two times more than marine water (Neff, 2002), and the potential risks of TPH toxicity for marine organisms is increased in areas with low salinity, such as such as estuaries and coastal zones (Shukla, Gopalani, Ramteke, & Wate, 2007).

In other cases, research has showed no significant differences in solubility (in two ranges of salinity zero to 4% and 33% to 36%)-unclear (Viamajala, Peyton, Richards, & Petersen, 2007; Whitehouse, 1983).

Temperature increases petroleum hydrocarbon solubility, bioavailability, and biodegradation, which causes an increase in the accumulation rate of petroleum hydrocarbon in aquatic areas (Feitkenhauer & Märkl, 2003; May, Wasik, & Freeman, 1978; Viamajala et al., 2007).

There is an inverse relationship between solubility and the molecular weight of petroleum hydrocarbons (Neff et al., 2000). Aromatics are more soluble than aliphatic hydrocarbons of the same molecular weight.

Several research studies have shown that solubility decreases when molecular weight and aromatic rings increase; thus, PAHs with high molecular weights have a greater tendency to leave the water phase and connect with the solid phase (Neff, Stout, & Gunster, 2005a; Varanasia, 1989). In addition, solubility is higher in PAH isomers with angular structures to comparison with the linear isomers and PAH Solubility invert relation with the length of molecule. For example the solubility of phenanthrene with an angular shape is 25 times more that of anthracene with a straight line shape (Whitehouse, 1983). The solubility of Alky PAHs is lower than the others, (Neff, 1979) although there are some exceptions such as the fact that the solubility of benza[a]anthracene is lower than that of methyl or ethylbenz[a]anthracene, and the solubility of chrysene is lower in comparison with dimethylchrysene. The solubility of the angular isomer of hydrocarbons is more than linear isomers.

For example, the number of carbons and aromatic rings are the same in the composition of phenanthrene and anthracene, but the solubility of phenanthrene with an angular shape is 25 times more than that of anthracenes with linear shapes. Also, the

solubility is directly increased when the length of hydrocarbons is decreased (MADEP, 2004).

Petroleum hydrocarbons may be degraded by bacteria and fungi in sediment. Linear alkanes with low weights have a greater degradation rate in comparison to branched alkanes and other petroleum hydrocarbons with higher molecular weights. Cyclic alkanes and PAHs have a low microbial degradation rate which is why they are so persistent in the environment. In general, natural environmental processes change the composition of petroleum hydrocarbon, and reduce their molecular weight and decrease the toxic effects of TPH fractions in contaminated sediments (MADEP, 2007). Hydrocarbons with low solubility are largely adsorbed by dissolved and suspended organic compounds in sediment, internal and external tissues, or organs of organisms (gill membranes and gut epithelium) in water columns, and benthic organisms which are able to accumulate hydrocarbons by lipid tissues (Neff, 2002). Hydrocarbons in sediment pore water are more bio-available and toxic (solution phase) compared to lipid tissues of benthic organisms (*e.g.*, petroleum, creosote, or tar) (Neff et al., 2005; Thorsen, Cope, & Shea, 2004).

2.3.2.2.4 Sources of petroleum hydrocarbon

Similar to other pollutants, the sources of TPH are divided into major groups, anthropogenic and lithogenic. Anthropogenic sources of TPH originate from pyrogenic and petrogenic sources. Pyrogenic TPH mainly includes more than three aromatic rings, and their original source is incomplete combustion of organic compounds, which form very rapidly at high temperatures (around 700°C)(MADEP, 2007).

Smoke fallouts significantly increase pyrogenic contamination; these contaminants originate from combustion of fossil fuels (heating oil, cooking, coal burning, vehicle emissions), biomass burning (fireplace, controlled burning) and

industrial centers which are located close to coastal water (Beyer, Jonsson, Porte, Krahn, & Ariese, 2010; Pies et al., 2008).

Petrogenic TPH involves unburned fossil fuels which include oil spills, and incineration of petroleum products that have originated from coal and crude oil sources (MADEP, 2004).

These sources formed very slowly, more than millions of years ago, at moderate temperatures (between 100°C - 300°C) (Beyer et al., 2010; Neff, 2002; Robertson, 1998). Pyrogenic sources are more toxic than petrogenic sources because of their high concentration of non-alkylated PAHs, which have more than three aromatic rings. Thus, the identification of petroleum hydrocarbon sources (TPH and PAHs) is essential. In recent years, the ratio of non-alkylated PAH and alkylated PAH has been applied to distinguish between different types of sources (Yunker et al., 2002; Zhang et al., 2004).

For example, if the alkylation concentration is more than that of non-alkylation, this means that petrogenic sources are predominant. Lithogenic sources of TPH seep of natural oil, coal erosion, forest and grass fires, biogenic and diagenic types (Beyer et al., 2010). Diagenic types originate from organic material in sediments with rapid formation during days or years.

Biogenic types form during the biosynthesis process by different organisms such as fungi and bacteria. Biogenic sources are not commonly considered to be true PAHs and main sources in marine environmental research, because they include just oxygen and nitrogen. Diagenic and biogenic processes are major sources for perylene, pimanthrene, phenanthracenes, tetra- and pentacyclic PAH (Beyer et al., 2010; Nahla, 2009; Neff, 1979, 2002; Whitehouse, 1983).

2.3.2.2.5 Enzymatic biotransformation

The toxicity and bioaccumulation of petroleum hydrocarbons, especially PAHs, are also closely dependent upon enzymatic biotransformation of marine organisms. Research has shown that organisms are less damaged by PAH toxins if their biotransformation capacity is poor, such as the blue mussel (*Mytilus sp*) (Anderson, Hunt, Hester, & Phillips, 1996).

In addition, these species are highly able to accumulate PAH and TPH in the environment because the bioaccumulation is related to low capacity of biotransformation (Porte & Albaiges, 1994). Therefore to assess exposure, estimation of petroleum hydrocarbon concentration in tissue and organs of mussels is more reliable to compare with fish and other vertebrates. Fish have the high capacity of biotransformation, and during metabolism, fish can convert PAHs to metabolites that are subsequently able to bind to other macromolecules (proteins, DAN, and RNA). This may cause adverse effects, such as teratogenesis, mutagenesis, and carcinogenesis, in organism tissues, and can also reduce growth and survival (Colavecchia, Hodson, & Parrott, 2007; Tuvikene, 1995). In fact, the levels of hydrocarbons that are estimated in the tissue and organs of fish are low, and poorly correlate with exposure because of the rapid biotransformation. This organism exposure in aquatic areas is influenced by sediment concentration, solubility of PAH, ingestion of suspended matter, types of habitats, and food source (Beyer et al., 2010; Budzinski et al., 2004).

2.3.3 Biological assessment

Benthic communities are useful biological indicators for monitoring the quality of marine environments, especially sediment, because of several aspects: (1) Benthos live in sediment where several types of contaminate accumulate, and hypoxia reactions occur. Thus, they directly or indirectly reflect the effect of environmental stressors

because they have low mobility and cannot easily relocate when influenced by contaminants; (2) to some extent, the variation in benthic species is predictable because their presence and absence are not influenced by diurnal cycles or tidal flux; (3) the benthic community is classified based on their sensitivity and resistance to contaminate and hypoxia conditions; (4) there are defined predictable patterns of response of benthic species to variations in marine quality (Borja, Franco, & Muxika, 2003; Malloy et al., 2007; Pearson & Rosenberg, 1978; Roesijadi & Robinson, 1994; Tarique, 2008); (5) Some species of benthic organisms (bivalves) are able to bioaccumulate contaminants in their soft tissues, and this sometimes causes an easier estimation of contaminant in their tissues compared to in marine water (Tarique, 2008). Several factors influence their bioaccumulation rate such as season, sex, size, reproductive cycle, and the hydrodynamic process (Bryan et al., 1977); (6) they have important ecological roles in recycling nutrients between sediment and water and their main food source of commercial fish (Cesar et al., 2006; Malloy et al., 2007).

Several monitoring programs have studied the accumulation, toxicity, distribution, and succession, to provide large-scale information about the exposure, trend, and status of species, populations and ecosystem effect over the long-term. This information has caused the development of several indexes and indicators based on the benthic community (Borja et al., 2000; Borja, Muxika et al., 2003; Burger, 2006; Cantillo & Connor, 1992; Jensen, Randlov, & Riisgard, 1981; Malloy et al., 2007; Shannon & Wiener, 1963). Bivalve (mollusks) have been successfully applied as biological indicators to assess heavy metals accumulation and toxicity in marine sediments, because of their effective bioaccumulation, high tolerance to variation in physicochemical parameters, low enzyme transformation, in addition to their dominance in wide geographical areas (Brown & Luoma, 1995; Gunther et al., 1999; O'Connor, 1992; Otchere, 2003).

Mussels, clams, fish (Denton & Burdon-Jones, 1986; O'Connor, 1992), colonial sea birds (Burger & Gochfeld, 2004), and barnacles (Fialkowski & Newman, 1998) are used as reliable bio-indicators.

In 1978, Pearson, Rosenberg, and Rhoads presented succession models of benthic communities in temporal and spatial scales, which showed that the biomass, abundance, and diversity of benthic communities vary in predictable patterns in response to organic compounds (**Figure 2.1**).

They indicated that the abundance of benthic communities increases along decreased gradients of organic materials (Pearson & Rosenberg, 1978; Rhoads, McCall, & Yingst, 1978). Several researchers have repeatedly tested this model that is now considered a universal applicable model for most disturbances (physicochemical and biological) in different sub-tidal and soft-bottom marine ecosystems (Christopher, Calabretta, & Oviatt, 2008; Heip, 1995; Rosenberg & Blomqvist, 2004; Rosenberg, Magnusson, & Nilsson, 2009).

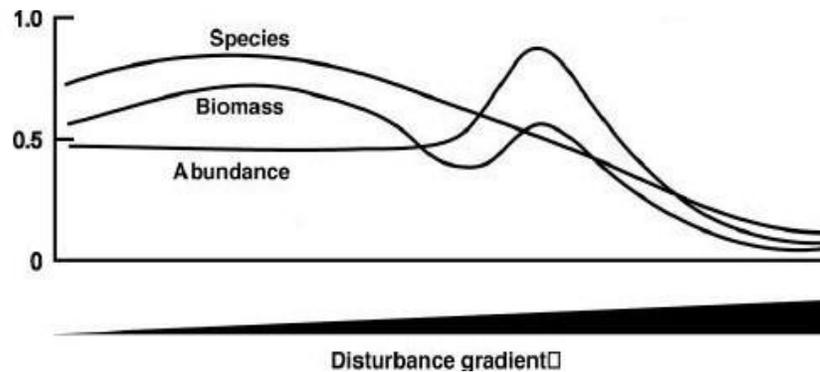


Figure 2.1, General distribution model of benthic faunal succession stage a gradient of increased environment disturbance from left to right (Pearson & Rosenberg, 1978)

In general, three main succession stages were described: the peak of opportunistic species: in early stages of succession there is degradation in size and number of first species, which are close to pollution sources (largely polluted) (Rhoads

& Boyer, 1982). When distance from a pollution sources increases (100 m), a peak is formed by opportunistic species with little diversity and high abundance. These species are usually polychaetes with small tubes that are tolerant to types of contaminants. These groups usually have some advantage in the environment such as changes in the physicochemical characteristics in surface sediment (a narrow oxidized and to restrict the interstitial area), improved food sources, and decreases in the biological interaction (Pearson & Rosenberg, 1978; Rhoads & Boyer, 1982).

Their high yield reproduction, rapid maturity, and non-selective deposit-feeder, are important characteristics for increasing great colonization, rapid changes in micro-structure by pelletizing compounds and extending the available surface area for the microbial community (Christopher et al., 2008; Dauer, 1993; Hargrave & Theil, 1983). The ecotone point: this stage along poorly polluted areas with low abundance and high diversity; because with further distance from pollution sources, the abundance of opportunistic species decreases to steady-state abundance of normal condition. At the same time, there is an increase both in the abundance of species in the community and the relative frequency of individuals between species (Christopher et al., 2008; Rhoads & Boyer, 1982). The transition zone: in this stage, there is an initial fluctuation of species developing towards the stability to provide the normal condition. Therefore, the benthic community is dominated by mature large-equilibrium species, which are deep-dwelling, and feed at depth layer of sediment; their fecundity is low and has a long life-span (Christopher et al., 2008; Rhoads & Boyer, 1982).

There are other variable effects on benthic distribution in the marine environment such as salinity, sediment types, and oxygen levels, via larva supply and specific flux. The effect of salinity is more than sediment types.

For example, along an estuary gradient, the diversity of species is high because of higher salinity and a high percent of silt and clay.

In the part of the estuary close to the river mouth, diversity is low due to the low salinity and high percentage of silt and clay. Dissolved oxygen reflects the quality of water and well-oxygenated sediment is essential for protecting the benthic population. The hypoxia condition is influenced by natural and anthropogenic sources (heavy metals, pesticides, and hydrocarbons) (Christopher et al., 2008; Malloy et al., 2007). Several attempts have been performed to describe an applicable set of indicator species for the extensive range of situations in the marine environment.

Therefore, several research studies have frequently reported that some benthic species can tolerate heavily polluted areas such as polychaetes, especially *Capitella capitata*, *Mediomastus ambiseta*, *Nereis caudate*, *Staurocephalus rudolphl*, *Audounia tentaculata* and in gastropod, *Polydora ciliate* and *Hydrobia ulyae* (Malloy et al., 2007; Pearson & Rosenberg, 1978; Reish, 1957; Reish, 1960; Swartz, 1972).

Moreover, on harbors with heavy polluted marine sediments, nematodes are introduced as some species and genus of nematodes such as *Deptonema*, *sabatieria*, and *Terschellingia* react sensitively to any pollutants, especially PAHs, heavy metals and organic compounds (Montagna & Harper, 1996; Moreno, Albertelli, & Fabiano, 2009; Schratzberger, Warr, & Rogers, 2006; Somerfield, Fonsêca-Genevois, Rodrigues, Castro, & Santos, 2003; Steyaert, Garner, van Gansbeke, & Vincx, 1999).

In general, Borja provided the comprehensive list of the benthic community based on their tolerance and sensitivity, that is so practical to estimate different indexes such as AMBI and BI (Borja et al., 2000) .

2.3.3.1 Assessment adverse biological effect

Since 1990, many scientists have focused on methods to define the direct correlation between the concentration of sediment contaminates (cause) and adverse biological effects.

Also, they have tried to find new methods to predict contaminate distribution, abundance, potential effects and an accumulation in the marine sediment (Nascimento, 2007). Thus, research studies have been done (Macdonald et al., 1996; U.S.EPA, 2000) to establish standard methods to conduct toxicity tests on sediment, sample collection, storage, and estimation of physicochemical and biological characteristics.

In recent years, sediment quality has been assessed based on several measurements, such as toxicity tests on specific biological communities, level of contamination in sediment, evaluating benthic communities, and biomarker assessment (Nascimento, 2007; U.S.EPA & NCA, 2005). Toxicity tests of sediments are commonly test based on bioassays that determine toxicity effect of contaminants on the organisms survival in different concentration of contaminants. In this method, specific organisms such as amphipods, sea urchins, tanaidacea, and penaeidae post-larva are selected according to their sensitivity, year round fertility, abundance, adaptability to salinity, and granulometric variation (Cesar et al., 2006; Evangelista et al., 2005; Green, Chandler, & Piegorsch, 1996; Nipper, Greenstein, & Bay, 1989). These organisms are exposed to different pollutants to describe levels of toxicities and biological responses, which are used to classify the potential of toxicity in marine sediment (Pearson & Rosenberg, 1978).

According to these studies, sediment quality standards are established in different chemical criteria to protect the health status in aquatic areas. These standards were modified to sediment quality guidelines (SQGs) such as Australian/New Zealand, Hong Kong, Canada, Netherland, Norway, Washington /Puget Sound, New York and Florida. Most SQGs are useful predictors according to the weight of evidence sources (Ralf Hubner, Astin, & Herbert, 2009). These practical methods are used to estimate the effects of contaminants in the environment, particularly at the population level, in light of the difficulty of analyses due to the effect of complex interferences on the abundance

and health status of organisms in temporal and spatial scales (Rosenberg, Blomqvist, Cnilsson, Cederwall, & Dimming, 2004). Many researchers have focused only on measuring the concentrations of chemical contaminants because toxicity tests are not easy, and are costly and time-consuming, sometimes leading to ambiguous results (Lehr & Keeley, 2005).

It is practical method to provide data about natural conditions and the extent of the contamination is also a useful tool to screen toxicity. Caeiro et al (2005) defined three methods for evaluating chemical contamination according to contamination indices (ratio of polluted /clean sites), background enrichment factors (ratio of sediment sample and background levels); and ecological risk indices(comparison to sediment quality guidelines). In general, if the ratio is lower than two mean, this indicates insignificant pollutants, causing little concern about the adverse effects of chemical pollutants (GIPME, 2003; Ralf Hubner et al., 2009).

The distribution and abundance of benthic communities are vital bio-indicators for evaluating the effects of contaminants, supporting quality standard criteria, and advancing the use of existing methods.

Several indices are frequently applied to study benthic communities which are described in **Table 2.3** (Pinto et al., 2009; Tarique, 2008). The biomarker approach is a typical method for assessing biological responses to the effects of contaminants on different organizational levels such as cellular, histological, and physiological. It is also a useful method for detecting contaminate problems (specially related to PAH), and it reveals the early adverse effects of contaminants on living organisms (Martins et al., 2005; Nascimento, 2007).

Despite of all of this research, there are no measurements that are able to reliably predict contaminate concentrations and their effect on marine sediment, leaving the researcher to face to much uncertainty.

Thus, much research has focused on integration methods, which link chemical analysis with biological effects to understand how benthic organisms respond to degradation of sediments (Anderson et al., 1996; Anderson et al., 2001; Carr et al., 1996).

Integration methods are so useful and practical because chemical analysis and biological approaches alone are not accurate to estimate and predict the adverse effects of chemical contaminants on biological communities.

Chemical analysis is not able to predict biological effects because of the complexity of physical and biological interactions that alter the bioavailability and concentration of contaminants. On the other hand, biological surveys cannot establish the relationship between cause and effect factors because it can perform toxicity bioassays in sediments and biological structures (Burton & Scott, 1992; Nascimento, 2007).

2.4 Ecological risk assessment

In recent decades, ecological risk assessments have been known as “technical support to make decisions for uncertainty” in environmental research. In 1992, the EPA stated that, “ecological risk assessment is a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors” (EPA, 1998; Suter, 2007).

The process is developed to organize information and uncertainties, in order to better evaluate and predict the relationship between stressors and their adverse ecological effects, which is practical way to make environmental decisions. An assessment can probably include physicochemical and biological stressors as an assessment of adverse effects dependent upon several parameters such as type and intensity of effects, scale of the effect, and the potential for recovery (Suter, 2007).

The general objectives of risk assessment have focused on managing environmental problem which mainly include chemical regulation, remediation of contamination areas, population control of exotic organisms, and management and protection of the environment (Jones et al., 1999; Suter, 2007).

The term, "environment risk" is usually used in Europe instead of the term, "ecological risk" which is used in the United States because of the similarity of their divisions.

In Europe, the term "ecological risk" describes the risks for nonhuman organisms, the ecosystem, and population (Barnt-house and Suter1986). Ecologists frequently use the term, "environment risk" to explain human risks which are influenced by pollution in the environment (Suter, 2007).

In the last two decades, numerous studies have been done to assess ecological risks such as ecological risk assessment of polyaromatic hydrocarbons (Brendehaug, Jhonsen, Bryne, & Gjose, 1992; Chen, Zhao, Lee, & Hannath, 2007; Fernández et al., 2005; Neff, 1979; Neff & Sauer, 1995; Neff, Stout, & Gunster, 2005; Stagg et al., 1996; Wang, Wang, He, Du, & Sun, 2011), and ecological risk assessment based on heavy metals (Bai et al., 2010; Chow, Gaines, Hodgson, & Wilson, 2005; Hakanson, 1980; He, Song, Zhang, Zhang, & Xu, 2009; Hope, 2006; Jones et al., 1999).

In general, most research indicates a quantity model to evaluate ecological risk. According to this model, ecological risk assessment is estimated by obtaining the ratio between predicted environmental concentrations (PEC) and predicted no-effect concentrations (PNEC) (Mahmoud, 2009).

PNEC are calculated based on sediment or water quality guidelines that are widely applied to signify threshold concentration of chemical compounds and their biological effects on the population (Hübner, Astin, & Herbert, 2009; MacDonald,

Ingersoll, & Berger, 2000; Pekey, Karakas, Ayberk, Tolun, & Bakoglu, 2004; Thompson, Kurias, & Mihok, 2005).

2.4.1 Framework of ecological risk assessment

The process of ecological risk assessment is based on a routine framework, which was developed by the National Research Council framework for assessing human health risk. This framework acts as a guide for performing risk assessment, showing the general structure of risk assessment, and preparing quality assurance based on main components. The framework of health risk assessment was modified to ecological risk assessment (Barnthouse & Suter, 1986), and the ecological risk framework has been described for several nations in the world, including Australia and New Zealand (ANZ 1995; NEPC 1999), the United Kingdom (UK Department of the Environment, Food and Rural Affairs 2000), Canada (CCME 1996), Africa (Claassen et al. 2001), and the Netherlands (Menzie and Freshman 1997; Power and McCarty 1998, 2002) (Mahmoud, 2009). Most eco-risk frameworks consist of several processes including problem formulation, analysis, risk characterization, and risk management (Suter, 2007).

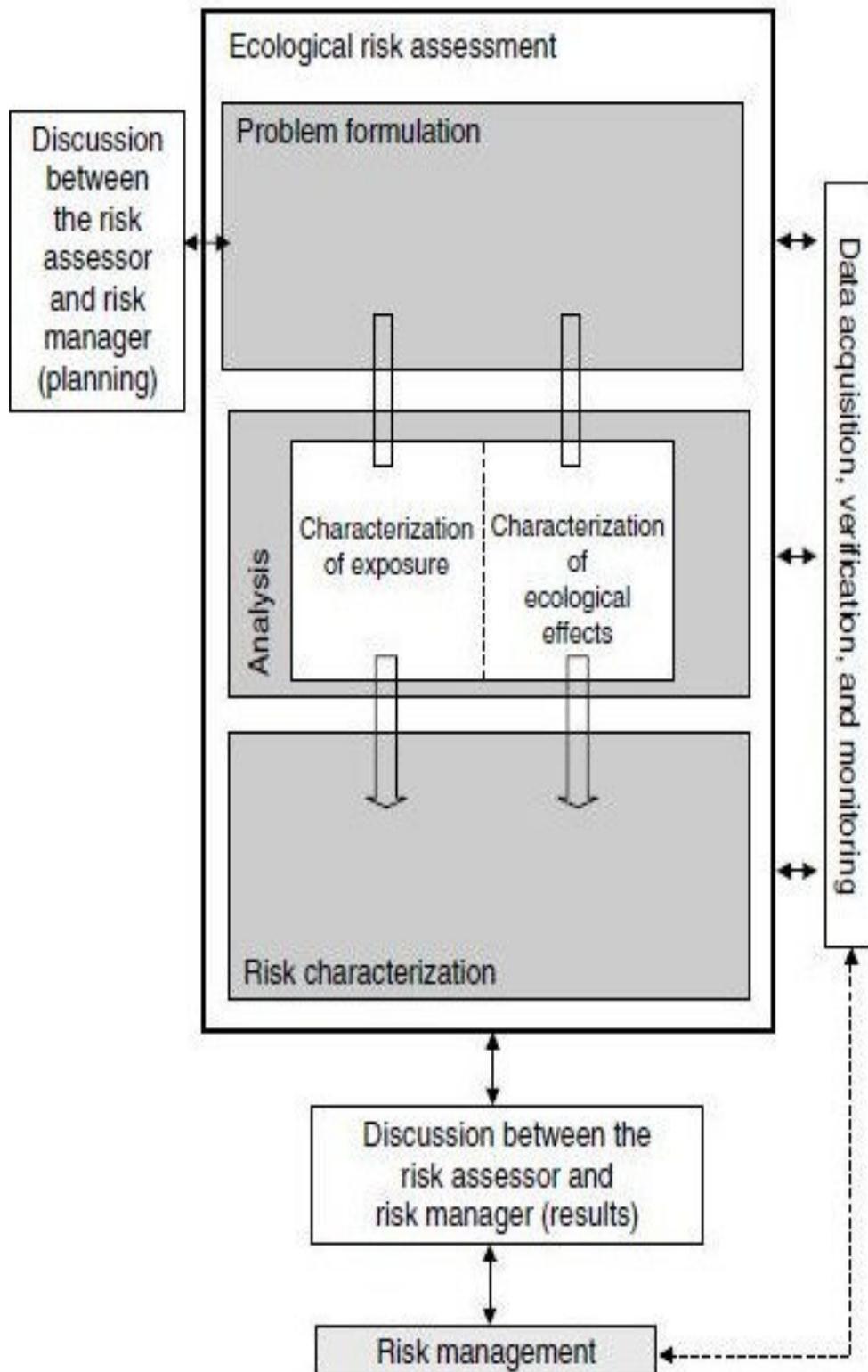


Figure 2.2, The framework for ecological risk assessment (EPA, 1998)

2.4.1.1 Problem formulation

Problem formulation, in which several inputs are provided to develop a plan for assessment by risk managers and risk assessors, is the first step in performing assessment. Those inputs include:

- Collecting and summarizing available information about stressors and their sources, effects, the physiochemical environmental condition, and receptor characteristics (receptor is “The ecological entity exposed to the stressor”). This information has helped to assess endpoints and conceptual models. ‘Endpoint’ is an explicit term of the environment which is attributed to valued ecological entities, and thus, must be protected (Suter, 1993). Therefore, this important characteristic should be considered in defining the endpoint, which includes biological and social relevance, and proven susceptibility, and a comprehensive operational definition must be easily measurable. However, these are not the same measurements to assess endpoints, but are generally estimated based on toxicity values or function as a dose response (for example 96-h LC50) and characteristic of the environment defined during temporal and spatial scales (e.g benthic population in sediment). In 1993, Suter defined two methods to estimate endpoints: those that estimate the level of effects to estimate exposure (dose-response), and only specific levels are applied such as LC01 (lethal threshold concentration), LC50, LD50 (median lethal dose), and EC50 (median effective concentration). The second method is related to hypothesis testing in which responses at unexposed concentrations (null concentration) or control responses are compared with responses at exposure concentrations such as no observed effect concentration (NOEC), and lowest observed effect concentration (Suter,1993). The conceptual model is a visual description to predict relationships between endpoints receptor and stressor.

- Defining the purpose, limitations, and scope of assessment.
- Analyzing a plan to collect information, and performing risk characterization.

2.4.1.2 Analysis

Analysis is the stage that is controlled based on the technical evaluation of data about characterization of exposure and effects. Characterization of exposure is a part of the analysis stage that evaluates the reaction between ecological entities and stressors. Exposure defined as “co-occurrence or contact, depending on the stressor and ecological component involved”. The exposure analysis is a process to describe the sources of contaminants (stressors), their spatial and temporal distribution in the environment, and contact with the ecological entities. Characterization of ecological effects is another part of the analysis stage that estimates the ability of stressors to make adverse effects under a specific set of situations. It indicates the relationship between endpoint responses and exposure variation, and quantifies the potential and type of endpoint effects that can be expected.

2.4.1.3 Risk characterization

Risk characterization includes the integration of results of the stressor-response and exposure to parameterize and perform the response of exposure model and estimate risk process, and analyze the scientific uncertainties and limitation. Risk characterization also includes the descriptive process used to interpret the results of uncertainty analysis, ecological adversity, and lines of evidence.

2.4.1.4 Risk management

Risk management is the process in which the results at all stages of eco-risk assessment are transferred to the risk manager to make decisions about remediation, and ratify the new regulation to improve environmental conditions (Mahmoud, 2009; Suter, 2007).

CHAPTER III: MATERIALS AND METHODS

3.1 Location and General Overview

3.1.1 Geographical Features

The Klang Strait is located on the western tropical coastal region (03°00 N to 101°24'E) of the Malaysia peninsula at the north end of the Malacca Strait (**Figure 3.1**) and over 573 km². This strait is divided into three main gateways that are also its busiest ports which include North, South, and West Port (**Figure 3.2**). There are 18 berths in the North Port, 8 in the South Port, and 22 in the West Port (berth information is described in Attachment I). These ports are situated about 70 km away from the Kuala Lumpur International Airport. A network of highways and railroads link these ports to other parts of Malaysia (Authority, 2008; Selangor Waters Management Authority, 2005).

Admiralty Chart No. 3453 in London describes the Klang Strait as “the narrow corridor between Klang Island and Che Mat Zin Island on west and Indah Island and the mainland on the east.” In 1970, hydrographic and topographic researchers showed that the Klang Strait is a channel that extends an additional distance of 45 km along the northwest (Coleman, Galiano, & Smith, 1970; Sasekumar & Chong, 2005). The northern part of the Klang Strait has been known as Pulau Angsa; it is located between the mainland on the east and a vast region of sand banks and mud flats (Angasa Bank) on the west. This is considered to be the northern entrance into Port Klang for shipping. The boundaries of Pulau Angsa are marked by two lighthouses and marine buoys (Authority, 2008).

The southern part of the Klang Strait lies between several mangrove islands (such as Pulau Klang, Pulau Che Mat Zin, and Pulau Pintu Gedong) on the west and Pulau Indah on the east. The border of the southern part of Klang Strait lies just off from the adjacent north lane of the Malacca Straits Traffic Separation Scheme.

This area is well marked by the lighthouse and South Fairway Buoy. The end of southern part is comprised of complex currents with tidal influence, which affect the Klang Delta. Thus, this is considered to be an open-ended estuary (Authority, 2008; Sasekumar & Chong, 2005). Klang River and Langat River are the two main rivers that drain into the Malacca Strait to form the Klang Strait and Klang Delta. These rivers cover 1,300 km² and 2,400 km² of the catchment area, respectively. This area is characterized by several interconnecting tidal channels that are completely surrounded by the mangrove islands and the mud flats (**Figure.3.2**).

As matter of fact, marine process, riverine, and climate were factors in the colonization of the Klang Strait coastal area including the mangrove islands with their high diversity of plants and marine organisms. In addition, there is scientific evidence that indicates that cross-shelf currents cause to transport material and living particles (e.g., fish and prawn larvae) toward the shore, and most of this marine life is trapped and retained by the mangrove system. However, these islands have lost most of their mangrove trees in recent decades because of the development of industrial centers and West Port (Sasekumar & Chong, 2005; Selangor Waters Management Authority, 2005).



Figure 3.1, Location of Klang Strait at the west coast of Peninsular Malaysia
(Port Klang Authority, 2008)

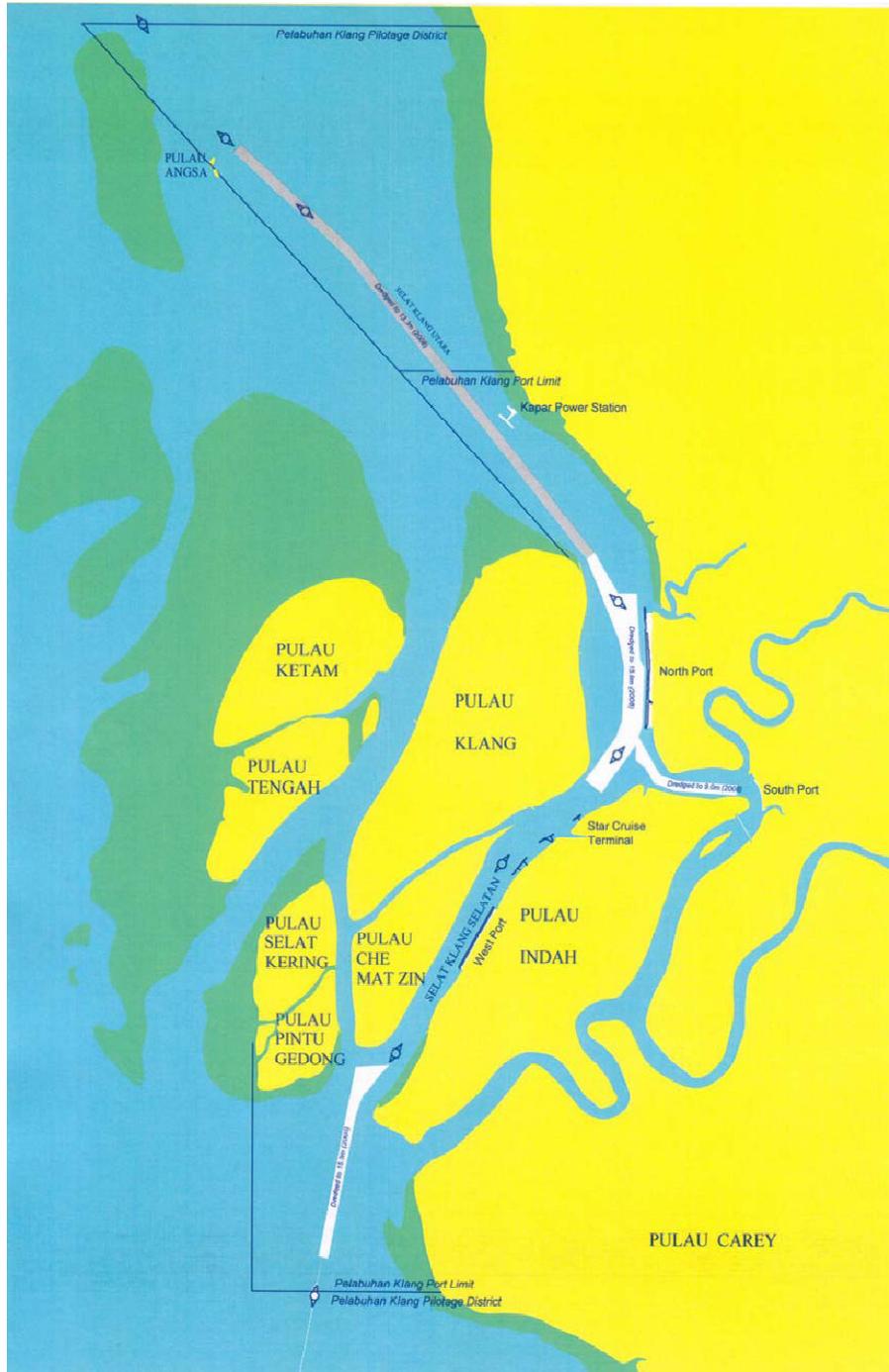


Figure 3.2, Location of Port Klang (Port Klang Authority, 2008).

3.1.2 Meteorology

The seasonal alternation between the northeast monsoon (November to March) and southern monsoon (May to September) causes the main rainfall pattern along the Klang Strait (Chong, 1993a). In general, the beginning of the northeast monsoon occurs between the 11th and 20th of November (Chong, 1993a). In the early part of the monsoon season, heavy rainfall usually occurs; dry spells happen later on, and at least eight cycles of dry and wet spells occur during the north monsoon (Cheang, 1988). The southwest monsoon occurs in May and causes a decrease in rainfall. During the monsoon break, which is often between July and September, heavy rainfall occurs because of converging low-level winds from the east or southeast, with the southwesterly winds coming from the Bay of Bengal and Sumatra Strait (DID, 2000). In general, three to four cycles of dry and wet spells take place during this monsoon. In the Klang Strait, two peak rainfall periods are reported each year; these peaks normally correspond to the inter-monsoon period (Chong, 1993b). **Figure 3.3** shows the average monthly rainfall based on reports of the Malaysian Metrological Service (MMS) between 1985 and 1987 (Cheang, 1988). The monthly average rainfall ranged between 15.5 and 370 mm, the average was 143.23 mm, and the annual rainfall was 1,719 mm. In addition, MMS recorded that the river discharge at Klang Strait correlates with rainfall pattern, and, as expected, the maximum river discharges would occur at the two peak rainfall periods in November, December, and April (Sasekumar & Chong, 2005).

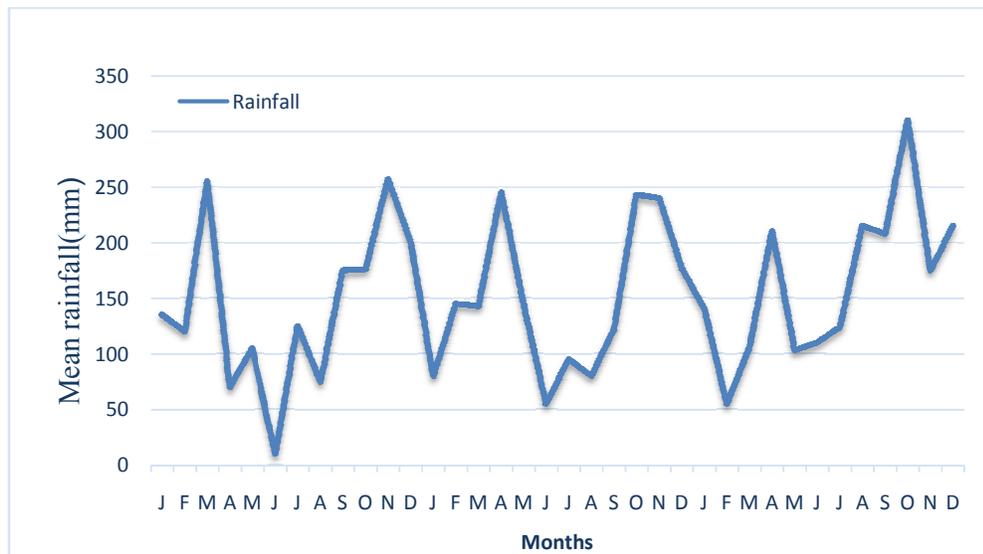


Figure 3.3, Monthly mean rainfall (mm) from January 1985-December 1987

Regional surface winds were assessed based on the research of the world Meteorological Organization’s Voluntary Ships Scheme (VOSS) and MMS. The wind data generally indicated that northwest winds are the prevailing winds during September to December, while the direction of the wind reverses to come from the southeast during April to July. Wind directions are variable during these two periods. The directions of winds are anomalous in the Klang Strait because of the Coriolis effect; e.g., northwest winds derive from the northeasterly trade winds during the northeast monsoon, and the southeast winds derive from southwesterly winds during the southwest monsoon (Sasekumar & Chong, 2005).

3.1.3 Tides and Tidal Streams

Tidal circulation is semidiurnal in the Klang Strait; the level of the surface water falls and rises with an average range of 1.4 m to 4.2 m within approximately 12.5 hours depending on the condition of the sun and the moon (DID, 2000).

In the 1970s, the British admiralty and the hydrographic directorate of the royal Malaysian navy reported tidal heights at mean high water spring, mean high water neap, mean low water neap, and mean low water spring were follows: 5.2 m, 3.9 m, 2.5 m, and 1.0 m, respectively(Authority, 2008; Sasekumar & Chong, 2005).

3.1.4 Water Parameters

The average of water parameters was measured for a period of 14 months in the Klang Strait by Chong (1993) and Zgozi (2000). Mean surface water salinity was recorded at 30.25‰ (± 1.36) and ranged between 26.0 to 33.0‰, whereas surface water temperature ranged from 28.2 to 31.9 °C and its mean was 30.04 °C (± 0.62). Bottom salinity (at a water depth from 2 to 17 m) ranged from 30.4 to 32.5‰, whereas the monthly average bottom temperature varied from 29.4 to 30.2°C. Thus, there was only showed small seasonal fluctuations of salinity and temperature.

The differences between salinity and temperature in surface and bottom waters did not exceed 0.5°C and 2.5‰ salinity respectively even at a depth of 20 m because the strong current, prevailing northern monsoon winds, ebb and flood tides, and high river discharge caused the marine water to be vertically well mixed in the Klang Strait (Chong, 1993; Zgozi, 2000).

The average concentration of surface dissolved oxygen (DO) was 5.38 mg/l (± 0.85). Chong (1993) reported that the range of DO concentrations in the surface and bottom waters in the Klang Strait varied from 4.2 to 6.4 mg/l and 3.7 to 6.2 mg/l, respectively.

Zgozi (2000) indicated that the range of mean concentrations of DO was between 4.84 mg/l and 6.76 mg/l (Zgozi, 2000). The monthly average pH value was 8.06 (± 0.17) and ranged from 7.85 to 8.25. However, Zgozi (2000) reported that the average pH value ranged between 8.20 and 8.44.

The lower value of pH was measured during a higher river discharge from October to January (Zgozi, 2000). The monthly mean turbidity values varied between 3.75 to 270 NTU, and the highest values were measured around the Klang River mouth and Angsa Island (Chong, 1993; Sasekumar & Chang, 2005; Zgozi, 2000).

3.1.5 Depositional Features

Lee (2005) indicated that the Klang Strait was submerged in late quaternary marine transgression and that the sea subsequently receded in the Holocene epoch (Ibrahim, 1988). During this period, vast alterations occurred in this area because the strong current in the rivers washed a huge amount of sediment downstream and dispersed it uniformly. Wide intertidal mud flats and offshore shoals deltaic island were formed as a result of the active fluvial deposition and marine process. The analysis of surface sediment (up to 4 cm deep) performed around the Angsa Bank (north of the Klang Island) determined that more than 70% of the sediment was very fine sand and that the fine sand/silt composition was 15 to 25% and the clay composition was less than 5% (Ibrahim, 1988). In the mud flats' sediment, the clay and silt composition was about 7 to 27% and 45 to 75%, respectively. Also, a high amount of coarse and finely broken shells were reported in the sediment of the Klang Strait (Sasekumar & Chong, 2005).

3.2 Sampling and Field Work

In this project, the study area was defined based on the definition of Admiralty Chart No. 3453 in London. A total of 21 sampling stations were selected at 3 sites including 6 stations in North Port, 6 stations in South Port, and 9 stations in West Port (**Figure 3.4** and **Table 3.1**). One station was selected 30 kilometers far from north of the Klang Strait as a control point. According to the location and bathymetry of each site, stations located inside the Klang Strait were arranged into three parallel transects at three different distances. The first transect was parallel to the berth line and industrial outlets, the second was the middle line of the strait, and the third was parallel to the mangrove line in the West Port and North Port. Water samples were collected at the 22 stations in the first week of every month from November 2009 to October 2010.

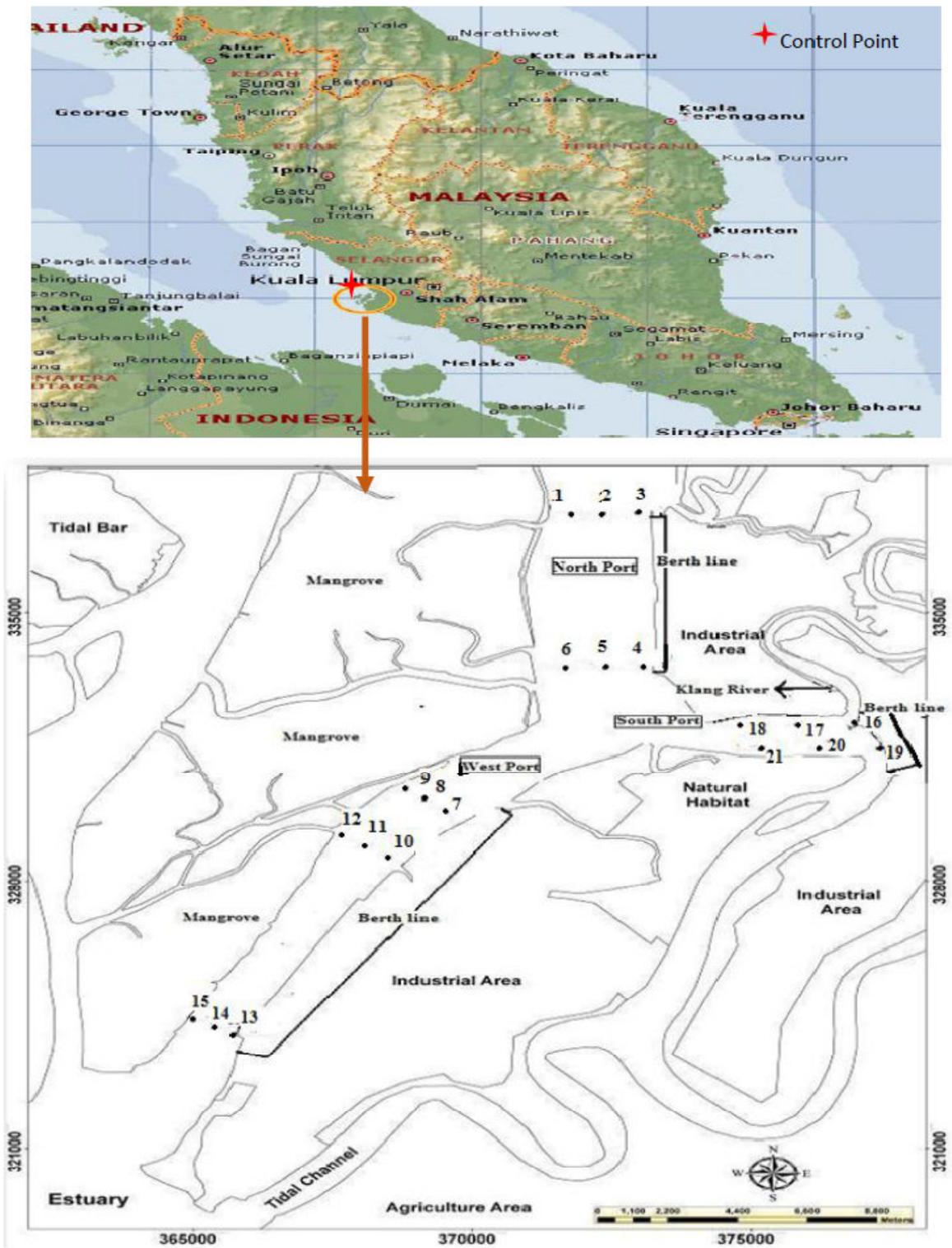


Figure 3.4, Map showing the sampling sites and stations

Table 3.1, Location, depth and description of stations along Klang Strait

Sites	Station code	latitude	longitude	Depth (m)	Description of stations
North Port	1-NL100	3° 3'1.49"N	101°21'18.70"E	14.3	liquid berth line
	2-NL700	3° 3'1.33"N	101°20'56.04"E	20.5	Remote
	3-NL1500	3° 3'1.47"N	101°20'33.11"E	10.3	Mangrove
	4-NC100	3° 0'53.11"N	101°21'20.25"E	13.5	Container berths
	5-NC700	3° 0'52.64"N	101°20'58.04"E	21.6	Remote
	6-NC1500	3° 0'52.49"N	101°20'34.54"E	11.2	Mangrove
West Port	7-WC100	2°58'44.00"N	101°19'21.02"E	12.5	cement berth
	8-WC500	2°58'54.12"N	101°19'9.06"E	19.5	Remote
	9-WC1000	2°59'3.12"N	101°18'58.38"E	7.8	Mangrove
	10-WL100	2°58'6.34"N	101°18'48.14"E	13.3	liquid berth
	11-WL500	2°58'14.90"N	101°18'34.56"E	20.3	Remote
	12-WL1000	2°58'23.07"N	101°18'20.99"E	8.8	Mangrove
	13-WT100	2°55'34.43"N	101°17'18.76"E	15.5	Container berths
	14-WT500	2°55'39.38"N	101°17'7.57"E	21.1	Remote
South Port	15-WT1000	2°55'45.02"N	101°16'55.55"E	6.8	Mangrove
	16-SK100	2°59'59.08"N	101°23'18.88"E	7.5	Dry berths, Klang River
	17-SK1000	2°59'58.17"N	101°22'45.35"E	10.5	Klang River
	18-SK2000	2°59'57.66"N	101°22'12.45"E	12.4	Semi-urban
	19-SL100	2°59'38.25"N	101°23'32.32"E	10.3	Liquid berth
	20-SL1000	2°59'37.70"N	101°22'57.93"E	11.3	industrial
Control Point	21-SL2000	2°59'37.23"N	101°22'23.78"E	10.4	Mangrove
	22-CP	3° 6'55.95"N	101°12'44.70"E	17.5	Remote

Water quality was evaluated based on the physical and chemical parameters, and the Rutner sampler was used to collect water samples. A multi-parameter probe (YSI 556 MPS) was applied to measured physical parameters such as temperature, salinity, dissolved oxygen, oxygen saturation, pH and total dissolved solids, from the surface water layer (50 cm deep). The multi-parameter probe was calibrated the day before the sampling using methods outlined in the YSI 556 MPS maintenance manual. The dissolved oxygen probe was re-calibrated in the field on the day of sampling. Water transparency was measured using a Secchi disc, and a fish finder was used to measure the water depth at each station. The current meter (RDI Ocean Surveyor ADCPs™) was used to measure current speed in this research. This equipment was installed on vessels to provide detailed maps of the distribution of water currents and suspended materials through the water column and along the ship's path. The system is completed with the new VMDAS Software.

Water samples of about 1 liter were taken from the same depth (one meter) to measure the total suspended solid and dissolved nutrients (nitrite, NO_2^- ; nitrate, NO_3^- ; ammonium, NH_4^+ ; ammonia, NH_3), soluble reactive phosphate (orthophosphates), and soluble reactive silicate (SRSi). These water samples were transferred into dark polyethylene bottle, which were filled about three-quarters full.

These samples were immediately filtered through a Millipore membrane filter (0.45 micrometer), using a vacuum pressure of < 400 mm Hg and analyzed as soon as possible after filtering within 48 hours. Additional water (1 liter) was collected to estimate suspended solids by Hach DR/2400 Spectrophotometry based on the photometric method (EPA, 2001; Parsons, Maita, & Lalli, 1984).

For measuring the chlorophyll a, a 1-liter water sample was poured into the opaque bottles and held on ice or at 4°C. These samples were immediately filtered after being transferred to the laboratory at the same day (Clesceri, Greenberg, & Eaton, 1998).

From November 2009 to October 2010, sediment samples were collected one every 3 months (two sampling per season) at low tide. The sediment samples were collected in triplicate from sediment by the Petersen grab sampler (0.07m²). Each replicate was rinsed through a sieve with a 0.5-mm mesh screen to sort benthic organisms including macro-infauna (greater than 0.5 mm)(GIPME, 2003). The organisms were then transferred into a plastic container, preserved in a 99.9% ethanol alcohol with Rose Bengal, and stored to identify their lowest practical taxonomic level (i.e., organisms were identified as species where possible and damaged organisms or juveniles were identified to genus and family) by a dissecting microscope. Then, the upper 2 to 3 cm of sediment were collected from additional grabs for chemical mechanisms because this layer controls the exchange of chemicals compounds between sediment and water (Praveena, Ahmed, Radojevic, Abdullah, & Aris, 2008).The samples were stored in clean aluminum foil and kept in an icebox at 4°C to decrease chemical and biological reactions. For extra analysis, samples were air dried and passed through sieve with a 2-mm mesh size and stored at -20°C until further analysis for measuring heavy metals, organic contaminants (PAHs), total organic carbon (TOC), and grain size (Clesceri et al., 1998; Paul, Scott, Holland, Weisberg, & Summers, 1992).

3.3 Experimental Methods

3.3.1 Water Quality Analysis

3.3.1.1 Nutrient:

A Hach DR/2400 spectrophotometer was used to measure the nutrients and suspended solids based on the methods which is published in Hach procedures manual June 2007 edition 2. These methods were denoted by USEPA as standard method for water and wastewater analysis ("Procedures manual of DR 2400 Spectrophotometer," 2007). Dissolved inorganic nitrogen (DIN) was estimated as the sum of nitrites, nitrates, and ammonium. The Redfield ratio (N:P, 16:1) was estimated based on the DIN: PO_4^{3-} to clarify potential N and P limitation for phytoplankton growth (USEPA, 1991).

Accuracy and precision was checked by using standard solutions and standard additions (USEPA, 1991). Some of these standards were made in the laboratory, and some of them were ordered as a chemical reagent. The standard solution was used instead of the sample water in the analysis process, and their percent recovery was estimated by the specific formula published by the USEPA SW-846. The reasonable percent recovery values ranged between 80 and 120%. Also, laboratory reagent blanks, laboratory duplicate analysis and calibrate tests were used to check performance (Clesceri et al., 1998; EPA, 2001).

Table 3.2, Standard analysis methods for nutrient based on the Hach procedures manual ("Procedures manual of DR 2400 Spectrophotometer," 2007).

Parameters	Name and number of Method	Concentration range (mg/l)	Accuracy Check	Preservation and Maximum holding time
Nitrate	Cadmium Reduction (8117)	0.1 to 10.0	10mg/l Nitrate Nitrogen standard solution	filter immediately cool 4° C for 48 hours
Nitrite	Diazotization method(8517)	0.002 to 0.300	0.30mg/l nitrite standard based on the method 4500-NO2 in standard method	
Ammonia	Salicylate (8155)	0.01-0.5	0.4 mg/l ammonia nitrogen standard solution	
Ammonium	380N,Ammonia, Ness	0.02-2.5	Nitrogen Ammonia Voluette Ampule, 50mg/l NH3-N	
Orthophosphate	Ascorbic Acid (8048)	0.02 to 2.5	2.0 mg/l phosphate standard solution	
Silica	Silicomolybdate (8185)	1.0-100	50.0 silica standard solution	cool 4° C for 7 days
Suspended Solid	Photometric (8006)	0-750 mg/l	-----	

3.3.1.2 Chlorophyll *a*:

In this research method, 446.0 USEPA (1997) was used to measure the concentration of chlorophyll *a*. One-liter water samples were concentrated by filtration through Whatman GF/C glass fiber filters at low vacuum (not exceeding 6 in. Hg [20 kPa]). The pigment extraction was performed in 90% acetone by aid of the Homogenizer HG-150 (macerate at 500 rpm for 1 minute), with an adjusted total volume of 10 ml by 90% acetone, and let to steep for at least 2 hours at 4°C in the dark. To clarify the solution, the extraction sample was centrifuged for 15 minutes at 675 g (or at 1,000 g for 5 minute), the clarified extraction was transferred into glass cell of UV, and UV-2100 spectrophotometer was used to measure the absorbance at the four wavelengths (750, 664, 647, and 630 nm) to estimate turbidity, chlorophylls *a*, *b*, and *c*, respectively (USEPA, 1991).

A specific equation was used based on the absorbance value to calculate the concentration of chlorophyll a based on the mg/l (pmm). Before calculation of the concentration of chlorophyll a, the absorbance value of 750 nm was subtracted from the other absorbance values because of the high sensitivity of this observed value at 750 nm to change in the water –to- acetone proportion. The concentrations of chlorophyll a, b, and c were estimated in the following equation.

$$a) C_a = 11.85(Abs\ 664) - 1.54(Abs\ 647) - 0.08(Abs\ 630) \quad (3.1)$$

$$b) C_b = 21.03(Abs\ 647) - 5.43(Abs\ 664) - 2.66(Abs\ 630) \quad (3.2)$$

$$c) C_c = 24.52(Abs\ 630) - 7.60(Abs\ 647) - 1.67(Abs\ 664) \quad (3.3)$$

Where:

C_a , C_b , and C_c = concentrations of chlorophyll *a*, *b*, and *c*, respectively, mg/l, in the extract solution analyzed). After determining the concentration of pigment in the extract, the amount of pigment per unit volume was calculated as follows (Chapman, 1996):

$$C = \frac{C_a \times \text{extract volume}(L) \times DF}{\text{sample volume}(L) \times \text{cell length}(cm)} \quad (3.4)$$

C = Concentration of chlorophyll a in the whole water sample ($\mu\text{g/l}$)

C_a = Concentration of chlorophyll a in the extraction solution analyzed (mg/l)

Extract volume = volume (l) of extract before any dilution

DF = any dilution factor

Sample volume = volume (l) of whole water sample that was filtered

Cell length = optical path length (cm) of cuvette used (typically 1 cm)

3.3.2 Sediment Quality Analysis

3.3.2.1 Sediment grain size:

Sediment grain size was determined using a multi-wavelength particle size analyzer (model LS 13 320), and the results were divided into sand ($>64\ \mu\text{m}$), silt ($2\ \mu\text{m} < \text{size} < 64\ \mu\text{m}$) and clay ($<2\ \mu\text{m}$) fractions for the determination of heavy metals and PAHs in the contaminated soil (Rauret, 1998; Tessier, Campbell, & Bisson, 1979). For extra analysis, samples were dried to decant water and humidity from sediment samples by a freeze dryer (Magnum™ Series Freeze Dryers) and each sample was held in a glass bottle for further analysis (Clesceri et al., 1998).

3.3.2.2 Heavy metals

Double distilled water was first used to wash sediment samples and remove halides from sediment. All Teflon bottles and crystal materials were washed with water and soap and rinsed with MilliQ and Ellox quality water prior to analysis (Clesceri et al., 1998).

The samples were dried in an oven at $60\ ^\circ\text{C}$ for overnight, and 0.5 g of the dried sediment sample was transferred to vessels for acid extraction analysis. The samples were digested in 3 ml of hydrofluoric acid (HF), 6ml Perchloric acid and 9 ml of nitric acid for 15 minutes using microwave heating (MASTER 40-vessel), while covering the sediment samples continuously for three hours. 18 ml of boric acid 99.99% was added to the cooled solution followed by centrifugation.

The solution from the centrifugal operation was filtered using filter-paper (Whatman No 0.45 μm), and the volume was brought to 50 ml with deionized water for the measurement of heavy metals concentrations. The preparation procedure described above for metal analyses was based on EPA method 3052 (EPA, 1996; Ilander & Väisänen, 2007).

After extraction process, heavy metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) were measured by the plasma mass spectrometry (Agilent technologies 7500 series ICP-MS) at Department of Chemistry and Geology in the University Malaya. Metals measured had all levels above detectable limits. ICP-MS was calibrated by the external standard solutions (Multielement standard ICP-68A-A 10 mg/l, Merk. Malaysia) to measure metals and the calibration was improved by using the rhenium and indium as internal standards. Standard reference materials (SRM) 2702 is a natural matrix of inorganic compounds collected from marine sediment with certified concentration values. The National Institute of Standards and Technology (NIST) and collaborating laboratories obtained certified values for the concentrations of 25 elements based on chemically independent analytical methods with the highest accuracy (Willie & May, 2002). In this study, data quality control and heavy metal concentrations were evaluated with the certified concentration of SRMs 2702 (Frankfurter, Germany) and matrix spike recoveries. The recovery was between 91.54 and 104.66. The standard methods suggest warning limits for matrix spike recoveries from 87 to 113%; therefore, the range of recovery was reasonable in this study (IDEM, 2002; Willie & May, 2002). Mercury was estimated by both ICP/MS and with a milestone mercury analyzer (DMA-80 model) to produce accurate result. The specific equation was applied to calculate the final results of heavy metal concentration.

$$C = A \times \frac{V}{D} \quad (3.5)$$

C: Meta dry weight (mg/kg)

A: The concentration of the sample measured

V: Final volume of the collected sample.

D: Dry weight of the sample

3.3.2.3 Total organic carbon

TOC and nitrogen was measured in surface sediment by using a Perkin-Elmer 2400 carbon–hydrogen–nitrogen–sulfur (CHNS) elemental analyzer at 950°C combustion temperature. Two g of freeze-dried sediment sample was treated with an HCL (10%) solution in a specific container to remove the inorganic carbon and was dried overnight at 60°C. A 5- to 15-mg sample was put into a tarred 5.8-mm silver capsule, which was compressed with tweezers for CHNS analysis. The percent of organic carbon was measured in duplicate.

3.3.2.4 Polycyclic aromatic hydrocarbons (PAHs)

Authentic standard of 16 USEPA priority PAHs were applied which include naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*] pyrene (IcdP), dibenzo[*a,h*]anthracene (DahA) and benzo[*ghi*] perylene (BghiP).

The EPA PAHs mixed standards were prepared into different concentrations (**Table 3.3**) in acetonitrile: methanol (9:1) which purchased from Sigma-Aldrich (Bellefonte, PA, USA) and these standard solutions diluted by n-hexane to prepare working standards with appropriate concentrations. The concentrations of working solutions were varied from 5 –1000 ng ml⁻¹ based on the analyte. Organic solvents such as hexane and dichloromethane (SupraSoly) were provided from the Merck Company (Frankfurter, Germany) and the specific cartridges for the solid phase extraction (SPE) C18 (1 g, 3 ml) were purchased from International Sorbent Technology (Stevenage, Hertfordshire). For drying, nitrogen of 99.995% purity was purchased from Roham Co (Tehran, Iran).

Table 3.3, Concentrations of 16 EPA PAHs in the mixed standards solution

Concentration ($\mu\text{g mL}^{-1}$)	PAH Name	Retention time
500	naphtalene	6.02
500	acenaphthylene	8.96
1000	acenaphthene	9.46
100	flurene	11.03
40	phenantrene	14.75
20	anthracene	14.95
50	fluoranthene	20.61
100	pyrene	21.71
50	Benzo(a)anthracene	28.5
50	chrycene	28.7
20	Benzo(b)Fluoranthene	34.32
20	Benzo(K)Fluoranthene	34.44
50	Benzo(a)pyrene	35.85
200	(a,h)Anthracene	40.95
80	Benzo(g,h,i)Perylene	41.13
50	indeno(1,2,3)pyrene	41.95

Before use, the organic solvents were distilled in glass; the glassware was rinsed sequentially with methanol, acetone and distilled hexane to remove pollutants, especially organic compounds, and held in an oven at 60 °C.

Freeze-dried samples were homogenized and sorted with an 80-mesh (mesh size: 0.18 mm) stainless steel sieve. A weighed aliquot (10 g) of each sample was wrapped in a piece of pre-cleaned filter paper. After addition of activated copper strips for removal of elemental sulfur, samples were Soxhlet-extracted (Method SW-846 of EPA) with 200 ml of a mixture of hexane: acetone (1:1 in volume) for 48 h. Since the quantitative results were reproducible (RSD < 10%), the internal standard was not used in the analyses.

The extract was concentrated to 0.5 ml and the remaining solvent was set in hexane. The SPE columns (ISOLUTE[®] SPE column-NH₂) were conditioned with hexane (8 ml). The hexane extract (0.5 ml) was applied to the column. Interferences were eluted with pentane (2 × 1.5 ml). PAHs trapped on SPE cartridges were eluted with 6 ml of n-hexane containing 3.4% (v/v) isopropanol at a flow rate of 1–2 ml min⁻¹ using a solid-phase extraction (SPE) system under a vacuum pump. Then extracts were concentrated to nearly dry by rotary evaporation, and the solvent was exchanged into n-hexane. Samples were concentrated to about 100 µl under a stream of pure nitrogen and stored at -4 °C prior to instrumental analysis.

Some sediment samples were polluted with sulfur; thus copper powder was used for desulfurization. Hydrochloric acid (HCl, 1N) was used to activate the copper powder, which was then washed with acetone, hexane and water.

For all samples, a standard solution and a procedural blank consisting of all the reagents was run to test interferences and cross-contamination. The equipment was calibrated with the standard mixture at seven different concentrations to make a standard curve for external calibration.

The applied method of extraction and clean-up was checked, based on the sediment reference material (IAEA-417). Results of recovery were summarized in **Table 3.4**. The results of recovery ranged between 78% and 94%. Sediments have certified concentrations of PAHs. Since the certified reference material (CRM) was used, spiking of the working standard solution had not been used for the assessment of recovery. Concentration of the target compounds consistently showed the 95% confidence interval of the allocated reference value for concentrations of known hydrocarbons.

The accuracy of the estimation achieved through replicates of the reference materials was better than 10% for all target compounds. The method of detection limit (MDL) was measured according to the USEPA and ranged from 0.095 to 1.018 for sediment (**Table 3.5**). The RSD percentage of all PAHs was lower than 10% in the fortification analyses, and the replicate was used to estimate the MDL.

Table 3.4. Average concentration, standard deviation and percent recovery (RSD) of certified references IAEA-417

PAH Name	Assign Value Con:ng/g	Reported Standard Deviation	Recovery (\pm RSD)%
naphtalene	150	110	78(\pm 7)
acenaphtylene	42	35	83(\pm 5)
acenaphthene	180	62	79(\pm 7)
flurene	230	110	81(\pm 3)
phenantrene	3900	1500	95(\pm 3)
anthracene	630	240	91(\pm 6)
fluoranthene	7700	3000	84(\pm 6)
pyrene	6000	2200	87(\pm 5)
Benzo(a)anthracene	3200	1200	94(\pm 2)
chrycene	3600	1700	93(\pm 4)
Benzo(b)Fluoranthene	4100	2000	80(\pm 5)
Benzo(K)Fluoranthene	2000	300	95(\pm 3)
Benzo(a)pyrene	2800	1200	89(\pm 2)
(a,h)Anthracene	1100	1100	92(\pm 4)
Benzo(g,h,i)Perylene	2300	1300	78(\pm 5)
indeno(1,2,3)pyrene	2700	370	88(\pm 3)

Table 3.5, Detection limit of 16 USEPA priority PAHs

Name	MDL
naphthalene	0.09551
acenaphthylene	1.018327
acenaphthene	0.064122
fluorene	0.28086
phenanthrene	0.089409
anthracene	0.174339
fluoranthene	0.064886
pyrene	0.229757
Benzo(a)anthracene	0.114942
chrycene	0.203589
Benzo(b)Fluoranthene	0.292616
Benzo(K)Fluoranthene	0.145181
Benzo(a)pyrene	0.169257
(a,h)Anthracene	0.186419
Benzo(g,h,i)Perylene	0.247436
indeno(1,2,3)pyrene	0.241637

Quantification and qualification of 16 USEPA priority PAHs were performed, based on the modified method of USEPA 8270 by a capillary gas chromatograph (GC; Agilent 6890) equipped with a mass spectrometer (Agilent 5973 MS; Quadrupole mass analyser) using electron ionization and operating in a selected ion-monitoring mode.

The Gas chromatography (GC) was equipped with a column coated with HP-5MS (30 m by 0.25 mm; 0.25-mm film thickness). The oven temperature programme was as follows: isothermal at 70 °C for 2 min, 30 °C per min to 150 °C, and 4 °C per min to 300 °C. It then remained at 300 °C for 10 min.

Helium was used as the carrier gas at 1.0 ml per minute at a constant flow, and a Split/Splitless injector was used for the injection of samples. The injection port temperature was 300 °C and the mode of injection was split-less.

The GC–MS condition was at 70 eV ionization potential with electron multiplier voltage at 2000 V. The ion source temperature was 150 °C, and the transfer line temperature was 250 °C. Solvent delay time was 4 min. Selective ion monitoring was used to increase sensitivity. PAHs were monitored using ions 152, 153, 166, 178, 202, 228, 252, 276 and 278. Identification of PAHs was done on the basis of the relation between the retention time of PAH and the retention time of mixed standard and the m/z ratio of an authentic PAH mixed standard (Sigma). The integrated peak area was used to quantify the PAH compound based on the comparison between the peak area of the selected ion and the peak area of the ISTD (a known standard), and the concentration of PAHs was calibrated according to the standard calibration curve.

3.3.3 Biodiversity and species richness

Biodiversity study is an essential part of the environmental assessment because the diversity values act as an indicator of the health of ecological systems (Vollenweider et al., 1998). There are several indices and models to measure diversity; it is difficult to select which method is best for estimating diversity. A scientific method to use when selecting a diversity index is to make the decision on the basis of whether it has the ability to fulfill certain function criteria to distinguish between study sites, dependence on sample size, what component of diversity is being measured, and whether the index is widely used and understood (Vollenweider et al., 1992).

In present study, Shannon–Wiener Index was used (Shannon & Wiener, 1963) to assess diversity of benthic organisms. Shannon diversity is frequently used to compare diversity between various ecological systems (Clarke & Warwick, 2001).

This index is based on the theory that individual species are randomly sampled from indefinitely large populations, and it also assumes that all the species are represented in the sample (Jørgensen et al., 2005).

The index takes the form of:

$$H' = -\sum p_i \log_2 p_i \quad (3.6)$$

$$p_i = \frac{N_i}{N} \quad (3.7)$$

P_i is the proportion of individuals found in the species i , N_i is the number of individuals of the species i , and N is the total number of individuals. The value of index can take between 0 and 5. According to the literature (Vollenweider et al., 1998), low index values are considered to be indications of contamination.

High status: Greater than 4 bits/individual

Good status: 4 to 3 bits/individual

Moderate status: 3 to 2 bits/individual

Poor status: 2 to 1 bits/individual

Bad status: 1 to 0 bits/individual

Several researches have indicated valuable information on water quality based on the invertebrate communities, because at same time, diversity and abundance of benthic communities are affected by the changing condition of water and the sediment column. Also, invertebrate organisms have long lives with different life cycles, and their structures vary by anthropogenic stress (Kitsiou & Karydis, 2011). In recent decade suitable benthic index and models have been proposed to assess coastal and marine water based on benthic communities such as the AZTI Marine Biotic Index (AMBI), BI and M-AMBI.

3.3.4 AZTI Marine Biotic Index (AMBI)

This index was designed to classify the ecological quality of the estuary and coastal water according to the response of soft-bottom macro benthic population to changes in water quality (Borja et al., 2012).

The benthic organisms were divided into 5 ecological groups GI, GII, GIII, GIV and GV based on their sensibility and respond to anthropogenic stress (Borja et al., 2000). The AMBI scale ranges between the 0-7 which is described in **Table 3.6**.

The formula that expresses this index is given by,

$$AMBI = \left((0x\%GI) + (1.5x\%GII) + (3x\%GIII) + (4.5x\%GIV) + (6x\%GV) \right) / 10 \quad (3.8)$$

GI: Species very sensitive to organic enrichment and present under unpolluted conditions (initial state).

GII: Species tolerant to enrichment, always present in low densities with non-significant variations with time (from initial state, to slight unbalance).

GIII: Species tolerant to excess organic matter enrichment. These species may occur under normal conditions, but their populations are stimulated by organic enrichment.

GIV: Second-order opportunistic species (slight to pronounced unbalanced situations).

GV: First-order opportunistic species (pro-nounced unbalanced situations).

3.3.5 Multivariate- AMBI, M-AMBI

This index designed to define better the water bodies' ecological quality status (EcoQS) based on the benthic community integrity (abundance, biomass or diversity measures)(Pinto et al., 2009). Zettler et al., (2007) indicated that this index "is combination of the proportion of disturbance- sensitive taxa through the use of the Shannon-wiener index, which overcome the need to use more than one index to evaluate the overall state and quality of continental shelf and oceanic water bodies"(Zettler, Schiedek, & Bobertz, 2007).

These factors integrated through the use of Discriminative Analysis (DA) and Factorial Analysis (FA) techniques. This method compares monitoring results with reference condition by salinity stretch, for estuarine system, in order to derive an ecological quality ratio.

The final values describe the relationship between the observed values and reference condition value. This values ranged between 0 and 1 which imply the five ecological states (Muxika, Borja, & Bald, 2007; Pinto et al., 2009).

A main advantage of these indices is that, it is possible to detect the impact of anthropogenic pressures in marine environment because these indices can be applied to estimate the evaluation of ecological status of different geographical sites because these indices have been tested in different geographical sites and provided strong agreement percentage with local indices (Borja et al., 2000; Muniz, Venturini, Pires-Vanin, Tommasi, & Borja, 2005; Muxika, Borja, & Bonne, 2005).

As so, these indices can be practical as sound tool for environment management due to its capacity to evaluate ecosystem health. Other advantage of both index is that these are easily estimated by the software can be freely download at <http://www.azti.es> (Pinto et al., 2009).

Table 3.6, AMBI scales and classifications

AMBI	M-AMBI	Disturbance Classification	EcoQS (WFD)
$0.0 < \text{AMBI} \leq 1.2$	> 0.82	Unpolluted	High Status
$1.2 < \text{AMBI} \leq 3.3$	$0.62 - 0.82$	Slightly polluted	Good Status
$3.3 < \text{AMBI} \leq 5$	$0.41 - 0.61$	Moderately polluted	Moderate Status
$5.0 < \text{AMBI} \leq 6$	$0.21 - 0.4$	Heavily polluted	Poor Status
$6.0 < \text{AMBI} \leq 7.0$	< 0.2	Extremely polluted	Bad Status

3.3.6 Tropic Level of Water

There are several indices proposed to assess water quality and trophic status based on the single and multiple parameters such as annual phosphate, DIN, DO, and chlorophyll a as indicators. Table 2-5 and 2-6 show the trophic classification in estuary and coastal water based on the single parameters. Multimetric eutrophication indices have also been suggested (Primpas & Karydis, 2010).

3.3.6.1 TRIX Trophic Index:

Vollenweider et al (1998) suggested the use of the trophic index (TRIX) for the monitoring of trophic status. This index uses a linear combination of four parameters related to primary production and nutritional condition; namely, dissolved inorganic nitrogen, total phosphorus or inorganic phosphorus (as a nutritional compound), chlorophyll a (as a proxy for phytoplankton biomass), and oxygen saturation (as a biotic component or measure of productivity).

This index was classified to 5 trophic scales from 2 to 8, which are shown in **Table 3.6**. The estimation of the TRIX index from the water bodies image can be computed by,

$$TRIX = \left[\log(chla \times \%DO \times DIN \times P \times 1.5) \right] / 1.2 \quad (3.9)$$

Table 3.6, Assessment of trophic status using TRIX

TRIX value	Tropic status	Condition	Reorganization for study
<2	ultra-oligotrophic	Very poorly productive	Excellent
2-4	Oligotrophic	Poorly productive	High
4-5	Mesotrophic	Moderately productive	Good
5-6	Mesotrophic to eutrophic	Moderate to highly productive	Moderate
6-8	Eutrophic	Highly productive	Poor

3.3.6.2 Eutrophication Index (EI)

In 2010, Primpas proposed another multimetric index to assess trophic status on a five-point scale; namely, the Euthrophic Index (EI). This index was tested in three standard sets of water types (oligotrophic, mesotrophic, eutrophice) and it was effective and valid (Primpas & Karydis, 2010).

The formula that expresses that this (EI) index is given by,

$$E.I = 0.297C_{PO_4} + 0.261C_{NO_3} + 0.296C_{NO_2} + 0.275C_{HN_3} + 0.214C_{Chla} \quad (3.10)$$

Where,

C is a concentration for nutrient and chlorophyll a. This index was also divided into five levels, which are described below:

- Less than 0.04 is high quality
- 0.04 to 0.38 is good quality
- 0.38 to 0.85 is moderate quality
- 0.85 to 1.51 is poor quality
- Greater than 1.51 is bad quality

3.3.6.3 Operational indicators

Table 3.7 shows operational indicators were introduced in the several scientific literature to assess trophic level of marine and coastal water (Hakanson & Blenckner, 2008; Håkanson, Bryhn, & Hytteborn, 2007).

Table 3.7. Operational indicators to assess trophic status of marine and coastal water

Operational indicator and indices	Secchi depth(cm)	Chl-a (µg/l)	Total-N (mg/l)	Total-P (mg/l)
Tropic status and Oligotrophic (high quality)	>1100	<2	<0.110	<0.015
Mesotrophic (good quality)	600-1100	2-6	.011-0.29	0.015-0.04
Eutrophic (Bad quality)	200-600	6-20	0.29-0.94	0.04-0.130
Hypertrophic (Poor quality)	<200	>20	>0.94	>0.13

3.3.7 Sediment Quality Assessment

Enrichment factor (EF) and geo-accumulation are specific indices that are used to estimate the anthropogenic source and contamination degree of heavy metals on estuarine and coastal waters. These indicators provide simple ways to assess the contamination status of surface sediments (Sinex & Helz, 1981).

EF is estimated based on total resistant elements, such as Al, Li, Fe, Rb, Sc and Cs (Balls, Hull, Miller, Pirie, & Proctor, 1997; Qin, Zhao, & Chen, 1989; Rubio, Nombela, & Vilas, 2000). In recent decades, Al and Fe were widely used as normalising element to estimate the enrichment factor (Ackermann, Bergmann, & Schleichert, 1983; Loring, Naes, Dahle, Matishov, & Illin, 1995; Rubio et al., 2000).

Several comparative arguments exist on the use of Al or Fe as normalising elements. Some studies have selected Fe as the normalising element because Fe has the same geochemical reaction under oxic and anoxic conditions with other heavy metals in sediment and also because the natural concentration is more uniform compared with Al (Goldberg, GRIN, Hodge, Koide, & Windom, 1979; Siddique et al., 2009).

The stability of Fe in sediment is lower than Al due to the mobility and ability of this element to accumulate in the food chain (Daskalakis & O'connor, 1995; Din, 1992; Rubio et al., 2000; Zwolsman, van Eck, & Burger, 1996), which indicates that Fe is affected by anthropogenic contaminants. Aluminium was selected as a normalising element in this study because this metal is commonly inactive in marine sediment with little or no chemical reaction and, therefore, is not easily affected by anthropogenic contamination and diagenetic changes (Rubio et al., 2000).

Zubir indicated that Al has a strong linear correlation with other trace metals (with: 0.89-0.93) in the Melaka Strait coastal water (Din, 1992). EF is the concentration ratio of measured heavy metals to normalising elements (Al, Fe, Cs,Rb, Li, Si) in sediment samples that is divided by the ratio of metal background to the normalising elements (Rule, 1986).

Enrichment factor can be written as:

$$EF = [C_{metal} / C_{normaliser}]_{soil} / [C_{metal} / C_{normaliser}]_{back\ ground\ values} \quad (3.11)$$

Where $[C_{metal} / C_{normaliser}]_{soil}$ are the metal concentrations in the sediment sample and $[C_{metal} / C_{normaliser}]_{back\ ground\ values}$ is the natural background of the heavy metals and normalising elements. According to the enrichment factor, sediment is classified into groups by river, estuary and coastal environments. EF values of $0.5 \leq EF \leq 1.5$ indicate that the metals may be completely derived from natural or lithogenic processes.

EF values of more than 1.5 indicate that a large portion of trace metal is derived from non-natural processes or anthropogenic sources (Feng, Han, Zhang, & Yu, 2004; Siddique et al., 2009; J. Zhang & Liu, 2002; W. Zhang et al., 2009).

Han et al in 2006 defined the new ER value classification as follows: $EF \leq 2$ indicates that metal contamination might be entirely from natural sources ,an EF value of 2–5 indicates that a moderate portion of heavy metals originated from an anthropogenic source or non-natural process, an EF of 5–20 indicates that a significant portion are from anthropogenic sources, an EF of 20 to 40 indicates that a high portion of contamination is derived from anthropogenic sources, and an $EF > 40$ indicates an extremely high portion of contamination. In this research, the average concentration of heavy metals from 1996 to 2007 is used to estimate the background value from (Hakanson, 1979).

The PAH isomer ratio was used to infer the possible anthropogenic sources of PAH from the natural source. These ratio and their classification was defined in **Table 3.9** based on several studies such as: Budzinski (1997), Yunker (2002), Zhang (2004), wang (2011) and khairy (2009).

Table 3.9, PAH isomer pair ratio measurement

PAH isomer	ratio	Source
Anthracene/anthracene+ phenanthrene	<1.0	Petroleum
	>1.0	Dominance of Combustion of coal
Benzo(a)anthracenen/ Benzo(a)anthracenen+chrysene	<0.10	Petroleum input or diagenetic sources
	>0.1	Characteristic of combustion processes
Fluoranthene/ Fluoranthene + pyrene	< 0.4	Petroleum
	0.4-0.5	Petroleum and combustion
	>0.5	Combustion
Methylphenanthrene/phenanthrene	>1	Petroleum
Phenanthrene/ Anthracene	>10	Petrogenic
	<10	Pyrolytic
Fla/Pyr	<1.0	Petrogenic
	>1.0	pyrolytic

3.4 Ecological Risk Assessment

Ecological risk assessment was performed to assess adverse biological effects or the degree of toxicity of PAHs and heavy metals in the sediment. In this research, two methods were applied to estimate ecologic risk, which is described in the following paragraph.

3.5 Ecological risk assessment based on the sediment quality guidelines

The sediment quality guidelines (SQGs) that are applied to assess adverse biological effect (Khairy et al., 2009; Hubner et al., 2009). This method indicates that the relationship between the concentrations of contaminants in sediment samples and adverse biological effects is based on the specific values of effect range low or threshold effect level (TEL) and effect range medium or probable effects level (PEL).

The TEL value has been estimated as the concentration of contaminants with a relatively low effect on biological communities, and PEL is a concentration of contaminants with high toxic effects. Occasional toxic effects are expected to occur from contaminates Concentrations between TEL and PEL occasional toxic effect are expected (Hübner et al., 2009; Long, MacDonald, Smith, & Calder, 1995; Long & Morgan, 1990).

The overall toxicity of heavy metals and PAHs was estimated by PEL quotients (PELq's). The PELq factor is the average of the ratios between the heavy metal concentration in the sediment sample and the related PEL value (Alvarez-Guerra, Viguri, Casado-Martínez, & DelValls, 2007; Fdez-Ortiz de Vallejuelo, Arana, De Diego, & Madariaga, 2010; Khairy et al., 2009; Leorri, Cearreta, Irabien, & Yusta, 2008). This factor describes contamination effect on biological organisms in sediment which range as non-adverse effect ($PELq < 0.1$), slightly adverse effect ($0.1 < PELq < 0.5$), moderately effect ($0.5 < PELq < 1.5$) and heavily effect ($PELq > 1.5$) (Vallejuelo, Arana, Diege, & Madariaga, 2010).

3.5.1 Ecological risk assessment based on the Hakanson method

This method is based on the issue that a sediment-logical risk index for a toxic compound in estuary and coastal systems should account for the following requirements in several literature (El-Said & Youssef, 2012; Fu, Guo, Pan, Qi, & Zhou, 2009; Hakanson, 1979; Luo et al., 2010).

3.5.1.1 Contamination factor

To describe the contamination of toxic compound, a contamination factor (C_f^i) was defined accordingly:

$$C_d = \sum_{i=1}^n C_f^i = \sum_{i=1}^n \frac{C_{0-1}^i}{C_n^i} \quad (3.12)$$

Where,

C_d = the contamination degree

C_f^i = the contamination factor

C_{0-1}^i = the average content of the compound in question (i) from surface sediment (0 to 1 cm) at the accumulation area. The value should be estimated in $\mu\text{g g}^{-1}$ ds (ppm).

C_n^i = the background value of the compound

There are several discussions to estimate an accurate natural background level in all projects. This discussion can be treated by in two different ways. One is to use a general geological reference value such as an element's concentration in the earth crust, which was introduced by Turekian and Wedephol in 1961. The other way is to use per-industrial value or old previous studies (at least 10 years). In the first way, all local variations are ignored, and in the second way, all local differences are emphasized. In 1980, Hakanson proposed a method to estimate a natural background value based on the second approach.

$$C_n^i = x + S_x \quad (3.13)$$

Where, C_n^i is the natural background value, x is the mean of per-industrial data or old previous studies, and S_x is one (1) standard division. This contamination factor was ranged as low ($C_f^i < 1$), moderate ($1 \leq C_f^i < 3$), considerable ($3 \leq C_f^i < 6$), and very high ($C_f^i \geq 6$) (Hakanson, 1979).

The contamination degree (C_d) was estimated based on the sum of all contamination factors. The specific terminology is used to describe the contamination degree of sediment—low contamination degree ($C_d < 8$), moderate contamination degree ($8 \leq C_d < 16$), considerable contamination degree ($16 \leq C_d < 32$), and a very high contamination degree ($C_d \geq 32$) (Hakanson, 1979).

3.5.1.2 The toxic response factor and sensitivity requirement

The formula that expresses this model is given by,

$$RI = \sum_{i=1}^n Er^i = \sum_{i=1}^n Tr^i \cdot C_f^i \quad (3.14)$$

Where,

RI = Potential ecological risk index for the aquatic area ranges based on the following terminology: Low ecological risk ($RI < 150$), Moderate ecological risk ($150 \leq RI < 300$), high ecological risk ($300 \leq RI < 600$), and very high ecological risk ($RI > 600$) (Hakanson, 1979).

Er^i = the Potential ecological risk index for the given compound

Tr^i = the toxic-response factor for the given compound

To evaluate the toxic-response factor, the sediment-logical toxic factor (St^i -value) and bioproduction (BPI) should be estimated.

3.5.1.2.1 Sediment-logical toxic factor (St^i - value)

St^i - value provides information about the potential transport roads of the toxic compound to man and their complex threat toward the aquatic ecological system and man.

As a matter of fact, the “main road” in this method goes from contamination of water to sediment to biota to fish mail. Hakanson purposes a new concept about the toxic factor based on the “abundance principle.” He indicates that the potential toxicological effect of an element is proportional to the abundance of this element in nature. To measure the “abundance numbers,” this methodology should be used:

The abundance of various elements are provided at least in four different types of biological and geological media such as igneous rocks, soils, fresh or marine water, land animals, and land plants.

This information causes beneficial revision of the results given in this background media. The relative abundance of various elements is measured by following equations:

$$\text{relative abundance} = \frac{\text{element with high mean concentration}}{\text{mean concentration of other element}} \quad (3.15)$$

Once the abundance number has been obtained, the largest value of relative abundance should be omitted for every element in the different media, and the sum of these relative numbers should be estimated and divided into the lowest mean value of relative abundance. The abundance number is not equivalent to the St^i – value and sink-effect factor, and the problem of dimension should be measured.

The “sink-effect factor” means that the various elements make different “fingerprints” in sediment with different tendencies to be deposited in the sediment. This factor may depend on several reasons such as the chemical form of an element, the biogeochemical system of an aquatic area, and the presence of other elements.

The sink-effect factor has been obtained by comparing the “natural background values” for water with the natural background value for sediments.

The lowest “sink-factor” means that this element has “heaviest fingerprint” in the sediments and that its concentration is high in sediment when compared to the water.

Sedimentological toxic factors are obtained by multiplying the sink-factors with the abundance numbers. Hakanson indicated the following: “The problem of dimension which means that we must give the corrected abundance numbers an adequate dimension, order of magnitude, so that these numbers may be used subsequently as sedimentological toxic factors and be compared with the contamination factors. One possible to reduce dimension between St^i -value and the contamination factor is that, all corrected abundance should be divided to the lowest corrected abundance for making normation between elements.

Then to get reliable dimensions, the square-root should be taken from these figures and the values also rounded to emphasize the accuracy of the method. These values seem to be reliable sedimentological toxic factors for all elements.

3.5.1.2.2 Bio- production (BPI)

Several methods and equations have been proposed to measure the bioproduction value based on nutrients, bottom fauna, plankton, and morphometry (see Ahl and Wiederholm, 1977). Hakanson in 1975 and 1980 defined a specific method to measure the BPI value for aquatic systems.

He determined the BPI value by measuring the ignition loss (the IG value) and the nitrogen content (the N-value) of sediment. The BPI value was then described as “the N-content on the regression line for IG=10%.”

The N-content should be given in mg/g (ds) and the IG content should be given in $\%ds$ (dry substance). Most of the research showed a high correlation between the N and IG and the relationship between total P and BPI , which was applied to measure trophic levels (see Wetzel, 1975).

The sensitivity of organisms to toxic material is extremely controlled by bioproduction value. All heavy metals except arsenic showed a specific relation with the degree of bio-production in the aquatic area. The negative effect and toxicity degree of metals tend to increase with reducing bio-production. Also, there is negative effect of PCB, and PAH are increased with increasing the degree of bio-production. Thus, Hakanson defined a factor named the toxic response factor (Tr -value) according to the sedimentological toxic factors and the sensitivity requirement (given by the BPI value). Tr^i -value is determined by multiplying the St -value with the BPI value (**Table 3.8**). The Tr^i -value is analogous to the contamination factor. Most of the research showed the high correlation between the N and IG and the relationship between total-P and BPI , which is applied to measure trophic level (see Wetzel, 1975). The sensitivity of organisms to toxic material is extremely controlled by bioproduction value. All heavy metals, except arsenic showed specific relation with bioproduction degree in aquatic area. The negative effect and toxicity degree of metals tend to increase with reducing bio-production. Also there is negative effect of PCB and PAH are increased with increasing bio-production degree. Thus Hakanson defined a factor named the toxic response factor (Tr -value) according to the sedimentological toxic factors and the sensitivity requirement (given by the BPI -value) Tr^i -value is determined by multiplying the St -value with BPI -value (**Table 3.10**). Tr^i -value is analogous to the contamination factor.

Table 3.8. The toxic-response factor (Tr^i) have been established for the nine substances based on the Hakanson 1980

Substance	$St^i - value$	$Tr^i - value$
Hg	40	$40 \times 5/BPI$
Cd	30	$30 \times \sqrt{5}/\sqrt{BPI}$
As	10	$10 \times \sqrt{5}/\sqrt{BPI}$
Pb	5	$5 \times \sqrt{5}/\sqrt{BPI}$
Cu	5	$5 \times \sqrt{5}/\sqrt{BPI}$
Cr	2	$2 \times \sqrt{5}/\sqrt{BPI}$
Zn	1	$1 \times \sqrt{5}/\sqrt{BPI}$
PBC	40	$40 \times BP1/5$
PAH	40	$40 \times BP1/5$

3.6 Statistical Methods

Statistical analyses were performed using Microsoft Excel and SPSS 17 software (SPSS, Chicago, IL) to estimate statistical tests on monitoring and bioassays data.

For the data assessment, significant difference from control was evaluated with via Kruskal-Wallis one-way nonparametric ANOVA (level of significant is 0.05). The methods were selected based on the results of the Shapiro-Wilk Normality Test, the test for homogeneity of variances, and Bartlett's test of equal variances. Normally distributed data were evaluated via one-way ANOVA, with an alpha level of 0.05.

Data that did not pass tests of normality and homogeneity evaluated with the Kruskal-Wallis one-way nonparametric ANOVA. Differences were determined to be significant where $p < 0.05$. Nonparametric correlation method (Kendall's tau-b) was used to obtain the correlation coefficient and the significance of the correlation among physicochemical parameters in water and sediment.

Variation of spatial and temporal data were analyzed by multivariate techniques such as cluster analysis (CA) and principal components analysis (PCA).

These methods are practical to estimate structure and relationships in multivariate data (Bierman, Lewis, Ostendorf, & Tanner, 2011). PCA is known as dimensional reduction because this method is able to decrease the dimensionality of the primary set of data and compress data into a lower dimensional matrix (Kitsiou & Karydis, 2011). PCA is frequently used to assess water quality of rivers and estuaries and to quantify anthropogenic stresses. Primpas recently published the new application of PCA to evaluate eutrophication in the marine and coastal areas (Primpas & Karydis, 2010). CA analysis was used to classify a set of data into different groups based on similarity.

This method has been widely applied to environmental assessment to classify the data into temporal and spatial scales (Kitsiou & Karydis, 2011). Geo-statistical analysis was performed using Surfer 8 software (GPS value of stations) based on the geospatial methods to better understand contaminant pathways and to provide a comprehensive contour map of the spatial distribution of contaminants over a large area (Cressie, 1990; Sparks, 2000).

CHAPTER IV: RESULTS AND INTERPRETATIONS

4.1 Sediment quality assessment

4.1.1 Analysis of surface sediment components

Some characteristics of the surface sediment of the Klang Strait are shown in **Table 4.1**. Analysis of the sediment grain size demonstrated that fine-grained sediment predominated at almost all stations (41.1%- 95.39%). The highest proportions of fine fractions were estimated for the stations close to the mangrove edge and the mouth of the Klang River, whereas stations 8 and 11 exhibited the highest proportions of the sand fraction. The TOC of the sediment samples was estimated at 22 stations, and these results are summarized in **Table 4.1**.

The TOC varied between 5.35%- 24.88% and was synchronous with fine-grained sediment in most parts of the study areas, with the highest value in the South Port around the mouth of the Klang River and lower concentrations at stations 8 and 11.

Table 4.1, Characterization of surface sediment in Klang Strait

Site	Station	Silt and clay (<64µm)%	Sand %	TOC %	Depth meter
North Port	1. NL100	58.20	41.79	12.49	14.30
	2. NL700	49.63	50.36	10.13	20.5
	3. NL1500	73.77	26.22	17.04	10.3
	4. NC100	59.78	40.21	11.41	13.5
	5. NC700	50.89	49.10	10.08	21.6
	6. NC1500	65.19	34.80	14.71	11.2
West Port	7. WC100	53.57	46.42	10.24	12.5
	8. WC500	45.96	54.03	7.74	19.5
	9. WC1000	63.42	36.57	11.98	7.8
	10. WL100	56.33	43.66	9.14	13.3
	11. WL500	41.10	58.89	7.55	20.3
	12. WL1000	70.81	29.18	12.76	8.8
	13. WT100	52.31	47.68	10.63	15.5
	14. WT500	50.69	49.30	10.15	21.11
South Port	15. WT1000	70.36	29.63	15.49	6.8
	16. SK100	95.39	4.60	22.65	7.5
	17. SK1000	93.16	6.83	21.55	10.5
	18. SK2000	64.69	35.30	15.59	12.4
	19. SM100	69.50	30.49	13.79	10.3
	20. SM1000	69.72	30.27	14.91	11.3
Control Point	21. SM2000	57.73	42.26	11.89	10.4
	22. CP	51.60	48.39	10.46	17.5

According to the Kruskal-Wallis test, there were significant differences ($p < 0.05$, $df=21$, $sig=0.00$) in TOC among different stations, whereas the concentration of fine-grained sediment shows significant differences both among stations ($p < 0.05$, $df= 21$, $sig=0.00$) and among seasons ($p < 0.05$, $df= 3$, $f=3.62$, $sig= 0.00$).

Figure 4.1 illustrates a cluster analysis that clearly classified the stations into three clusters based on TOC concentration. The first plot cluster (C) includes 14 stations with low percentages of TOC (7.55% -12.76%). The second plot cluster (B) includes 6 stations with intermediate percentages between 13.79 to 17.04 %, and the third cluster includes the stations with the highest percentages of TOC, which includes stations 16 and 17.

The dendrogram in **Figure 4.2** classified the stations into three clusters based on the percentage of fine-grained sediment. The first cluster (A) represents the low range of fine-grained sediment (41.10-53.57%) and includes 12 stations.

The second cluster (B) includes 8 stations that range between 63.42% and 73.77%, and the third cluster (C) includes two stations with high values of percentage of fine-grained sediment (93.16 and 95.39).

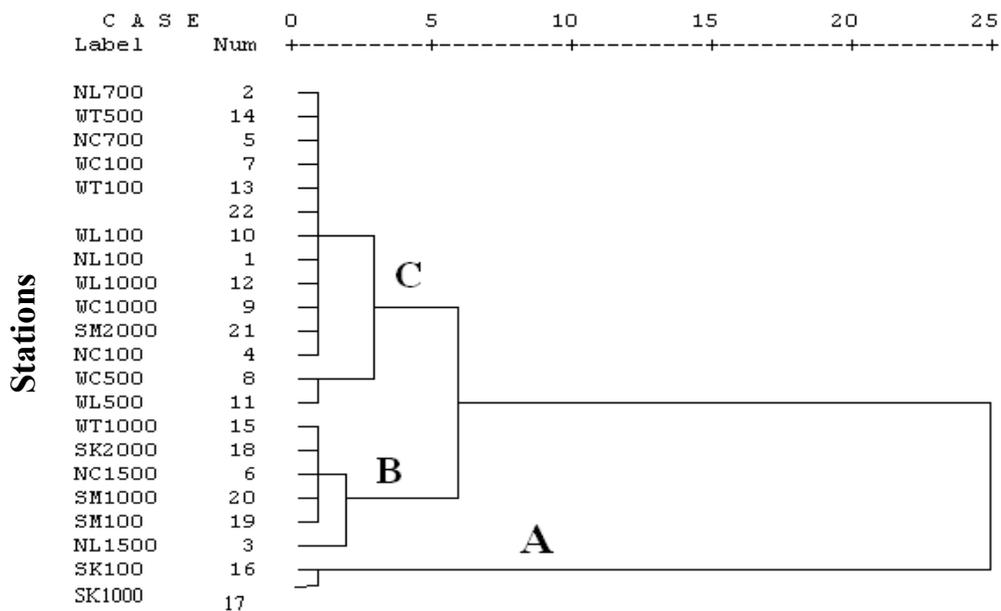


Figure 4.1, Cluster analysis to classify the different stations based on the total organic carbon percentage

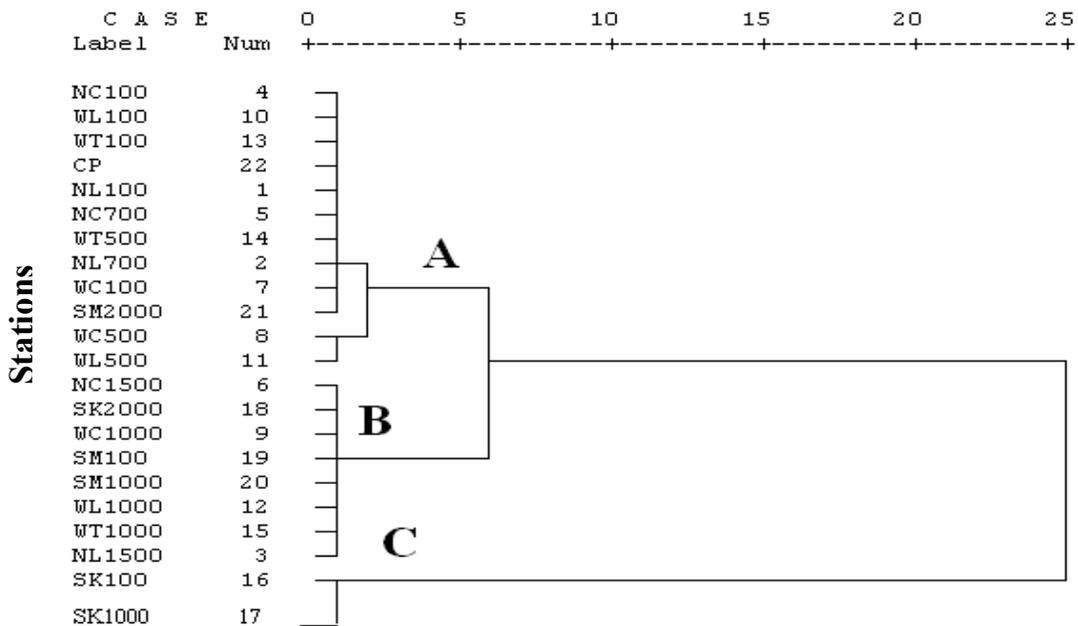


Figure 4.2, Cluster analyses to classify the different stations based on percentage of the fine grained sediment

In the present study, some metals and TOC exhibited a significant positive correlation ($0.4 < r$, $P < 0.01$), with the following percentage of fine particles: Al ($r=0.541$), Cd (0.406), Cu (0.447), Fe (0.418), Ni (0.432), V (0.411), Zn (0.493) and TOC(0.716) (Table 3). Moreover, TOC showed significant positive correlations with heavy metals such as Al ($r= 0.582$), Cd (0.504), Cu (0.557), Fe (0.438), Ni (0.404), V (0.462) and Zn (0.406) (Table 4.1).

Table 4.1, Correlation coefficient between heavy metals, TOC and fine particular size fraction

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	V	Zn	Fine fraction	TOC	PAHs
Al	1.00														
As	0.26	1.00													
Cd	0.38	0.32	1.00												
Cr	0.37	0.27	0.26	1.00											
Cu	0.33	0.15	0.29	0.32	1.00										
Fe	0.63	0.35	0.39	0.52	0.29	1.00									
Hg	0.20	0.37	0.21	0.29	0.21	0.29	1.00								
Mn	0.13	0.23	0.19	0.11	0.03	0.10	0.10	1.00							
Ni	0.29	0.32	0.30	0.29	0.34	0.34	0.52	0.18	1.00						
Pb	0.31	0.58	0.36	0.22	0.21	0.39	0.37	0.16	0.27	1.00					
V	0.30	0.29	0.51	0.36	0.22	0.34	0.18	0.31	0.24	0.28	1.00				
Zn	0.68	0.26	0.55	0.32	0.38	0.58	0.28	0.08	0.38	0.27	0.27	1.00			
Fine fraction	0.54	0.37	0.40	0.28	0.44	0.41	0.25	0.10	0.43	0.20	0.41	0.49	1.00		
TOC	0.58	0.36	0.50	0.25	0.55	0.43	0.23	0.11	0.40	0.23	0.46	0.40	0.71	1.00	
PAHs	0.16	0.06	0.13	0.18	0.06	0.22	0.30	0.09	0.29	0.28	0.06	0.09	0.15	0.11	1.00

4.1.2 Heavy metals analysis

In this study, the data quality for heavy metals was controlled with the certified concentration of SRMs 2702 and matrix spike recoveries. The percentage recovery was between 91.54 and 104.66 (Table 4.2). The standard methods suggest warning limits for matrix spike recoveries from 87 to 113%; therefore, the range of recovery in this study was reasonable (IDEM, 2002; Willie and May, 2002).

Table 4.2, Average concentration (mg/kg dry weight, except AL and Fe as %wt) Standard deviation and percent recovery (%REC) of certified references

Metals	Certified	Measured± S.D	% Recovery
Cu	117.7	118.34 ± 2.56	100.54
Cd	0.817	0.810 ± 0.09	99.14
zn	485.3	492.39 ± 35.56	101.46
Pb	132.8	128.98 ± 6.56	97.12
Mn	1757.0	1838.93 ± 102.34	104.66
Ni	75.4	74.56 ± 2.34	98.88
Co	27.76	25.21 ± 1.3	90.81
Cr	352.0	388.84 ± 48.21	110.46
V	357.6	371.13 ± 31.23	103.76
Hg	0.438	0.424 ± 0.26	96.8
As	453.0	475.26 ± 47.32	104.91
Al	8.4%	7.69 ± 0.39	91.54
Fe	7.91%	8.14 ± 0.22	102.90

4.1.2.1 Spatial variation of heavy metals

The mean concentration and range of heavy metals measured at different stations are provided in **Table 4.4**. These results showed that the concentrations of all metals (except for Cu, Ni, Hg and Fe) vary widely among stations, and the ranges are as follows: Al, 6148.98-42586.5 µg/g; Fe, 2380.00-17569 µg/g; Mn, 66.15-468 µg/g; As, 17.34 -142.3 µg/g; Cu, 5.60–57.01 µg/g; Cr, 15.29-83.20 µg/g; Cd, 0.00 -2.1 µg/g; Pb, 20.76-104.87 µg/g; Ni, 3.93-23.5 µg/g; Hg, 0.10-0.45 µg/g; V, 15.23-130 µg/g and Zn, 17-192.9 µg/g.

In this research, the Klang Strait was divided into three specific geochemical partition sites (the North, West and South Ports) to describe the distribution of metals.

In the North Port, the mean values of the metal concentrations (Al, Fe, Mn, As, Cu, Cr, Cd, Pb, Ni, Hg, V, and Zn) were 13357.75, 5417.1, 241.57, 55.49, 1643, 39.01, 0.82, 54.03, 9.87, 0.19, 46.45 and 47.13 µg/g, respectively.

In the West Port, these values were 12381.18, 5985.98, 254.21, 61.4, 14.59, 47.14, 0.72, 58.43, 12.14, 0.25, 53.29 and 39.03, respectively. In the South Port, these values were 20906.66, 8988.88, 186.23, 69.91, 24.28, 54.54, 1.03, 68.57, 12.61, 0.24, 60.52 and 76.68, respectively.

The Kruskal-Wallis test revealed significant differences in the concentrations of heavy metals among stations. According to **Figure 4.3** the highest concentrations of all metals except for Mn were recorded in the South Port (at stations 16 and 17), and the lowest concentrations of all metals were recorded at the control point (Station 22). The spatial distribution maps confirm these results; these maps are attached in appendix two.

Table 4.3, Average, minimum and maximums of the metal concentrations ($\mu\text{g/g}$ dry weight) in surface sediment at different stations

Stations		Al	Fe	Mn	As	Cu	Cr	Cd	Pb	Ni	Hg	V	Zn
1	Mean	12021.77	5215.73	224.41	75.64	17.43	44.41	.79	58.59	11.14	.24	48.63	52.34
	Minimum	8546.83	4183.00	195.80	43.30	12.40	39.50	.42	41.20	4.50	.11	30.23	29.00
	Maximum	18983.40	6480.00	286.00	109.23	23.80	53.87	1.10	92.67	17.60	.37	70.30	77.00
2	Mean	8765.43	3711.07	171.90	60.35	13.60	37.22	.67	47.58	7.14	.17	31.56	35.27
	Minimum	6740.43	2380.00	137.00	36.40	10.34	27.00	.22	31.30	4.16	.11	22.34	26.60
	Maximum	12983.43	4700.00	210.00	91.00	16.93	50.98	1.00	73.40	9.60	.23	47.00	47.00
3	Mean	17217.90	6787.07	276.20	76.22	20.97	44.55	.89	68.52	10.51	.20	54.56	56.57
	Minimum	12597.98	4672.00	245.00	42.00	14.20	37.90	.50	47.60	6.23	.10	40.40	30.50
	Maximum	24804.56	8278.00	289.10	121.20	30.40	49.11	1.30	98.90	13.89	.29	71.25	83.00
4	Mean	14120.80	6213.00	244.34	38.05	16.57	39.97	.93	53.24	12.42	.19	46.59	46.18
	Minimum	11303.59	4000.00	230.00	22.30	12.80	28.90	.51	42.57	8.45	.10	30.09	23.45
	Maximum	16784.50	9247.00	289.00	46.00	20.80	52.67	1.32	62.60	17.90	.29	67.50	72.00
5	Mean	13604.83	4806.49	201.66	34.17	12.41	30.27	.80	47.37	6.24	.17	38.13	42.28
	Minimum	10024.45	2760.00	177.14	21.00	10.34	20.34	.35	31.85	4.43	.10	27.12	26.00
	Maximum	20875.30	6890.00	216.60	41.00	14.70	46.70	1.40	60.25	10.00	.24	62.50	62.90
6	Mean	14415.78	5769.29	330.91	48.55	17.62	37.69	.89	48.90	11.81	.19	59.29	50.17
	Minimum	10768.54	4095.59	299.00	25.52	12.34	31.45	.58	32.70	9.34	.11	42.67	28.45
	Maximum	23923.30	8081.00	352.09	76.70	24.89	45.87	1.32	68.93	14.90	.27	73.90	73.80
7	Mean	9520.56	4368.03	207.99	35.82	16.11	58.64	.68	54.97	11.64	.25	43.46	49.51
	Minimum	7845.87	2855.98	162.87	27.20	11.50	50.35	.32	45.67	6.20	.13	29.45	30.40
	Maximum	12584.45	6298.00	289.70	47.60	24.26	66.98	1.20	64.90	14.30	.36	69.34	70.50
8	Mean	9337.92	7464.68	175.35	51.62	11.35	47.06	.81	52.55	8.83	.20	65.18	36.47
	Minimum	7401.68	5135.00	96.80	24.50	8.60	31.60	.40	35.70	6.45	.14	49.10	20.40
	Maximum	10123.45	10560.00	234.00	95.60	13.93	66.90	1.18	75.30	10.93	.34	77.90	60.90
9	Mean	11132.26	4529.76	310.41	68.13	14.72	48.91	.89	51.31	10.49	.20	53.66	37.19
	Minimum	9684.34	3400.00	244.78	40.27	10.21	33.46	.42	43.03	7.20	.14	33.40	22.34
	Maximum	13608.34	6298.00	390.56	124.71	17.54	58.50	1.30	58.90	14.50	.29	73.34	57.70
10	Mean	10617.89	4647.12	250.15	67.49	13.96	37.20	.28	57.71	13.03	.25	38.54	37.32
	Minimum	8783.50	3000.00	179.19	43.90	12.34	28.50	.20	44.95	7.89	.12	21.30	20.70
	Maximum	12808.42	6382.12	325.67	125.00	16.78	48.90	.40	67.20	17.80	.37	62.00	51.40
11	Mean	8702.30	4487.59	185.06	47.64	13.00	36.08	.28	54.07	12.44	.30	29.81	32.82
	Minimum	7103.68	3150.00	128.62	29.30	10.20	22.00	.16	41.56	8.70	.21	16.30	18.90
	Maximum	10474.97	6652.00	220.71	63.90	16.98	51.90	.52	64.30	18.20	.45	50.30	49.00
12	Mean	12983.55	5491.64	263.68	50.31	15.69	47.05	.62	58.23	16.02	.31	53.31	35.11
	Minimum	10804.67	4016.00	142.00	38.63	11.40	38.80	.14	46.80	10.30	.21	30.67	21.98
	Maximum	16032.82	6730.80	365.50	57.45	20.99	61.50	1.10	66.10	20.80	.42	72.70	52.87

Table 4.4 (continued)

Other stations		Al	Fe	Mn	As	Cu	Cr	Cd	Pb	Ni	Hg	V	Zn
13	Mean	18685	8529.6	280.38	94.24	16.81	60.56	0.95	72.11	13.84	0.30	82.4	49.8
	Minimum	15318.6	6626.5	201.60	43.40	14.03	54.80	0.40	50.90	10.34	0.19	64.3	28.7
	Maximum	23830.4	10660	342.76	134.20	21.80	66.17	1.60	104.87	19.40	0.44	130	73.6
14	Mean	12805.4	6820	260.10	59.07	12.13	42.79	0.73	53.46	9.64	0.21	45.4	33
	Minimum	8087.3	4001	174.00	43.78	10.34	33.56	0.21	36.60	6.12	0.20	26.5	17
	Maximum	20999.4	10156	321.00	87.20	14.90	50.30	1.80	62.13	12.70	0.25	73.2	46.8
15	Mean	17645	7535.3	354.77	78.31	17.60	45.98	1.26	71.55	13.38	0.28	67.8	40
	Minimum	12102.6	4000	280.20	54.23	11.50	40.90	0.50	62.23	10.34	0.20	31.3	21.4
	Maximum	24930.4	10370	468.00	137.53	28.90	52.90	1.90	89.98	14.87	0.34	127	70.6
16	Mean	31182	13206	217.88	112.81	40.67	74.87	1.55	85.92	17.83	0.35	96.9	126.7
	Minimum	20578.2	10020	193.34	84.34	29.20	63.00	1.14	78.23	8.67	0.26	65.4	76.4
	Maximum	42586.5	17569	282.00	142.38	57.01	83.20	1.94	97.80	23.50	0.42	127	192.9
17	Mean	30588.5	13035	201.10	106.01	38.54	68.29	1.45	79.39	16.08	0.32	95.2	126.9
	Minimum	20478.4	10002	181.00	78.45	25.03	57.34	0.96	60.34	8.74	0.25	63.2	74.3
	Maximum	40849.4	15908	248.50	138.00	51.92	73.10	2.10	98.56	21.40	0.40	121	189.4
18	Mean	18122.9	8626.2	196.17	42.38	16.30	45.07	0.91	74.72	9.80	0.22	41.9	52.7
	Minimum	15287	6023	167.00	30.30	14.40	40.50	0.83	60.20	6.56	0.21	28.4	38.6
	Maximum	22287.3	11023	238.00	54.60	19.45	53.70	1.10	91.30	12.40	0.23	52.4	69.6
19	Mean	15571.2	6870	177.98	67.81	14.92	50.00	0.84	50.81	12.23	0.20	46.1	52.1
	Minimum	10484.5	3567.3	118.31	37.98	12.20	39.50	0.40	36.23	6.50	0.13	35.4	22.6
	Maximum	20776.4	9292	208.02	112.26	18.45	78.81	1.45	66.09	17.50	0.27	72.1	70.8
20	Mean	15095.4	7194.2	159.36	50.27	19.03	47.68	0.89	68.21	12.18	0.21	47.3	53.9
	Minimum	11103.4	4604.3	128.40	40.31	14.50	41.59	0.54	54.56	8.50	0.13	35.7	28.8
	Maximum	19439.3	8802	219.10	63.20	24.89	60.19	1.46	96.02	15.09	0.30	74.1	72.2
21	Mean	14879.8	5000.4	164.93	40.20	16.27	41.34	0.57	52.40	7.58	0.19	35.6	47.5
	Minimum	10104.8	3103.7	118.00	30.00	11.23	34.00	0.52	37.89	3.96	0.19	24.5	31.7
	Maximum	21056.4	6241	209.00	57.60	19.30	48.00	0.73	68.30	10.30	0.19	46.3	61.8
22	Mean	9745.8	4009.4	84.39	27.57	8.87	18.70	0.05	31.18	5.77	0.15	21.1	29.5
	Minimum	6148.9	2870	66.15	17.34	5.60	15.29	<ND	20.76	3.93	0.14	15.2	21.4
	Maximum	15873.6	4982	98.34	38.40	14.23	26.67	0.13	39.45	8.89	0.16	30.1	39.5

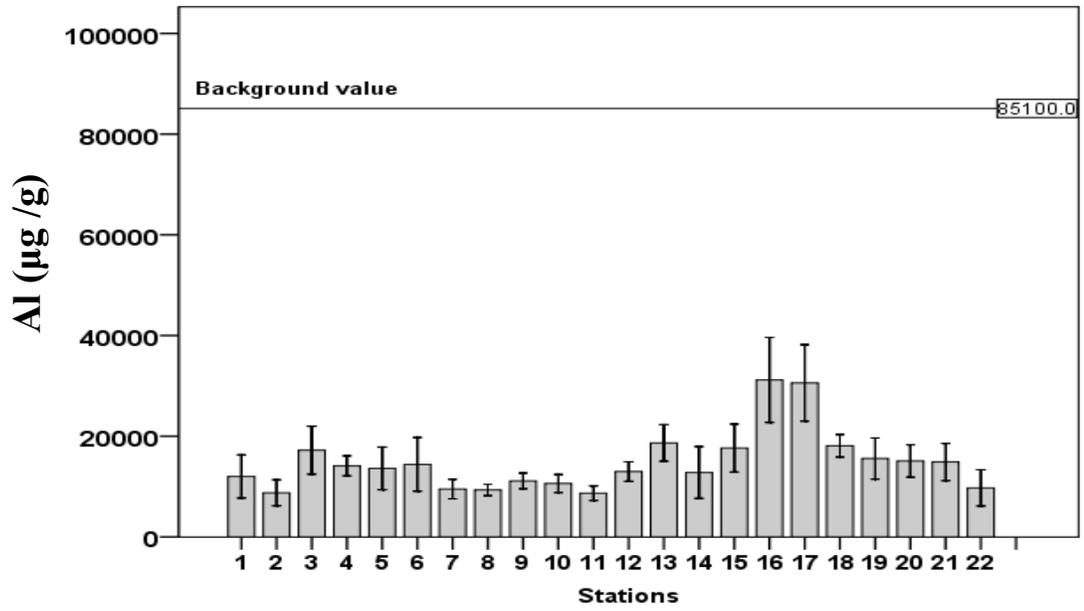


Figure 4.3(A), Spatial variation of mean concentration of aluminum in surface sediment ($\mu\text{g/g}$ dry weight)

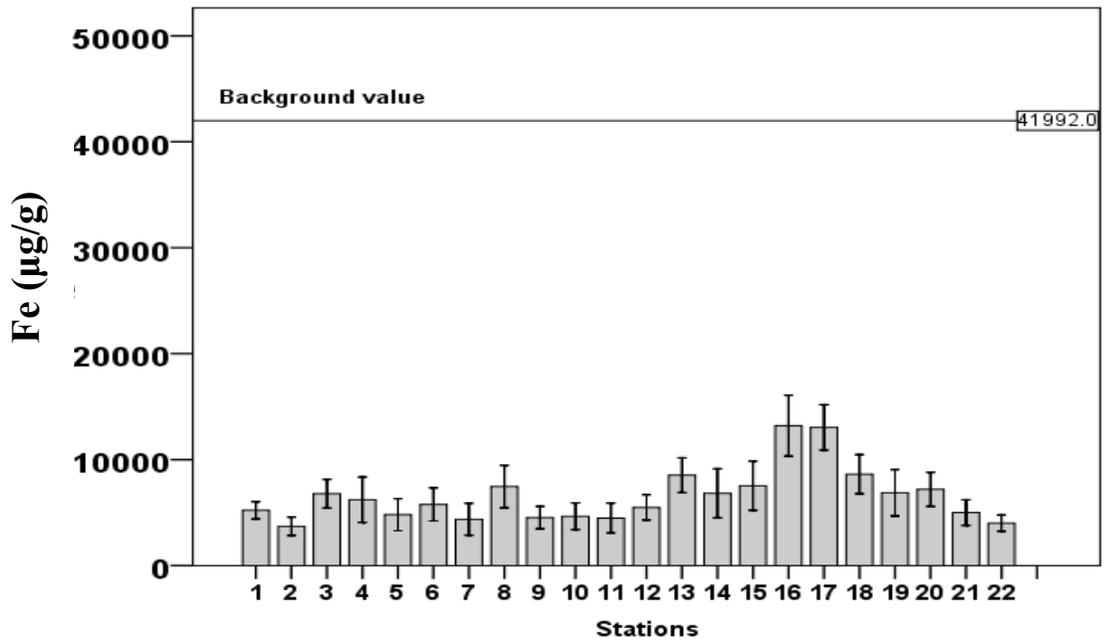


Figure 4.3(B), Spatial variation of mean concentration of iron in surface sediment of ($\mu\text{g/g}$ dry weight)

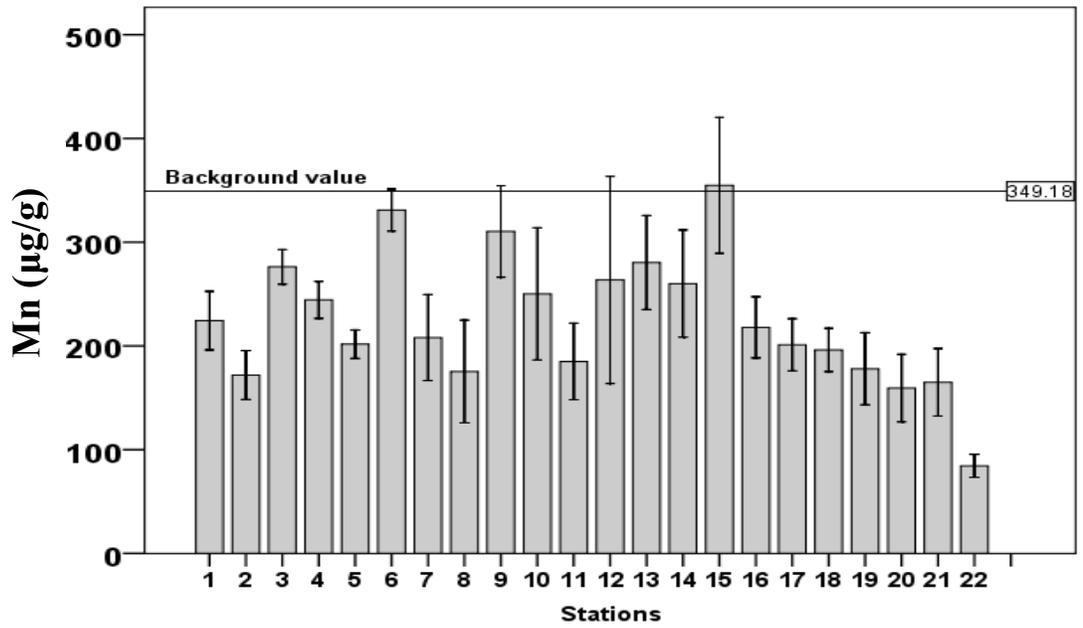


Figure 4.3 (C), Spatial variation of mean concentration of manganese in surface sediment (µg/g dry weight)

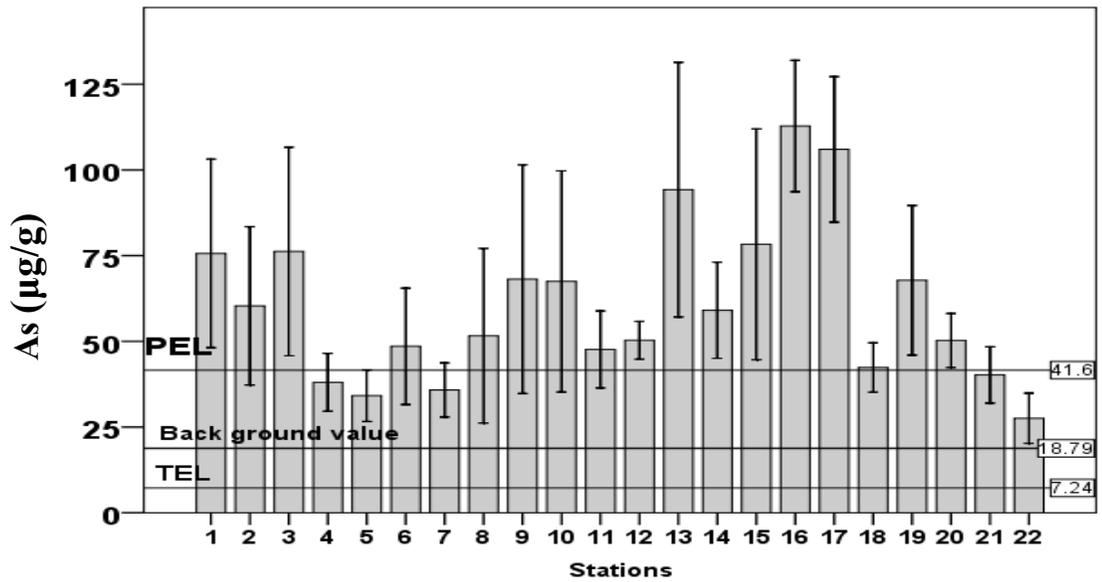


Figure 4.3(D), Spatial variation of mean concentration of arsenic in surface sediment (µg/g dry weight)

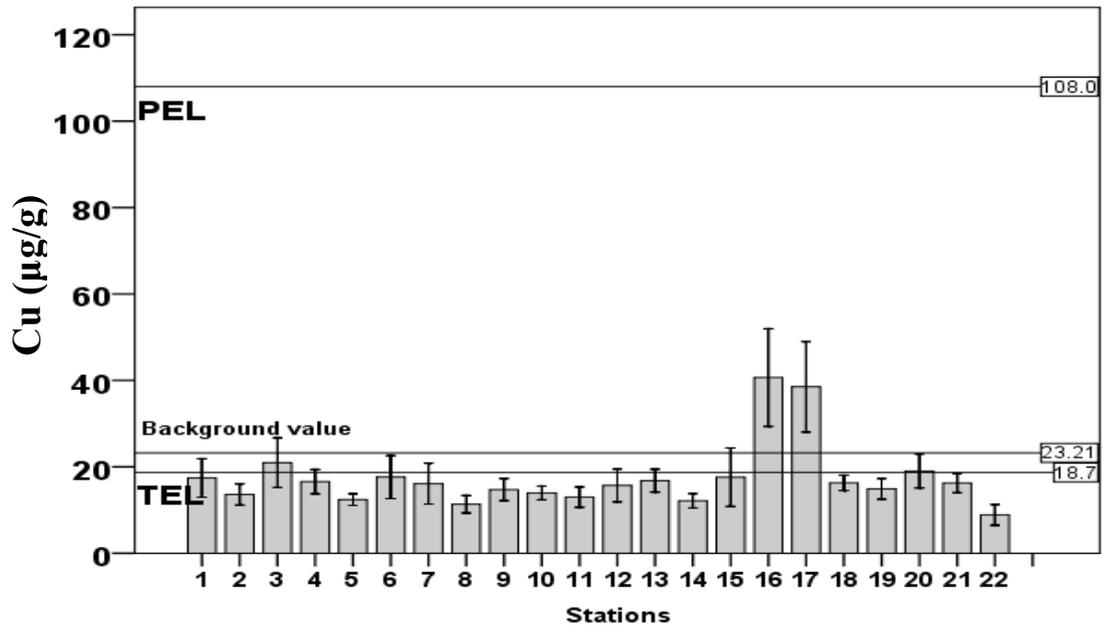


Figure 4.3(E), Spatial variation of mean concentration of copper in surface sediment ($\mu\text{g/g}$ dry weight)

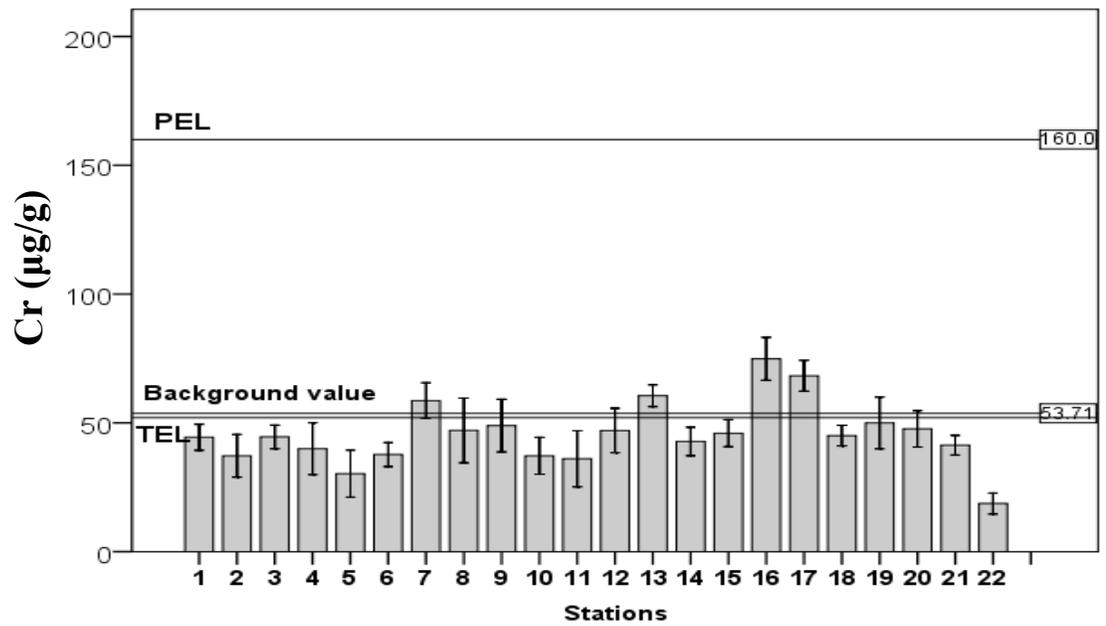


Figure 4.3(F), Spatial variation of mean concentration of chrome in surface sediment ($\mu\text{g/g}$ dry weight)

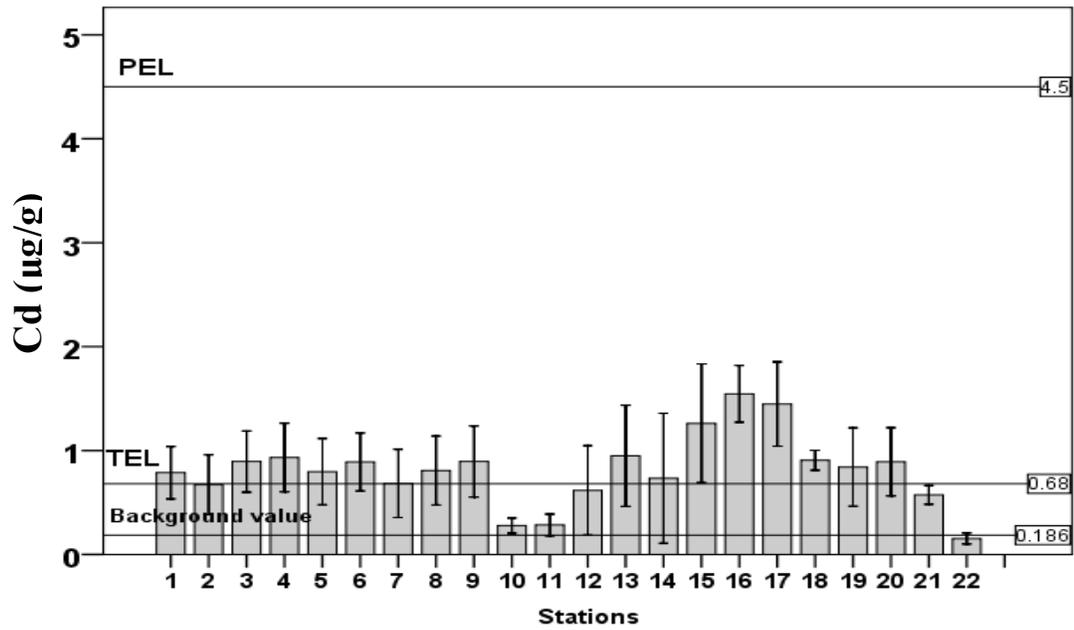


Figure 4.3(G), Spatial variation of mean concentration of cadmium in surface sediment ($\mu\text{g/g}$ dry weight)

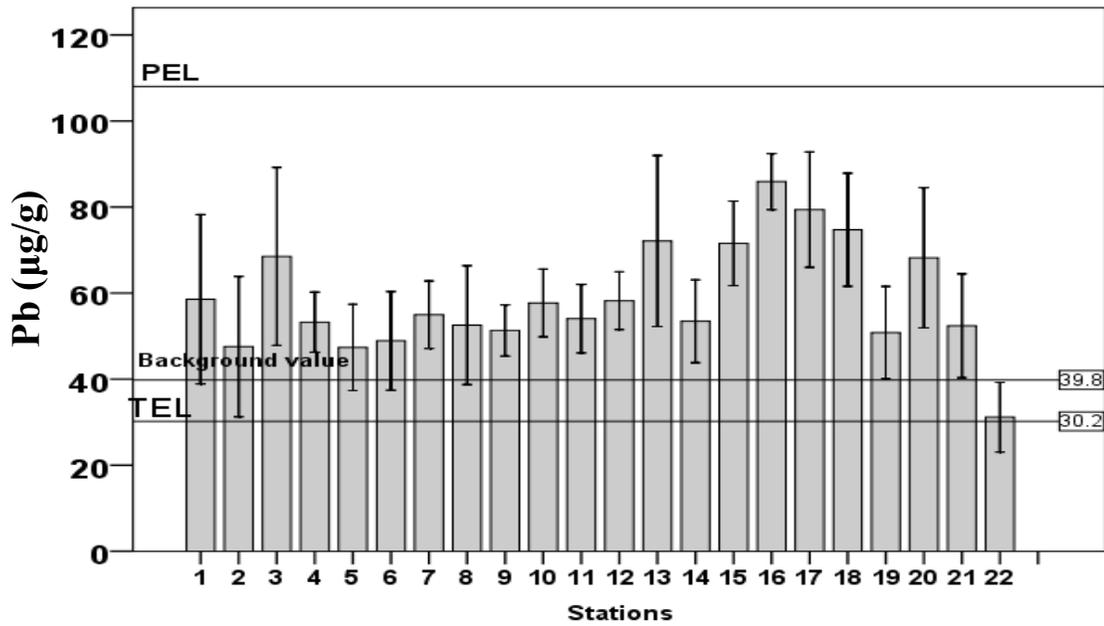


Figure 4.3(H), Spatial variation of mean concentration of lead in surface sediment ($\mu\text{g/g}$ dry weight)

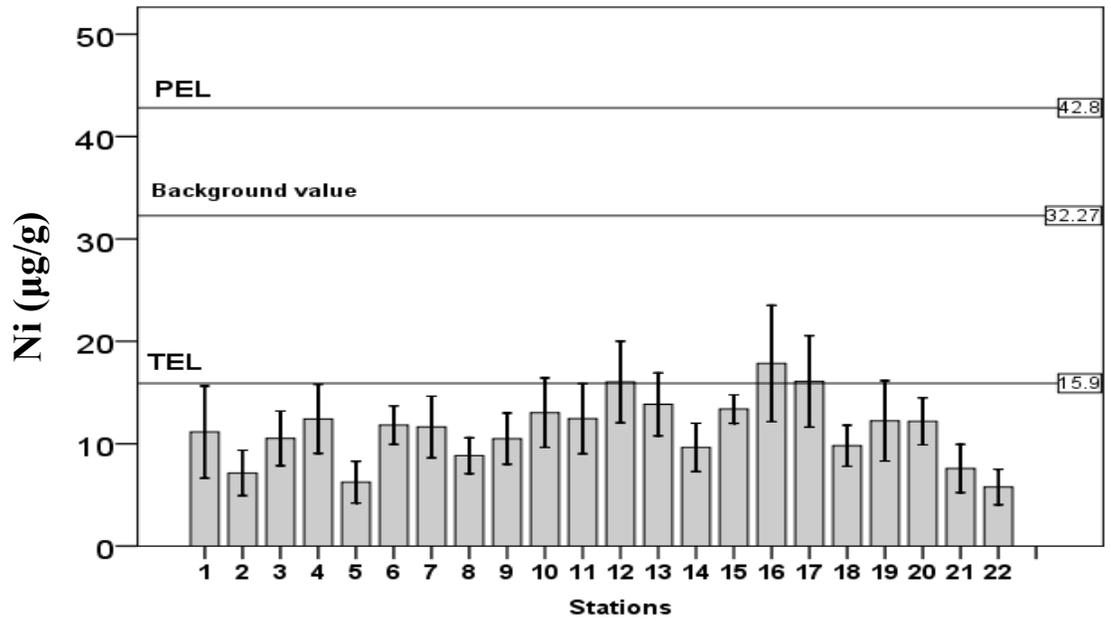


Figure 4.3(I), Spatial variation of mean concentration of nickel in surface sediment (µg/g dry weight)

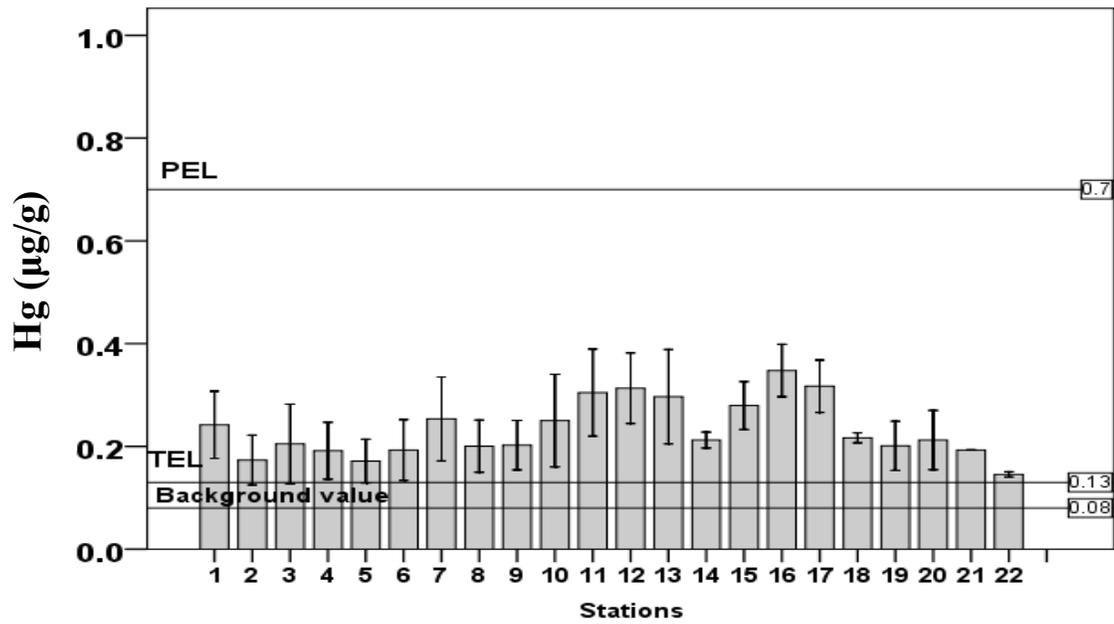


Figure 4.3(J), Spatial variation of mean concentration of mercury in surface sediment (µg/g dry weight)

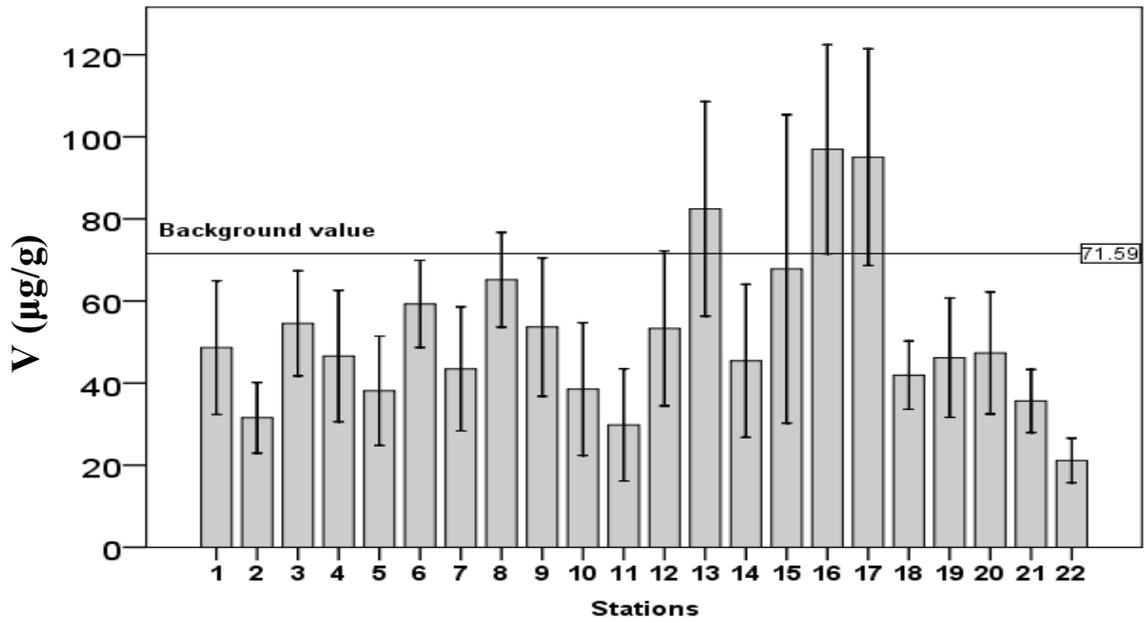


Figure 4.3(K), Spatial variation of mean concentration of vanadium in surface sediment ($\mu\text{g/g}$ dry weight)

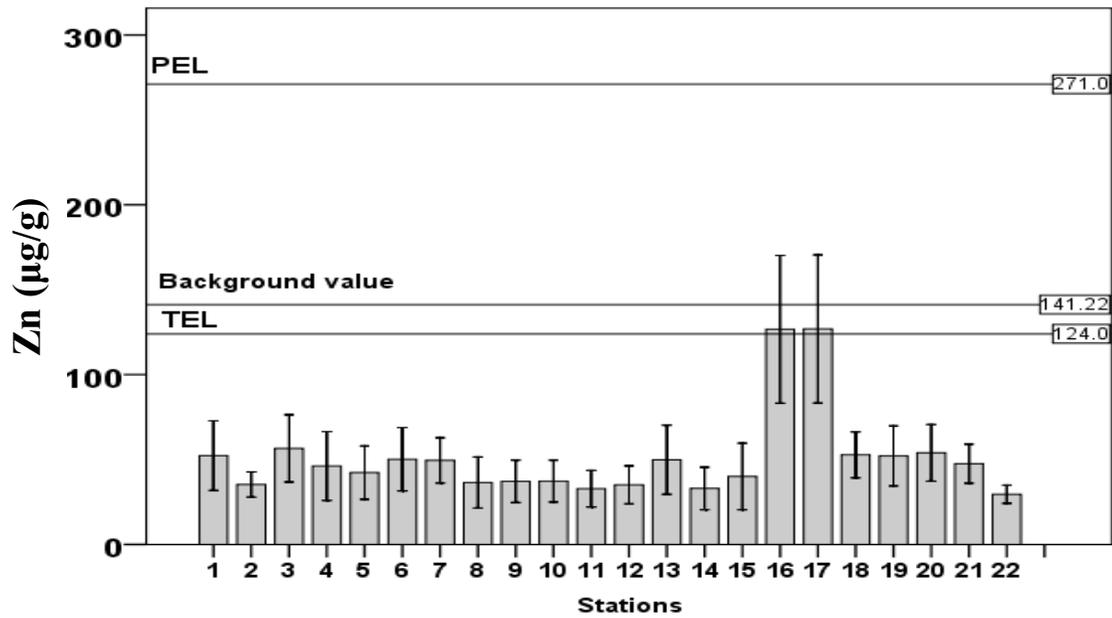


Figure 4.3(L), Spatial variation of mean concentration of zinc in surface sediment ($\mu\text{g/g}$ dry weight)

4.1.2.2 Temporal variation of heavy metals

Figure 4.4 illustrate the temporal variation in the concentrations of heavy metals over one year. According to the Kruskal-Wallis test, the concentrations of all of the heavy metals (except Cr and Mn) changed significantly over the year. Most of metals such as Al, Fe, Mn, Cd, Ni, Cr and Hg had same temporal pattern in surface sediment with significant reductions in their concentrations in November 2009 and May 2010 and high concentration in February 2010 and August 2010. Some metals include Pb, V and As had an increased trend toward high concentration from November 2009 to August 2010 and others metals (Cu and Zn) showed a different pattern in temporal scale.

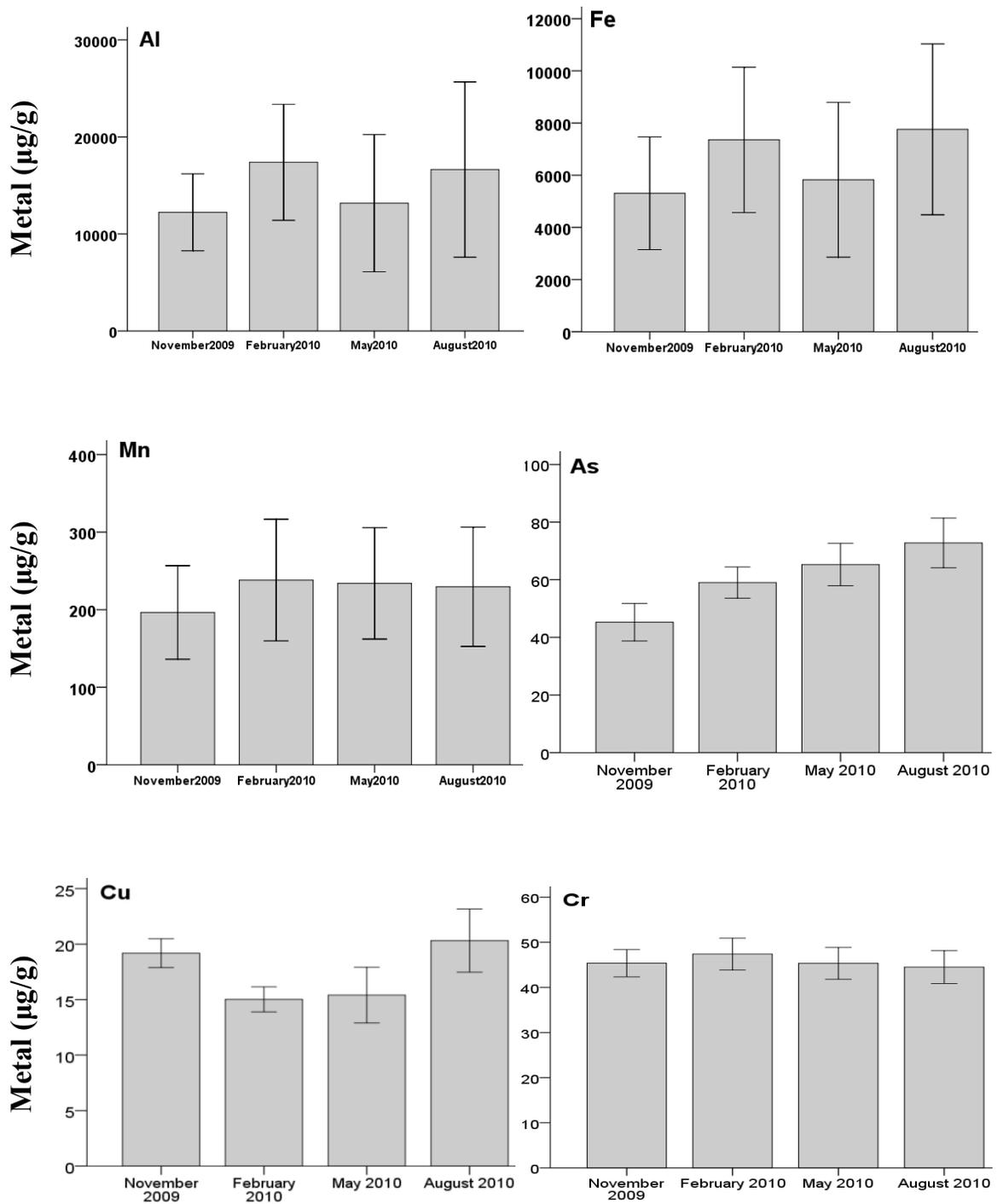


Figure 4.4(A), Temporal variation of heavy metals in surface sediment ($\mu\text{g/g}$ dry weight)

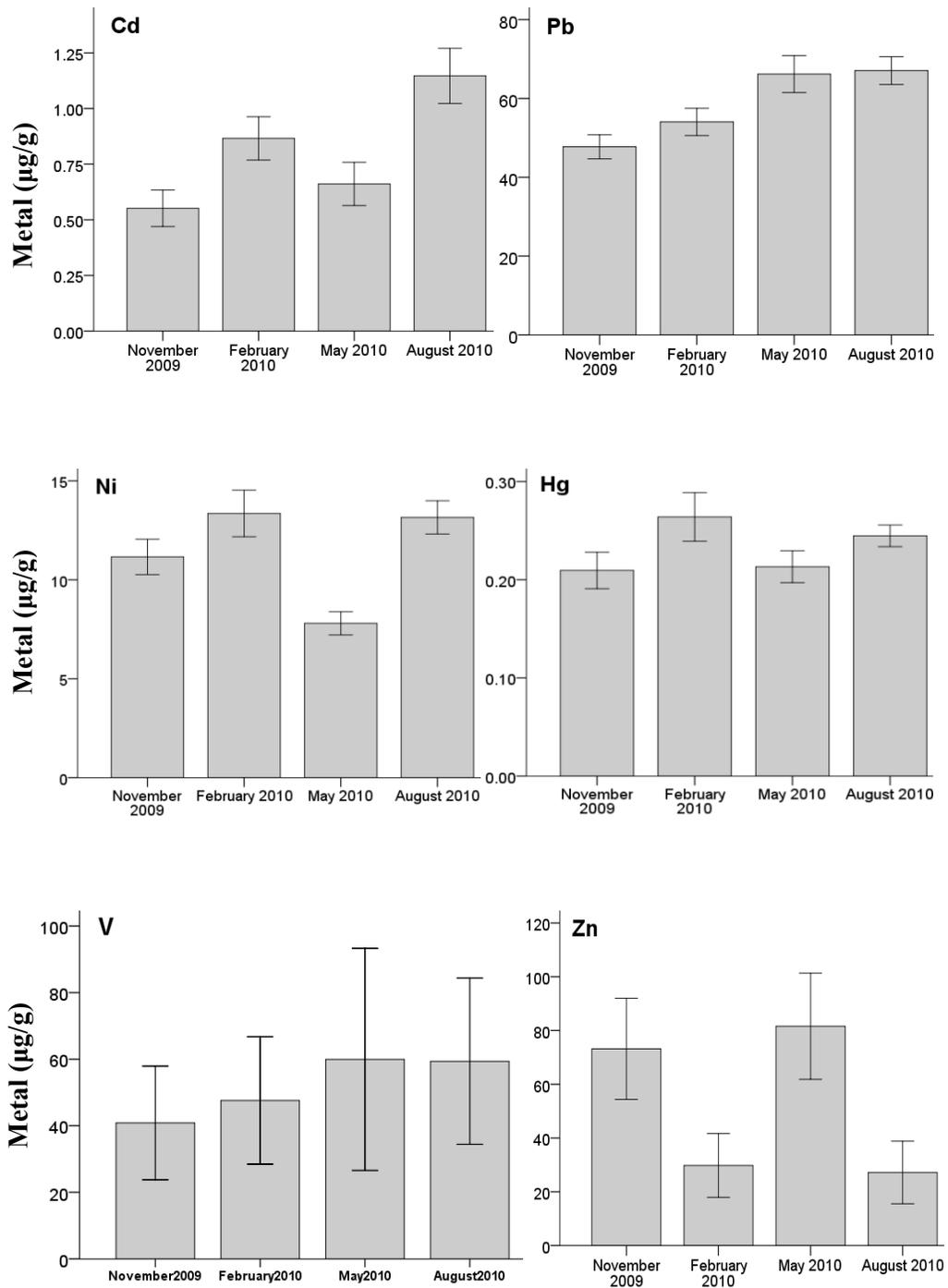


Figure 4.4(A), Temporal variation of heavy metals in surface sediment (µg/g dry weight)

4.1.2.3 Heavy metal contamination factor (CF) and contamination degree (Cd)

Figure 4.5 shows the variation in the contamination factor for each metal; the C_f -values for all metals based on the following sequence:

$$Cu < Fe < Al < Ni < Zn < Mn < V < Cr < Pb < Hg < As < Cd$$

The highest values of contamination degree and contamination factor for all metals except Mn were estimated at stations 13, 15, 16 and 17, whereas the lowest values were estimated for the control point (**Figure 4.6**).

Table 4.5 provides a better view of the sediment contamination status of all stations by describing the ranking order based on the contamination factor and contamination degree. The C_f -values for Al, Fe, Mn, Cu, Cr, Ni and Zn were less than 1 and were categorized as unpolluted levels at all stations. The contamination factor for Pb was estimated to be moderate at all stations except the control station, and the C_d -values for V was on the borderline between unpolluted and moderately polluted. The contamination factor for Cd at all stations except stations 10, 11 and 22 (CP) was categorised as highly to very highly pollute. Hg and As were between moderately polluted and highly polluted. A cluster analysis classified all of the stations into three groups based on the degree of sediment contamination (**Figure 4.7**).

According to this classification, stations 13, 15, 16 and 17 were arranged in a separate cluster (cluster C), and station 22 (the control point) was completely separated from the other stations.

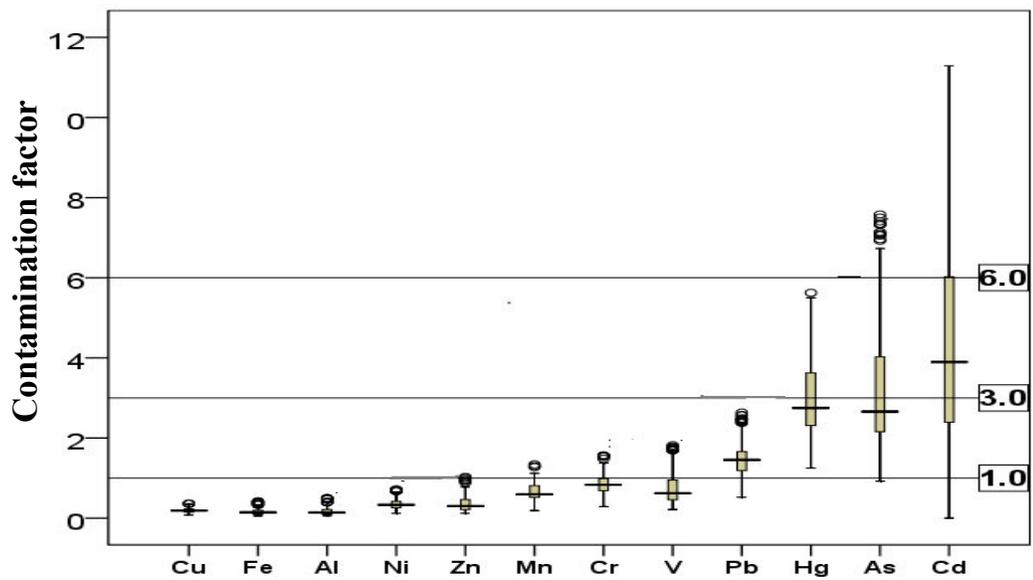


Figure 4.5, Whisker plots of the contamination factor of metal in surface sediments (The whisker shows the minimum and maximum concentration and the line of each plot is the mean value)

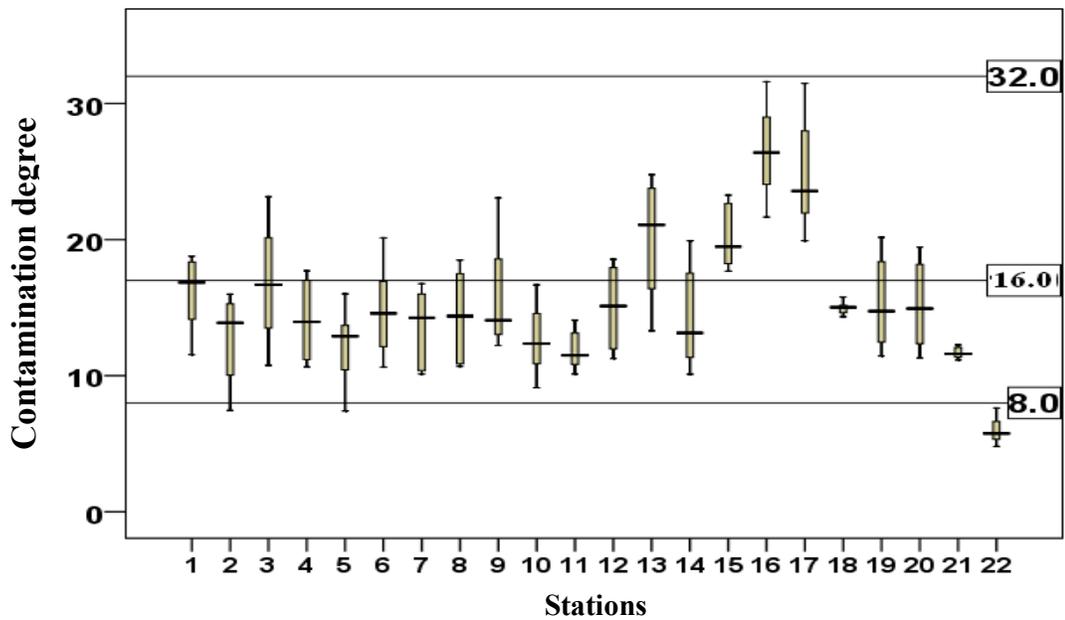


Figure 4.6, Box-Whisker plots of the contamination degree of metals for sediments in 22 stations

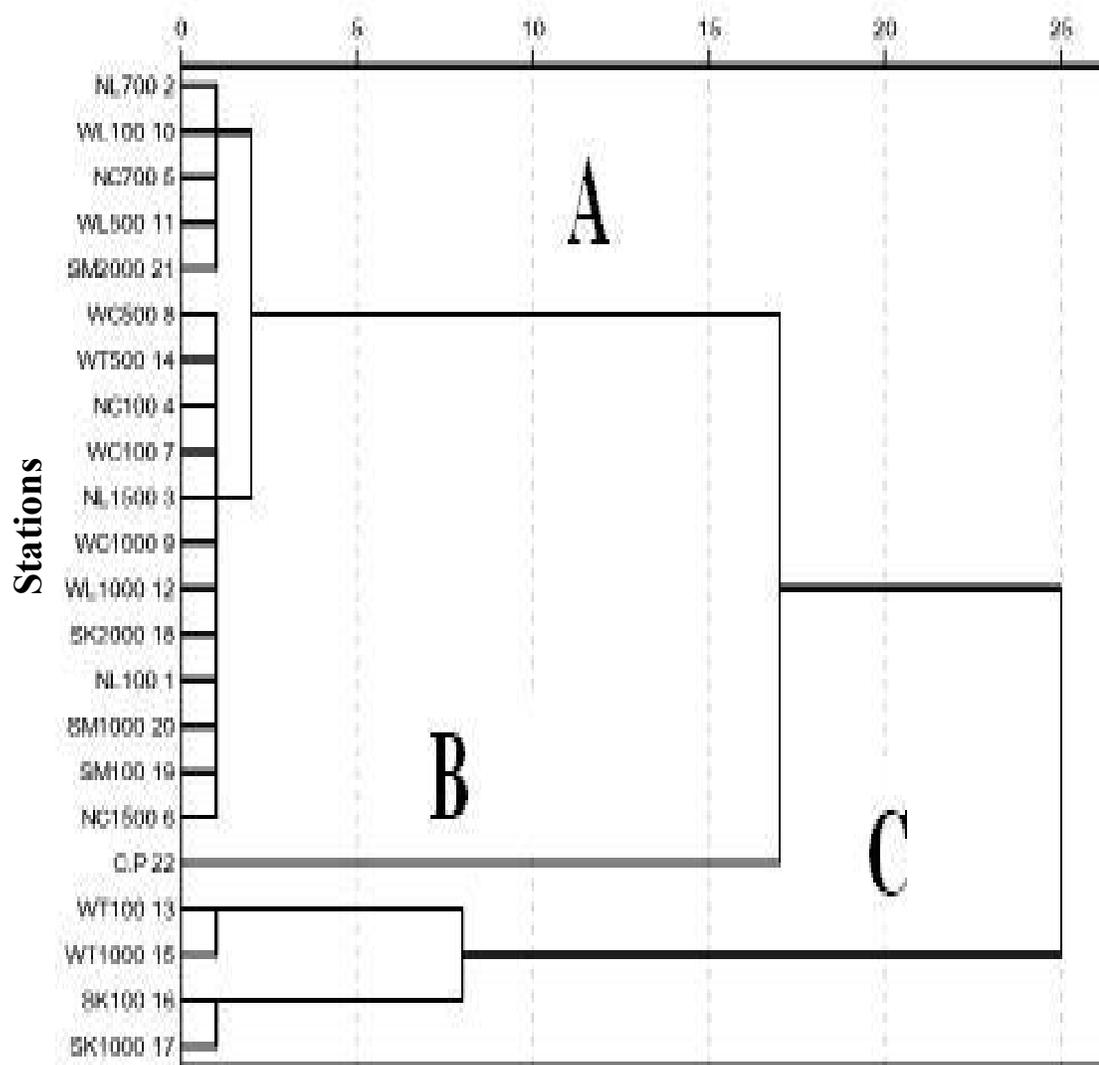


Figure 4.7, Cluster analysis to classify stations based on the contamination degree of heavy metals in surface sediment

Table 4.4, Illustrating the values of contamination factor (C_f) and contamination degree (C_d) at all stations in Klang Strait

Station	Al, Fe, Mn, Cu, Cr, Ni and Zn	Pb	As	Cd	Hg	V	$C_d = \sum_{j=1}^n C_f^j$
1	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
2	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
3	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$16 \leq C_d < 32$ Moderate
4	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
5	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
6	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
7	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
8	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
9	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
10	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
11	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
12	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
13	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$16 \leq C_d < 32$ High
14	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
15	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$(C_f \geq 6)$ very high	$3 \leq C_f < 6$ high	$C_f < 1$ unpolluted	$16 \leq C_d < 32$ High
16	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ ³ high	$(C_f \geq 6)$ very high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$16 \leq C_d < 32$ High
17	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$(C_f \geq 6)$ very high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$16 \leq C_d < 32$ High
18	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
19	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
20	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
21	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate
22	$C_f < 1$ unpolluted	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$C_d < 8$ unpolluted
Total	$C_f < 1$ unpolluted	$1 \leq C_f < 3$ moderate	$3 \leq C_f < 6$ high	$3 \leq C_f < 6$ high	$1 \leq C_f < 3$ moderate	$C_f < 1$ unpolluted	$8 \leq C_d < 16$ Moderate

4.1.2.3.1 Enrichment factor

The metal enrichment factor (EF) was also used to assess the anthropogenic proportion of the heavy metal load in surface sediments. In this study, the variations in the enrichment factor were significantly different for different heavy metals (**Figure 4.8**).

The EF value of Fe was lower than 2 at all stations, indicating that Fe may originate entirely from natural processes or crustal materials; the EF-value for Zn indicated natural process origins at most stations, but some stations showed a moderate proportion of anthropogenic pollutants. The enrichment values of Cu, Mn, Ni, V and Zn were between $2 < EF < 5$, indicating that the sediment at all stations had moderate anthropogenic inputs of these heavy metals. The EF value for Cr indicated a moderate to significant proportion of anthropogenic pollutants. There was significant enrichment of Pb and As in the sediments, which suggests that a high proportion of these metals were from anthropogenic sources. The EF values for Hg and Cd were determined to range between significant and high proportions of anthropogenic sources. In general, the EF-values for all metals obeyed the following sequence:

$$Fe < Zn < Ni < Mn < V < Cu < Cr < Pb < As < Hg < Cd$$

Figure 4.9 illustrates the variation in anthropogenic inputs of heavy metals at the different stations. Generally, the sediments of all stations had moderate ($5 < \text{Enrichment factor} < 20$) anthropogenic inputs of all metals. A cluster analysis classified the heavy metals into two major groups based on the proportions derived from anthropogenic sources (**Figure 4.10**).

The first cluster (A) represents high enrichment factor values (9-11) and includes 10 stations. The second cluster (B) includes 12 stations that range between 6.5 to 8.87. Additionally, station 22 (the control point) had the lowest value (5.2) of enrichment factor and was completely separated from cluster B.

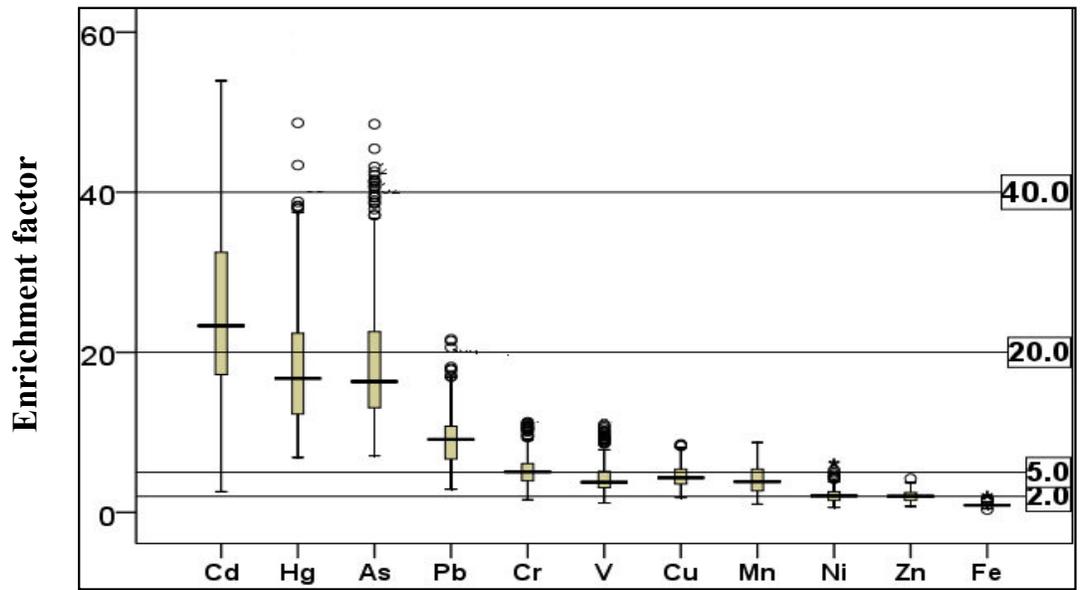


Figure 4.8, Box-Whisker plots of the enrichment factor (EF) of heavy metals in sediment (The whisker shows the minimum and maximum concentration and the line of each plot is the mean value)

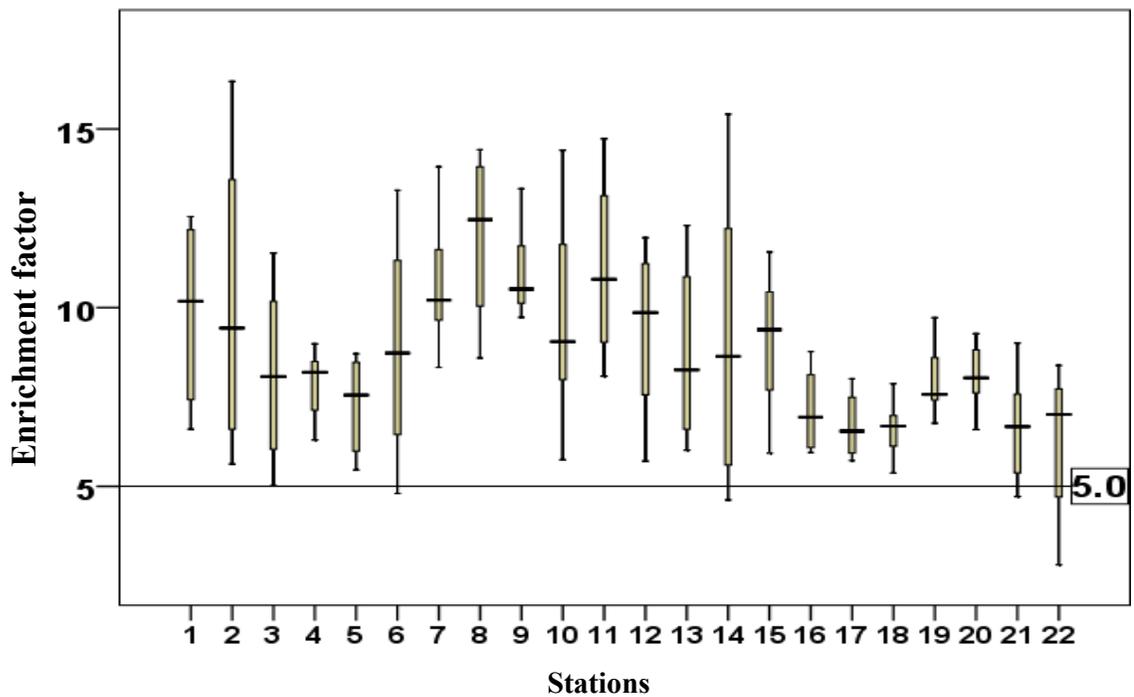


Figure 4.9, Box-Whisker plots of the enrichment factor (EF) of heavy metals in surface sediment of different stations (The whisker shows the minimum and maximum concentration and the line of each plot is the mean value)

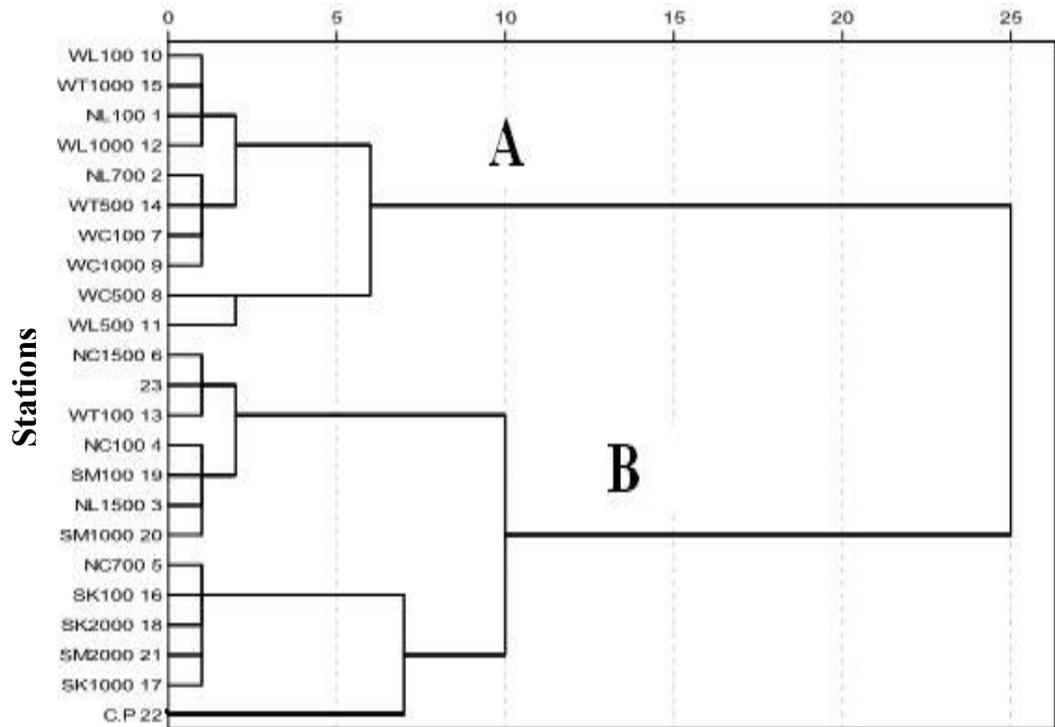


Figure 4.10, Cluster analysis to classify stations based on the enrichment factor of heavy metals in surface sediment

4.1.3 Poly Aromatic Hydrocarbons (PAHs)

4.1.3.1 Spatial variation of poly aromatic hydrocarbons (PAHs)

In the Klang Strait, the concentration of PAHs ranged from 98.2 to 3630.2 $\mu\text{g}/\text{kg dw}$ with an average concentration of 1030.3 $\mu\text{g}/\text{kg dw}$. The maximum concentration of PAHs was estimated at station 13, and the lowest concentration was observed at the control point. The PAH contamination was estimated for surface sediments all over the Strait, with higher concentrations observed at the stations close to the berth line (except station 12), especially in front of the container terminal in the West Port (station 13: 3545.9 $\mu\text{g}/\text{kg dw}$), in front of the dry and liquid terminal in the North Port (station 1: 2829.0 $\mu\text{g}/\text{kg dw}$ and station 4: 2851 $\mu\text{g}/\text{kg dw}$) and in stations located close to the

mouth of the Klang River in the South Port (16: 2497.1 µg/kg dw and 17: 3202.1 µg/kg dw).

PAH concentrations were generally lower in more remote stations except for station 12, which had an elevated concentration of PAHs (1448.8 µg/kg dw). The PAH concentration showed an insignificant correlation with percentage of TOC and fine-grained sediment ($p < 0.05$, $r = 0.15$ and $r = 0.11$) in the surface sediment of the Klang Strait (**Table 4.1**). A Kruskal-Wallis test showed that there are significant differences ($p < 0.05$, $df = 21$, $sig = 0.003$) among the concentrations of PAHs at all of the stations. In the present study, there was a significant positive correlation ($0.4 < r$, $P < 0.01$) among some individual PAHs, which was highlighted in **Table 4.6**.

Table 4.6, Correlation coefficient between individual PAHs compounds

	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	DibA	BghiP	InP	PAH
Nap	1.00																
Acy	0.28	1.00															
Ace	0.40	0.44	1.00														
Flr	0.55	0.40	0.76	1.00													
Phn	0.28	0.40	0.57	0.54	1.00												
Ant	0.24	0.27	0.64	0.58	0.75	1.00											
Fla	0.40	0.42	0.54	0.71	0.53	0.61	1.00										
Pyr	0.07	0.24	0.44	0.50	0.16	0.20	0.12	1.00									
BaA	0.23	0.19	0.15	0.27	0.28	0.42	0.08	0.28	1.00								
Chy	0.08	0.10	0.07	0.00	0.03	0.16	0.10	0.04	0.25	1.00							
BbF	0.01	0.19	-0.26	-0.31	-0.17	-0.24	-0.10	-0.36	-0.15	-0.11	1.00						
BkF	-0.06	0.52	0.20	0.27	0.27	0.46	0.42	0.12	0.09	-0.21	-0.18	1.00					
BaP	0.47	0.45	0.16	0.21	0.20	0.44	0.53	0.04	0.20	0.16	0.18	0.07	1.00				
DibA	-0.11	-0.11	-0.20	-0.33	-0.26	-0.18	-0.10	-0.27	-0.03	0.27	0.29	-0.06	0.04	1.00			
BghiP	0.44	0.75	0.44	0.28	0.05	0.26	0.23	0.07	-0.01	-0.14	0.00	0.21	0.54	-0.16	1.00		
InP	0.09	-0.14	-0.16	-0.18	-0.28	-0.14	-0.09	-0.36	-0.16	-0.05	0.21	-0.28	0.12	0.50	0.15	1.00	
PAHs	0.05	0.50	0.25	0.14	0.49	0.50	0.05	0.18	0.52	0.44	0.04	0.25	0.58	0.14	0.09	0.00	1.00

Table 4.7, Concentration of the PAHs ($\mu\text{g}/\text{kg dw}$) in surface sediments of Klang Strait

Station	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BeA	Chy	BbF	BkF	BaP	DibA	Bghip	Inp	Σ PAHs
1	ND	ND	2.1	34.2	47.5	100.4	ND	482.8	613.0	ND	ND	ND	ND	ND	ND	ND	1280.4
2	1.3	ND	ND	9.7	13.3	12.7	ND	131.3	31.5	ND	ND	ND	ND	ND	ND	ND	199
3	1.7	ND	8.1	118.5	89.0	58.8	42.7	62.9	ND	ND	ND	ND	ND	ND	ND	ND	381.7
4	0.4	ND	ND	1.1	10	59.8	12.5	12	66.7	50.0	852.8	ND	1495.8	190.2	ND	99.8	2851.0
5	0.8	ND	0.3	16.8	12.6	12	10	195.6	ND	ND	11.0	ND	ND	ND	ND	ND	259.1
6	4.0	ND	0.4	57.3	36.2	37.9	26.0	31.8	179.4	ND	ND	ND	ND	ND	ND	42.3	415.2
7	1.3	ND	ND	27.6	127.6	267.8	10.3	12.7	204.0	ND	ND	47.6	ND	ND	ND	ND	698.9
8	5.7	ND	1.0	39.0	6.8	71.4	13.5	15.8	50.5	ND	ND	ND	122.1	ND	64.2	77.4	467.4
9	1.2	ND	ND	7.7	5.1	8.2	ND	28.1	191.3	198.0	ND	ND	ND	67.8	ND	ND	507.4
10	0.8	ND	ND	23.7	5.0	10.1	ND	236.5	278.8	ND	ND	ND	ND	ND	ND	68.7	623.7
11	0.7	ND	0.7	48.8	15.6	37.8	17.6	25.1	29.5	ND	ND	367.6	ND	ND	ND	ND	543.4
12	2.0	ND	1.0	39.8	24.8	233.9	21.5	341.5	774.7	ND	ND	1.3	1.0	7.3	ND	ND	1448.8
13	16.1	645.3	14.8	520.8	225.0	308.0	166.5	243.8	390.9	ND	11.6	28.6	825.2	ND	49.4	ND	3446.9
14	3.0	ND	0.5	33.8	75.8	181.3	15.8	14.0	146.3	ND	11.3	ND	59.9	ND	ND	31.8	573.5
15	2.2	ND	ND	8.7	9.6	3.8	ND	ND	78.3	ND	12.8	ND	ND	130.2	ND	348.4	594.0
16	109.0	ND	1.2	120.6	66.3	100.5	92.2	99.7	974.8	116.0	ND	ND	716.8	ND	ND	ND	2397.1
17	9.6	ND	4.0	225.6	94.3	501.2	ND	226.2	1292.0	549.2	ND	ND	ND	ND	ND	ND	2902.1
18	1.3	ND	ND	20.8	8.5	11.6	ND	119.3	191.8	ND	378.6	ND	ND	ND	ND	ND	731.9
19	2.2	ND	ND	35.6	39.7	33.3	16.5	17.1	267.3	ND	10.2	ND	103.9	ND	ND	ND	525.8
20	2.1	ND	ND	37.1	38.6	30.2	16.3	17.0	226.8	ND	9.3	ND	89.9	ND	ND	ND	467.5
21	2.4	ND	ND	37.2	16.7	16.5	16.0	11.2	194.6	ND	22.0	ND	ND	129.6	ND	36.6	483.5
22	1.8	ND	ND	12.5	1.7	4.1	ND	ND	56.8	ND	23.4	ND	ND	ND	ND	ND	100.3
Mean	7.7	29.3	1.6	67.13	43.6	95.5	21.2	105.7	282.7	41.5	61.0	20.2	155.8	23.9	5.2	32.0	994.02
SD	22.6	135.9	3.453	131.0	53.01	142.3	38.0	144.0	363.8	121.7	191.9	77.5	377.7	53.7	16.7	76.1	918.1
Min	ND	ND	ND	1.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100.3
Max	110	650.4	15	621.6	225.6	601.2	169	599	1516.5	549.2	889.6	367.56	1524	199.2	72	360.8	3446.9

ND= below the method detection limit; Nap = naphthalene; Acy = acenaphthylene; Ace = acenaphthene; Flr = fluorene; Phn = phenanthrene; Ant = anthracene; Fla = fluoranthene; Pyr = pyrene; BaA = benzo(a)anthracene; Chy = chrysene; BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; BaP = benzo(a)pyrene; InP = indeno[1,2,3,(c,d)]pyrene; DibA = dibenzo(a,h)anthracene; BghiP = benzo(g,h,i)perylene.

4.1.3.2 Source of PAHs

High-temperature combustion processes are the primary sources of high-molecular-weight PAHs (HMWPAH) with 4 or more rings. Thus, the concentrations of high-molecular-weight PAHs (Fla, Pyr, BaA, Chy, BbF, BkF, BaP, InP, DibA, BghiP) are typically estimated to assess the combustion value (Khairy et al., 2009). In our study, combustion values ranged from 80 µg/kg dw to 2767.8 µg/kg dw with an average concentration of 767.2 µg/kg dw (**Table 4.5**).

High-molecular-weight PAHs represented between 26.4% and 95.9% of the total concentration of PAHs, with a mean value of 74.46%.

Moreover, the combustible PAHs constituted a significant portion of the total PAHs at stations 13 and 15 (in front of container terminal) in the West Port, stations 1 and 4 in the North Port and stations 16 and 17 in the South Port, which reflect a recent input of PAHs at these stations.

Some high-molecular-weight PAHs such as BaA, Chy, BbF, BkF, BaP, InP and DibA are known as toxic PAHs because of their mutagenic and carcinogenic effects on humans and other organisms (Hale et al., 2012; Khairy et al., 2009; Pahila et al., 2010). The concentrations of these PAHs ranged from 11 µg/kg dw to 2755.3 µg/kg dw, with a mean concentration of 631.1 µg/kg dw (**Table 4.5**). Their concentration made up an average of 61.25% of the total concentration of PAHs, ranging from 0 to 97.3%. These concentrations were highest in stations 1, 4, 13, 15, 16 and 17, whereas at some remote stations (2, 3, 5 and 22), toxic PAH concentrations were significantly lower.

Pyrogenic and petrogenic sources are typically distinguished based on the ratios of individual PAHs, which are identified based on molecular mass, such as Phn/Ant ($m=178$) and Fla/Pyr ($m=202$). The results related to the source identification of PAHs are summarized in **Table 4.5**.

According to the ratio of Phn/Ant, all of the stations are mostly exposed to pyrogenic sources of contamination because the Phn/Ant ratio was below 10 at all stations, whereas the ratio of Fla/Pyr revealed only stations 4, 14 and 21 to be mainly exposed to pyrogenic sources (Fla/Pyr >1) and others stations with ratios below 1.

Table 4.5, Molecular indices of PAHs, content in surface sediments of Klang Strait

Station	$\sum PAH_{combust}$	$\sum PAH_{toxic}$	Phn/Ant	Fla/Pyr	Ant/Ant+Phn	Fla/Fla+Pyr	L/H-PAH
1	1195.8	613.0	0.47	0.00	0.68	0.00	0.15
2	162.8	31.5	1.05	0.00	0.49	0.00	0.23
3	105.6	0.0	1.51	0.68	0.40	0.40	2.61
4	2767.8	2755.3	1.5	1.03	0.86	0.51	0.03
5	206.6	11.0	1.1	0.11	0.49	0.05	0.20
6	279.4	221.7	0.95	0.82	0.51	0.45	0.49
7	274.6	251.6	0.48	0.81	0.68	0.45	1.55
8	343.5	250.0	0.09	0.86	0.91	0.46	0.36
9	485.2	457.1	0.63	0.00	0.61	0.00	0.05
10	584.1	347.6	0.50	0.00	0.67	0.00	0.07
11	439.8	397.1	0.41	0.70	0.71	0.41	0.24
12	1046.8	784.3	0.11	0.09	0.90	0.08	0.29
13	1715.9	1256.3	0.73	0.68	0.58	0.41	1.07
14	279.2	249.3	0.42	1.13	0.71	0.53	1.05
15	569.7	569.7	2.54	0.00	0.28	0.00	0.04
16	2099.5	1907.6	0.66	0.93	0.60	0.48	0.19
17	2267.4	2041.3	0.16	0.00	0.86	0.00	0.41
18	689.7	570.4	0.74	0.00	0.58	0.00	0.06
19	415.0	381.5	1.19	0.97	0.46	0.49	0.27
20	359.4	326.1	1.28	0.96	0.44	0.49	0.30
21	410.1	382.8	1.01	1.42	0.50	0.59	0.18
22	80.3	80.3	0.41	0.00	0.71	0.00	0.25
Mean	767.2	631.1	0.44	0.19	0.70	0.16	0.33
SD	233.2	213.8	0.58	0.48	0.22	0.28	0.32
Min	80	11	0.16	0.19	0.28	0.4	0.04
Max	2767.8	2755.3	2.54	1.42	1	1	2.61

Figure 4.11 revealed a clear pattern in the sources of PAHs. Most of the investigated sediment samples presented a mixed pattern of contamination from pyrogenic and petrogenic origins. At the same time, just three sediment samples (4, 14 and 21) had pyrogenic-origin PAHs. Moreover, ratios of PAHs such as Ant/Ant+ Phn and Fla/(Fla+ Pyr) had been applied to provide an accurate estimation of PAH sources. The ratio of Ant/Ant+ Phn was greater than 0.1 for all stations, implying that the origin of the PAHs in the sediments of the Klang Strait is primarily combustion; either wood, coal or grass combustion or petroleum combustion. The PAH ratio Ant/(Ant+ Phn) was plotted against Fla/(Fla+ Pyr) to distinguish the possible source of PAHs.

Figure 4.12 showed a mixed pattern of combustion and petroleum sources (vehicle and crude oil) at some of the stations (3, 6, 7, 8, 11, 13, 16, 19 and 20). At the same time, combustion fingerprints (more frequent PAHs representing wood, coal and grass combustion) were strongly present in stations 4, 14 and 21. Other stations (1, 2, 5, 9, 10, 12, 15, 17, 18 and 22) have primarily originated from combustion, although petroleum-derived contamination cannot be ignored. The ratio between low-molecular-weight and high-molecular-weight PAHs (L/H-PAHs) was lower than 1 at all stations except stations 3,7,13 and 14.

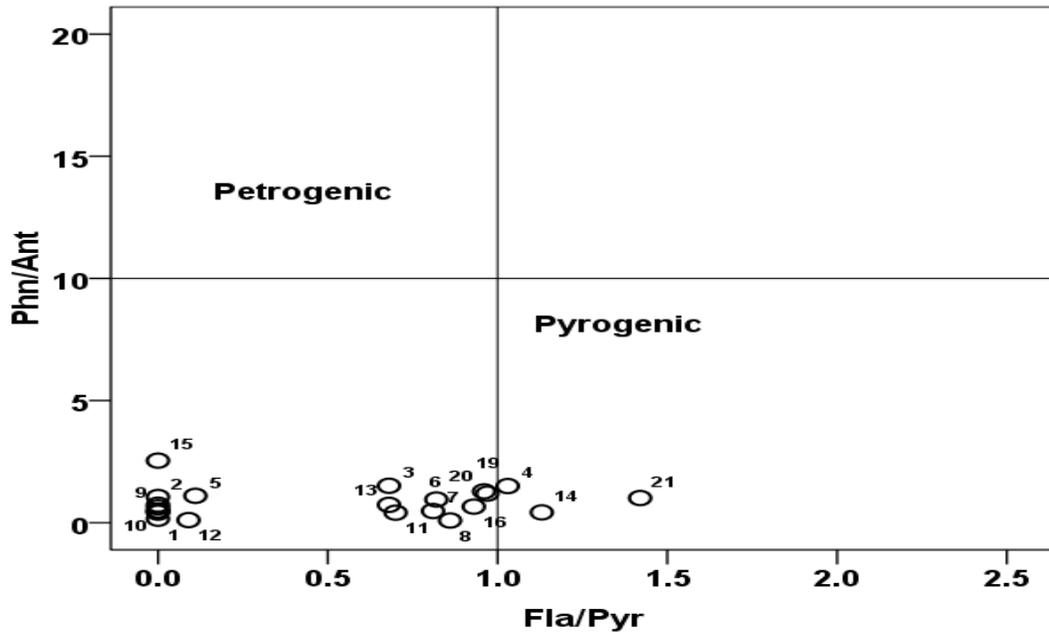


Figure 4.11, Plots of PAH isomer pair ratios for source identification Phn/Ant versus Fla/Pyr

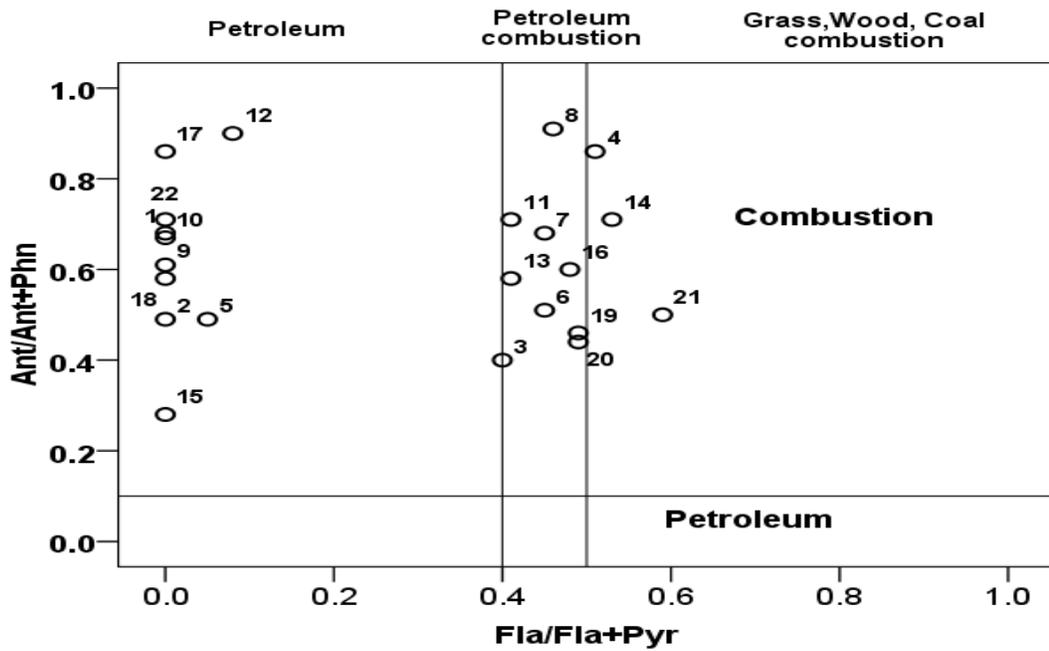


Figure 4.12, Plots of PAH isomer pair ratios for source identification $\text{Ant}/(\text{Ant}+\text{Phy})$ versus $\text{Flu}/(\text{Flu}+\text{Pyr})$.

Principal component analysis (PCA) was used to identify the occurrence sources of PAHs and quantify the percentage of contribution of individual PAH sources. As shown in **Table 4.6**, PCA analysis classified the dataset of PAHs into 5 principal components (PCs) that control 80.6% of changes in PAH contamination in the surface sediments of the Klang Strait.

PC1 described 30.81% of the variance in the data. This factor was strongly related to Acy, Ace, Flr, Phn, Flr and Bghip, of which Flr, Phy, Flu and Bghip are known to derive from the incomplete combustion and pyrolysis of fuel whereas Acy and Ace are used as tracers for contamination from oil spills. This could possibly be due to oil tanker operation in the Malacca Strait (Sakari et al., 2008; Sakaria et al., 2010).

PC2 explained 16.8% of the total variance and showed a strong relationship with Ant, BeA and Chy, which are used in an index to assess contamination by combustion sources.

The third factor (PC3), responsible for 16.037% of the total variance, was strongly related to BbF, BaP, DibA and InP, which are understood to be toxic PAHs. PC4 explained 10.27% of the total variance, with a high correlation with Nap. Nap is used as a tracer of oil spills, such as Acy and Ace. It can also originate from termite activities on vascular land plants and woody material in tropical areas and the Amazon region (Ekpo, Oyo-Ita, Oros, & Simoneit, 2011; Okere & Semple, 2012).

However, the total variance explained by PC5 was equal to 9.15% and was not strongly related to any PAH, indicating unknown sources. The PCA analysis is concordant with the pair isomer ratio of PAHs, which revealed a mixture of pyrogenic- and petrogenic-derived PAHs in the Klang Strait.

Table 4.6, Rotated component loadings of three principal components (PCs) for PAH compositions in the sediments of Klang Strait

PAHs	PC1	PC2	PC3	PC4	PC5
Nap	.105	.165	.025	.964	0.532
Acy	.955	-	.089	-	-
Ace	.917	.147	.002	.137	-
Flr	.936	.270	.010	.104	.084
Phn	.828	.298	-	-	.082
Ant	.390	.851	-	-	.081
Fla	.866	-	-	-	.448
Pyr	.154	.241	-	-	.177
BaA	.064	.849	0.10	-	.303
Chy	-	.929	.016	.052	.057
BbF	-	-	.944	.043	-
BkF	.02	-	-	-	-
BaP	.355	.009	.823	.051	.383
DibA	-	-	.778	.593	.109
BghiP	.788	-	-	.196	-
InP	-	-	.853	-	-
Variance(%)	30.18	16.81	16.37	10.27	9.15

Note: Only loading values with moduli large than 0.01 are presented and those higher than 0.7 are in bold.

4.1.4 Biological assessment

4.1.4.1 Spatial and temporal distribution of benthic communities

The results of the analysis of the spatial and temporal distributions of benthic composition are summarized in

Table 4.7 and **Table 4.8**. Overall, 23 species of Mollusca, 4 species of Arthropods, 3 species of Echinodermata and 3 species of Annelida (2 polychaetes and one oligochaete) were identified at the 22 sampling stations across four sampling periods. Individual species of Mollusca constituted 48.6% of the total abundance, followed by Arthropods (26.01%), Annelida (22.35%) and Echinodermata (3.03%). Large standard deviations in the total number of individuals indicated that temporal changes or inter-replicate differences varied strongly (**Figure 4.13** and **Figure 4.14**).

The results of Kruskal-Wallis analysis of phylum-level abundance indicated that replicate sediment samples taken in the Klang Strait exhibited a significant ($p < 0.05$) difference in the composition of the macro-benthic community between stations during the year. Duncan analysis indicated that the greatest separation of benthic composition occurred between stations 12, 16, 17, 22 and other remaining stations. Between-season differences in average abundance were not statistically significant ($p < 0.05$) over the 4 sampling periods (**Table 4.12**).

The spatial distribution data on species-level abundance showed different patterns of benthic species. Stations 1-5, 9, 12, and 18- 22 were numerically dominated by Mollusca species, which constituted more than 50% of the total abundance at these stations; this dominance was very stable over the four sampling periods (**Figure 4.15**). With respect to average abundance, the Mollusca includes *Anadara nodifera*, *Nassarius jacksonianus* and *Cerithium sp* were also conspicuous members of the benthic community at these stations.

Crustacean species dominated at stations 6, 10 and 11, especially *Xenopthalmus pinnotheroides* and *Excirrolana sp*, whereas Annelida species (Lumbrineridae) were numerically dominant at stations 7, 13, 14 and 15 over the different seasons surveyed (**Figure 4.15**). In temporal scale, Mollusca were dominant while Echinodermata showed the lowest concentration in all sampling periods (**Figure 4.16**).

Table 4.7, Total abundance (individuals m^{-2}) of macrofaunal taxa in different stations over different time intervals

Taxa and ecological groups	1	2	3	4	5	6	7	8	9	10	11	12
Mollusca	31.25	38.75	51.75	32.75	7.5	49	0	13.7	17.5	23.7	15	45
Mactra sp (I)												
Mactra luzonica(I)	23.25	9.75	41.25	28.75	23.75	45	11.2	8.75	25	5	5	31.2
Mactra Pellucida(I)	10	12	17.5	0	0	21.25	0	0	12.5	0	15	0
Spisula ravenal(I)	12.5	13.7	6.25	1.25	0	12.5	0	0	0	1.25	0	11.2
Merona cornucopiae(I)	22.5	15	31.25	32.5	25	41.25	0	0	0	11.2	0	11.2
Codakia tigerina(I)	33.75	23.7	42.5	13.75	1.25	56.25	11.2	0	15	27.5	11.2	62.5
Arcuatula arcuatula(I)	14.25	7.25	29	6.25	25	18.75	0	0	0	5	6.25	6.25
Tellina foliacea(I)	23.25	12.5	31.25	8.75	0	13.75	0	0	15	6.25	15	25
Barantolla sp(I)	25	20	28.75	26.25	0	20	0	0	8.75	0	0	18.7
Barbatia fusca(I)	7.5	7.5	20	6.25	6.25	13.75	20	15	25	0	0	32.5
Tellina sp(I)	18.75	22.5	25	6.25	0	12.5	0	0	0	12.5	6.25	18.7
Tellina tenuis (I)	33.75	15	27.5	11.25	22.5	31.25	0	0	0	10.2	0	20
Tellina albenia(I)	0	7.5	11.25	16.25	35.25	13.75	0	0	0	0	0	12.5
Tellina staurella(I)	13.75	0	20	20	13.75	26.25	0	0	16.2	0	0	0
Donax sp(I)	0	0	0	0	0	0	0	0	6.25	0	0	1.25
Crassostrea sp (ns)	0	6.25	18.75	20	12.5	25	0	0	33.7	0	0	30
Anadar nodifera (IV)	140	72.5	137.5	116.2	108.7	120	23.7	75	125	51.2	15	61.2
Chlamys sp(I)	7.5	6.25	30	0	0	20	0	0	47.5	0	0	0
Litorina coccinea(I)	3.75	6	22	42	13.75	70	0	106	161	0	0	107.
Cerithium sp(II)	0	0	0	0	20	17.5	31.25	45	116	121	60	137
Nassarius jacksoniasus(II)	30	15	55	0	0	0	0	0	0	40	25	260
Natica sp(II)	0	0	0	0	0	0	0	0	0	30	13	42.5
Scaphander lignarius(I)	0	0	0	0	0	0	7.5	11.2	0	10	0	21.2
Echinodermata	18.62	28.7	70	50	70	0	0	0	0	65	37.5	35
Amphipholis gracillima(I)												
Salmacis sp (ns)	0	0	0	0	0	0	0	0	0	0	1.25	16.2
Balanus sp (ns)	0	0	0	6.25	3.5	14.25	16.5	38.7	61.2	16.7	0	67.5
Arthropoda	36.25	18.7	30	16.75	12.5	30	0	0	12.5	30	15	19.7
Alpheus sp (II)												
Uca sp (I)	0	0	0	0	0	0	0	0	0	51.2	3.75	42.5
Xenophthalmodes pinnothe roides	37.5	25	370.5	43.75	215	422.5	144	156	307	72.5	181	246
Excirolana hirsuticauda (II)	60	0	90	207.5	0	295	26.2	46.2	15	277.	0	122
Annelida	16.25	12	12.5	15	13.75	11.25	0	0	0	75	0	50
Lipiniella sp. (II)												
Lumbricillus sp (V)	12.5	11.2	11.25	15	25	30	210	210	170	297	140	145
Glycera alba (IV)	55	46.2	46.5	52.5	45	53.7	40	60	40	0	0	35

Table.4.10 (Continued)

Taxa and ecological groups	13	14	15	16	17	18	19	20	21	22	Mean	SD
MolluscaMactra sp (I)	0	0	11.25	0	0	15	11.25	15	37.5	142.5	25.3	35.2
Mactra luzonica(I)	0	10	20	0	0	41.25	0	0	30	138.75	22.6	31.8
Mactra Pellucida(I)	0	0	0	0	0	0	0	0	0	98.75	8.5	26.7
Spisula ravenal(I)	0	7.5	17.5	0	0	1.25	0	0	1.25	62.5	6.7	21.5
Merona cornucopiae(I)	0	0	0	0	0	11.25	11.25	11.25	23.75	118.75	16.0	31.6
Codakia tigerina(I)	0	0	0	0	0	28.75	0	0	33.75	138.75	22.7	36.2
Arcuatula arcuatula(I)	0	0	0	0	0	0	0	0	0	131.25	11.3	30.1
Tellina foliacea(I)	0	0	12.5	0	0	8.75	0	0	21.25	138.75	15.1	32.0
Barantolla sp(I)	0	0	20	0	0	6.25	8.75	7.5	7.5	103.75	13.7	32.3
Barbatia fusca(I)	0	0	0	0	0	7.5	13.75	13.75	12.5	115	14.4	30.6
Tellina sp(I)	0	0	0	0	0	0	0	0	0	105	10.3	27.0
Tellina tenuis (I)	0	0	0	0	0	31.25	11.25	6.25	26.25	97.5	15.6	27.8
Tellina albenia(I)	0	0	0	0	0	0	0	0	0	60	7.1	21.1
Tellina staurella(I)	0	0	0	0	0	1.75	0	0	0	115	10.3	27.4
Donax sp(I)	0	0	0	0	0	0	0	0	0	68.75	3.4	18.1
Crossostra sp (ns)	0	0	0	0	0	0	12.5	17.5	37.5	28.3	10.9	22.2
Anadar nodifera (IV)	197.5	105	92.5	0	0	50	137.5	77.5	12.5	0	78.1	70.2
Chlamys sp(I)	0	0	0	0	0	0	0	0	0	31.25	6.4	19.1
Litorina coccinea(I)	0	0	0	0	0	20	45	0	10	15	28.2	121.3
Cerithium sp(II)	0	0	42.5	0	0	0	90	72.5	105	120	43.4	77.5
Nassarius jacksoniasus(II)	80	60	42.5	0	0	0	156.25	85	0	30	39.9	138.7
Natica sp(II)	0	0	17.5	0	0	2.5	0	0	91.25	50	11.2	49.9
Scaphander lignarius(I)	0	0	0	0	0	0	0	0	0	0	2.3	22.6
Echinodarmata Amphipholis gracillima(I)	0	0	60	0	0	0	0	0	0	0	19.7	79.9
Salmacis sp (ns)	0	0	0	0	0	23.75	23.75	16.25	20	46.25	6.7	15.2
Balanus sp (ns)	0	0	0	0	0	0	0	0	0	20	11.1	33.4
ArthropodaAlpheus sp (II)	12.5	11.25	10	0	0	0	0	0	0	1.5	11.7	44.8
Uca sp (I)	0	0	20	0	0	0	0	0	0	73.75	7.9	52.1
Xenophthalmodes.pinnotheroides	41.25	42.5	101.75	0	0	0	11.25	0	27.5	90.5	115.3	191.7
Excirolana hirsuticauda (II)	117.5	105	320	0	0	0	26.25	15	0	40	81.1	183.5
AnnelidaLipiniella sp. (II)	151.25	126.25	225	0	0	0	0	0	0	0	32.5	133.8
Lumbriculus sp (V)	331.25	285	295	0	0	20	191.2	97.5	45	0	115.6	148.0
Glycera alba (IV)	143.75	132.5	78.75	0	0	12.5	127.5	60	11.25	0	47.3	59.4

Table 4.8, Temporal distribution of macrofaunal taxa (individual m^{-2}) over different time interval.

Taxa and ecological groups	November2009	February2010	May2010	August 2010
Mollusca				
Mactra sp (I)	21.1	22.8	26.6	31.0
Mactra luzonica(I)	20.1	27.3	20.2	23.0
Mactra Pellucida(I)	2.7	8.6	6.6	16.0
Spisula ravenal(I)	0.0	11.8	5.7	9.5
Merona cornucopiae(I)	16.8	12.0	4.5	33.2
Codakia tigerina(I)	18.2	16.8	28.4	27.5
Arcuatula arcuatula(I)	5.7	16.4	13.0	10.2
Tellina foliacea(I)	14.8	15.2	13.9	16.5
Barantolla sp(I)	0.0	15.9	13.6	25.2
Barbatia fusca(I)	9.1	13.6	14.5	20.2
Tellina sp(I)	8.0	13.0	6.8	13.6
Tellina tenuis (I)	9.5	15.0	6.4	31.6
Tellina albenia(I)	0.0	7.0	8.7	12.7
Tellina staurella(I)	12.3	6.8	12.4	9.8
Donax sp(I)	0.0	2.3	5.9	5.7
Crossostra sp (ns)	1.4	18.0	9.5	14.8
Anadara nodifera (IV)	47.3	74.1	85.9	105.2
Chlamys sp(I)	0.0	2.3	10.2	13.4
Litorina coccinea(I)	33.6	13.1	12.0	54.5
Cerithim sp(II)	27.6	43.2	34.5	68.5
Nassarius jacksoniasus(II)	48.2	0.0	65.5	46.1
Natica sp(II)	3.4	9.6	11.4	20.5
Scaphander lignarius(I)	1.8	3.4	1.1	2.7
Echinodarmata				
Amphipholis gracillima(I)	26.4	12.7	11.8	28.2
Salmacis sp (ns)	5.2	5.2	8.2	8.2
Balanus sp (ns)	0.0	5.4	9.6	29.5
Arthropoda				
Alpheus sp (II)	0.0	44.4	0.7	1.5
Uca sp (I)	0.0	5.9	10.7	18.2
Xenophthalmodes.pinnotheroides	155.3	104.7	70.3	141.0
Excirolana hirsuticauda (II)	103.2	90.0	36.4	81.8
Annelida				
Lipiniella sp. (II)	0.0	36.3	31.9	62.0
Lumbriculus sp (V)	126.4	92.3	101.8	141.8
Glycera alba (IV)	25.7	81.4	40.0	42.0

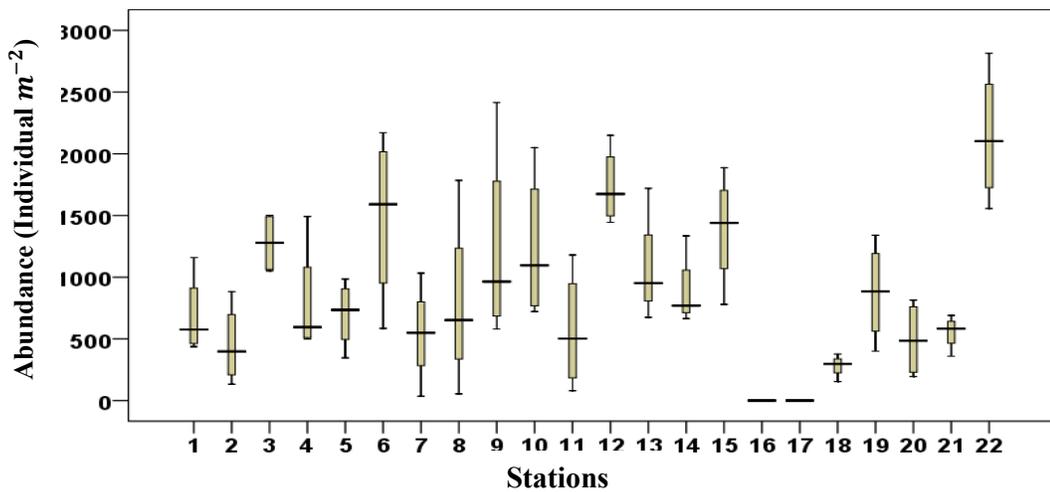


Figure 4.13, Box-Whisker plots of the spatial variation of benthic abundance (individual m^{-2}) at different stations (The whisker shows the minimum and maximum concentration and the line of each plot is the mean value).

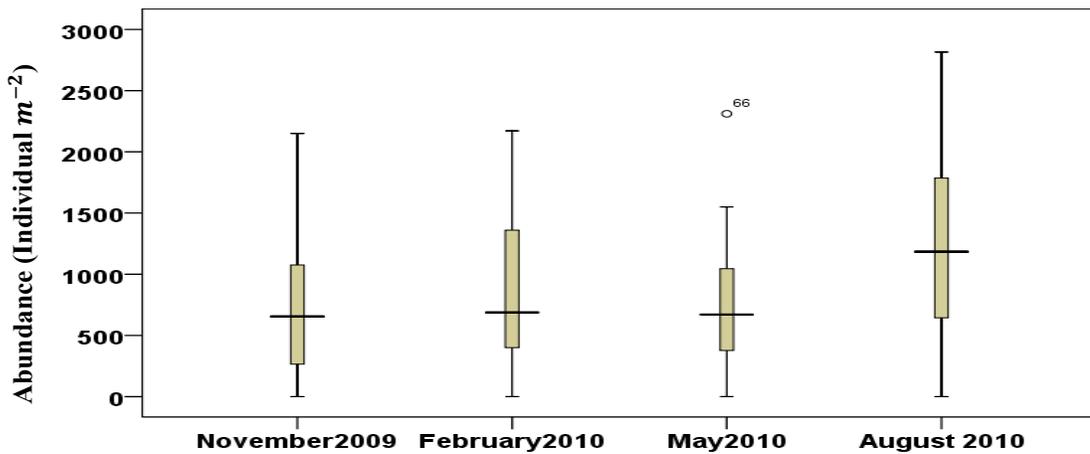


Figure 4.14, Box-Whisker plots of the temporal variation of benthic abundance (individual m^{-2}) during four times sampling

Table 4.9, Results of Kruskal wallis analysis of differences in composition of macro-benthic community assemblages between stations and Seasons

Phylum	Mollusca	Echinodermata	Arthropoda	Annelida	Benthos
a. Chi-Square	58.025	35.247	51.424	55.995	57.311
df	21	21	21	21	21
Asymp. Sig.	0.000	0.027	0.000	0.000	0.000
b. Chi-Square	7.807	0.566	3.072	3.549	7.032
df	3	3	3	3	3
Asymp. Sig.	0.050	0.904	0.381	0.314	0.071

Grouping Variable: Stations, Grouping Variable: Seasons

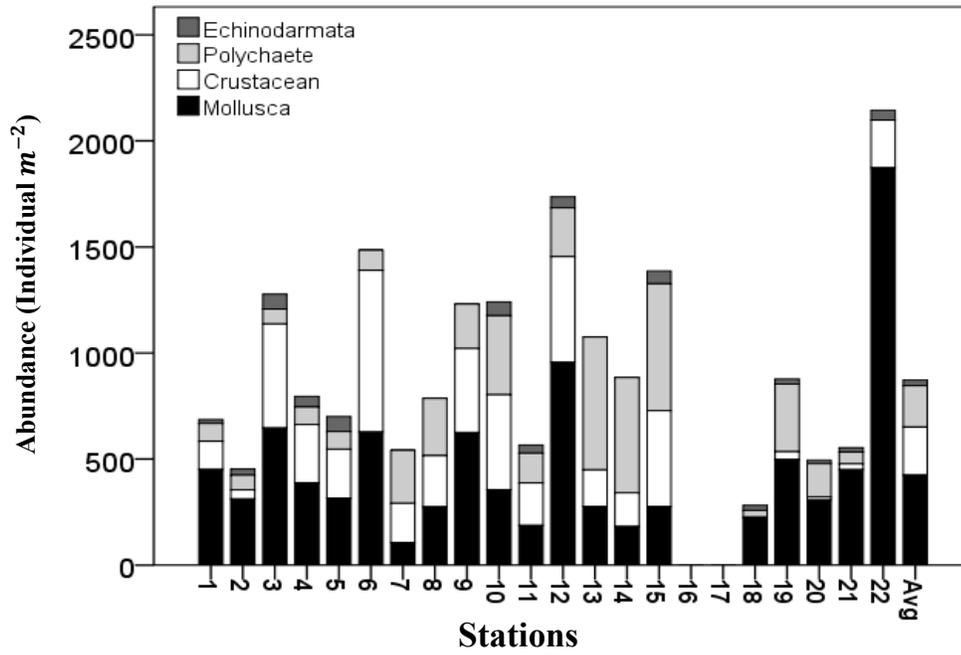


Figure 4.15, Total abundance (Individual m^{-2}) of different macro-benthic fauna present at 22 stations and the average number of species across one year

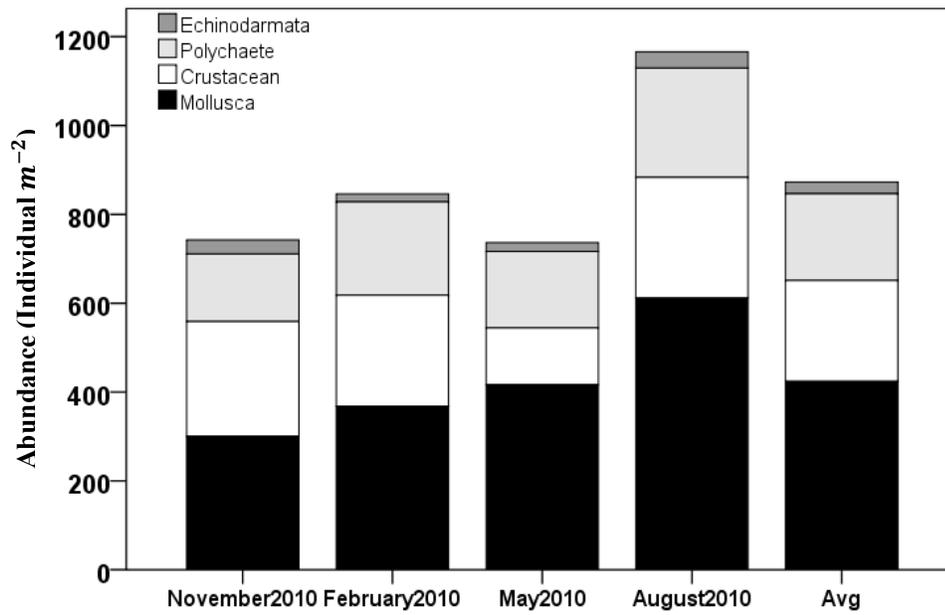


Figure 4.16, Total abundance (individual m^{-2}) of different macro-benthic fauna present at four sampling time and the average number of species across one year.

4.1.4.2 Disturbance analysis

Several ecological indices were applied to assess sediment quality based on the response of the soft-bottom macro benthic structure to changes in the environment. Average abundance, richness and diversity were significantly higher at stations 22 (2144.5 ± 543 , $H':4.41$, $J:25$) and 12 (1736 ± 313.39 , $H':4$, $J:28$), whereas the lowest abundance, richness and diversity were observed at stations 16 and 17. Some stations were significantly higher in terms of the average value of the total number of individuals, diversity or richness, such as stations 3, 6, 9, 12, 15 (along the mangrove edge in the North and West Ports), 10 (close to the liquid berth in the West Port) and 22 (control point). Other stations that were close to the berth line (1, 2, 4, 5, 7, 8, 11, 13, 14 and 20) showed relatively lower abundance, richness and diversity (**Table 4.10**).

There was significant variation of the pollution level according to the AMBI in different stations. In general, Klang Strait is classified as slightly polluted (BI:2, AMBI:2.1, M-AMBI:0.85) because the pollution level of most of the stations (1-6, 9-12, 15, 18, 21 and 22) varied between undisturbed and slightly polluted. At these stations, the benthic community was dominated by ecological group I and II (sensitive species), while there was low abundance (0-20%) in the area of group V (opportunistic species). Some stations, such as 7, 8, 13, 14, 19 and 20, are classified as moderately polluted, and the community was dominated (48.9-62.5%) by group IV and V. These ecological groups were also abundant in stations near the discharge point. Stations 16 and 17 were only classified as extremely polluted (BI:7, AMBI:7, M-AMBI: -0.05) because there is no benthic community present at these stations (**Figure 4.17**).

Ecological group III (tolerant to pollution) was not found in Klang Strait, which had an unbalanced benthic composition.

Table 4.10, Summary results of ecological indices to assess pollution level based on the benthic responds to disturbance in different stations.

Stations	Abundance individual m ⁻²	Diversity (H')	Species Richness (J)	* BI	** AMBI	Disturbance Classification	***M-AMBI	Status
1	686.8	4	22	2	1.86	Slightly disturbed	0.83	Good
2	453.25	4	22.00	2	1.72	Slightly disturbed	0.84	Good
3	1277.25	3.85	24.00	2	1.49	Slightly disturbed	0.85	Good
4	795.25	3.67	22.00	2	1.74	Slightly disturbed	0.79	Good
5	700	3.43	19.00	2	1.94	Slightly disturbed	0.73	Good
6	1484.50	3.43	19.00	2	1.94	Slightly disturbed	0.73	Good
7	541.75	2.49	10.00	3	3.95	Moderately disturbed	0.43	Moderate
8	786.25	2.89	11.00	3	3.88	Moderately disturbed	0.48	Moderate
9	1231.25	3.33	18.00	2	2.48	Slightly disturbed	0.68	Good
10	1241	3.42	21.00	2	2.46	Slightly disturbed	0.72	Good
11	566	3.03	17.00	2	1.81	Slightly disturbed	0.68	Good
12	1736	4	28.00	2	1.76	Slightly disturbed	0.85	Good
13	1075	2.64	8.00	3	4.01	Moderately disturbed	0.42	Moderate
14	885	2.75	10.00	3	3.80	Moderately disturbed	0.46	Moderate
15	1386.76	3.13	16.00	3	4.05	Slightly disturbed	0.55	Good
16	0	0.00	0.00	7	7.00	Extremely disturbed	-0.05	Bad
17	0	0.00	0.00	7	7.00	Extremely disturbed	-0.05	Bad
18	281.7	3.47	15.00	2	1.55	Slightly disturbed	0.70	Good
19	877.5	3	14.00	3	3.76	Moderately disturbed	0.54	Moderate
20	495.	3	12.00	3	3.60	Moderately disturbed	0.52	Moderate
21	553.7	3.67	17.00	2	1.43	Slightly disturbed	0.75	Good
22	2144.5	4.41	25.00	1	0.36	Undisturbed	0.96	High
Avg	872.66	4	33	2	2.1	Slightly disturbed	0.85	Good

*BI= Biotic index, **AMBI= AZTI marine biotic index, ***M-AMBI=Multivariate-AMBI

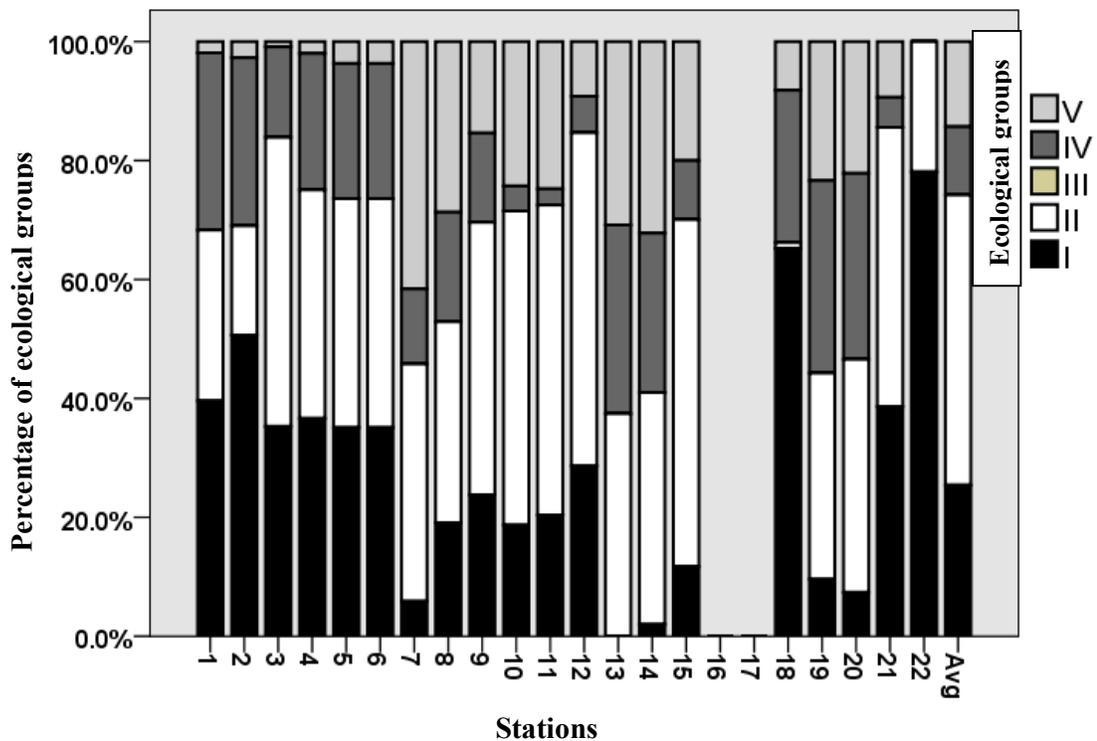


Figure 4.17, Range of ecological group percentage for different stations and average percentage of ecological groups across one year

Table 4.11 and **Figure 4.18** summarise the temporal variations of the ecological groups over a year. The results show that the area is generally slightly polluted, and the variations of the ecological groups are insignificant in a temporal scale. The abundance, diversity and richness changed in a small seasonal pattern, with an upward trend from November 2009 until August 2010 (**Figure 4.18**), but there was no significant temporal change in the ecological indices, and the macrobenthic species varied without an obvious temporal pattern. *Xenophthalmodes pinnotheroides* and *Lumbriculus sp* were the dominant species in all of the sampled months. Some species were occasionally dominant, such as *Anadara nodifera* and *Glycera alba*.

Table 4.11, Summary results of ecological indices to assess pollution level based on the benthic responds to disturbance in different sampling times

Seasons	Diversity	Richness	BI	AMBI	Disturbance Classification	M-AMBI	Status
November 2009	3.9	24	2	2.18	Slightly disturbed	0.74	Good
February 2010	4.3	32	2	2.21	Slightly disturbed	0.85	Good
May 2010	4.38	33	2	2.30	Slightly disturbed	0.85	Good
August 2010	4.42	33	2	2.03	Slightly disturbed	0.84	Good

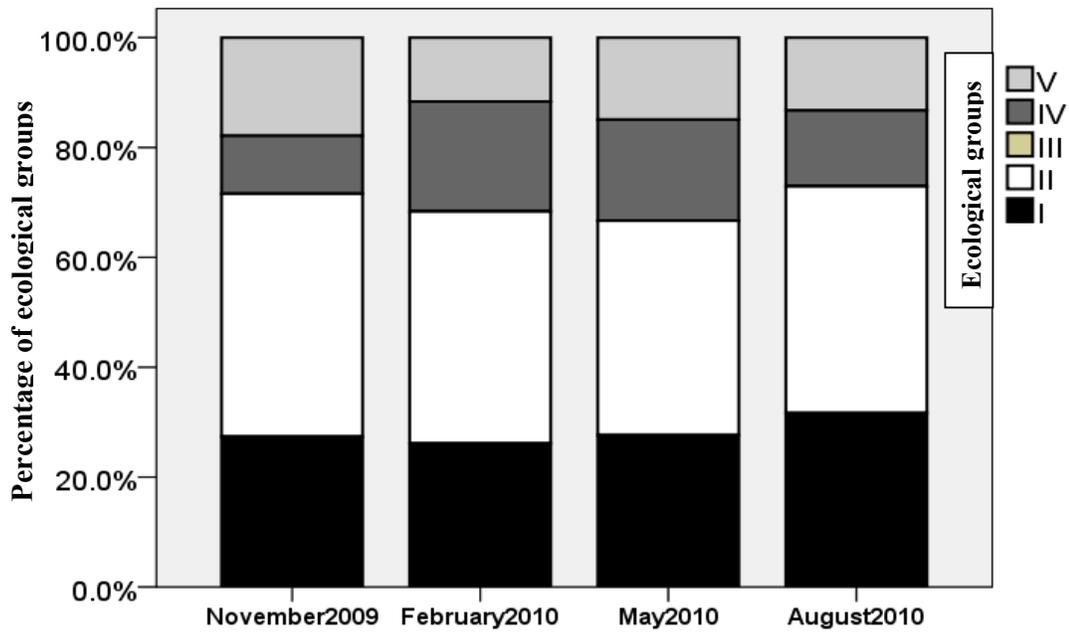


Figure 4.18, Range of ecological group percentage for different sampling times

The correlation analysis is good agreement to assess benthic faunal response to type variation in contaminant. It is individually estimated for each Site because of the differences in the physicochemical characteristic and contaminants sources. In South Port, there is strong negative correlation ($r > -0.5$) between benthic composition (abundance, diversity and richness) and other parameters except for PAHs, Mn and Ni.

In North and West Ports the significant negative correlations ($-0.4 < r < -0.5$) were found between benthic abundance and some parameters such as As, Cd and Cu. PAHs component had a significant negative correlation with diversity and richness of benthic structure. Fe, Mn, fine sediment fraction and TOC showed the significant positive correlation with benthic community (**Table 4.13**).

Table 4.12, Correlation coefficient between benthic community and physicochemical parameters of sediment at different sites

Physicochemical Parameters	South Port			North and West Port		
	Abundance	Diversity	richness	Abundance	richness	Diversity
Al	-0.76	-0.81	-0.69	0.24	-0.029	-0.01
As	-0.50	-0.74	-0.61	-0.45	-0.09	-0.01
Cd	-0.76	-0.74	-0.69	-0.48	-0.09	-0.14
Cr	-0.47	-0.81	-0.69	0.14	-0.24	-0.21
Cu	-0.76	-0.59	-0.54	-0.40	0.20	0.21
Fe	-0.76	-0.74	-0.69	0.42	-0.1	0.11
Hg	-0.69	-0.51	-0.47	0.28	0.24	0.17
Mn	-0.43	-0.29	-0.18	0.65	-0.067	-0.039
Ni	-0.47	-0.81	-0.69	0.35	-0.06	-0.019
Pb	-0.91	-0.59	-0.54	0.23	-0.12	-0.07
V	-0.54	-0.66	-0.61	0.32	-.14	-0.13
Zn	-0.69	-0.81	-0.76	0.12	0.16	0.11
Fine fraction	-0.61	-0.88	-0.83	0.58	0.53	0.55
TOC	-0.76	-0.74	-0.69	0.52	0.54	0.53
PAHs	-0.28	-0.29	-0.40	-0.08	-0.57	-0.46
Depth	-0.14	0.26	0.28	-0.51	-0.52	-0.54

4.2 Ecological risk-assessment

4.2.1 Ecological risk assessment based on the sediment quality guidelines

Heavy metal

In this study, the concentrations of heavy metals were compared with TEL and PEL values, and the PELq factor was used to estimate the toxic biological effects of heavy metals at different stations. PELq values were not estimated for Al, Fe, Mn, V and Co because these metals generally do not have toxic effects on biological communities in the environment (Hübner, et al., 2009; Vallejuelo, et al., 2010). **Table 4.13** shows a comparison between the heavy metal concentrations in the present study with background values in Klang Strait, igneous rock and guideline values (TEL and PEL). The mean concentrations for Zn, Ni, Cr and Cu were below the TEL value, and these compounds most likely have minimal toxic effects on biological communities in the studied region. Cd, Pb and Hg were found in the TEL and PEL range at which occasional toxic effects are expected. Only the As levels exceeded the PEL value, indicating highly toxic effects for biological organisms. In the present study, only the estimated Cd, Pb, Hg and As concentrations are significantly greater than the background and igneous rock values, while the concentrations of other metals were lower than these values.

Table 4.13. Comparison of heavy metal concentration in Klang strait with background, igneous rock and SQG ($\mu\text{g/g}$ dry weight) values

Concentration of heavy metals	Al	Fe	Mn	As	Cu	Cr	Cd	Pb	Ni	Hg*	V	Zn
Present study	14724.	6547.17	231.43	60.36	17.43	46.4	0.826	59.45	11.44	0.23	52.	51.05
Back ground value **	85100	41922	349.18	18.79	23.21	53.71	0.186	39.8	32.77	0.08	71.59	141.22
Igneous rock (Bowen, 1966)	82000	56300	950	1.8	55	100	0.2	12.5	75	0.08	135	70
SQG-based (Macdonald et al., 1996)												
TEL				7.24	18.7	52	0.68	30.2	15.9	0.13		124
PEL				41.6	108	160	4.2	112	42.8	0.7		271

*Mercury back ground value was estimated base on the concentration of igneous rock because there were no suffusion data in previous studies.

**Back ground value was estimated based on the previous studies from 1196 until 2007

The variation in estimated PELq values is shown in **Figure 4.19**. Three stations were considered to exhibit moderately toxic effects, including 16 and 17 (South Port) and 13 (West Port). The rest of the stations were considered to be slightly toxic. The dendrogram results allow for a better understanding of the patterns among the stations from the metal analyses **Figure 4.20**.

The dendrograms clearly classified the sampling stations into three clusters based on toxicity effects. All of the stations in first and second plot clusters are in the same range of slightly toxic effects ($0.1 < \text{PELq} < 0.5$). However, the average toxicity effects of heavy metals in the second cluster (stations 1, 3, and 15) were greater than those of the first cluster; the PELq values in second cluster were closer to 0.5 than the PELq values in the first cluster. The third cluster of the plot (cluster C), which includes stations 13, 16 and 17, exhibited a similar toxicity effect (moderately toxic). The average PELq of the third cluster was significantly different from those of the other stations.

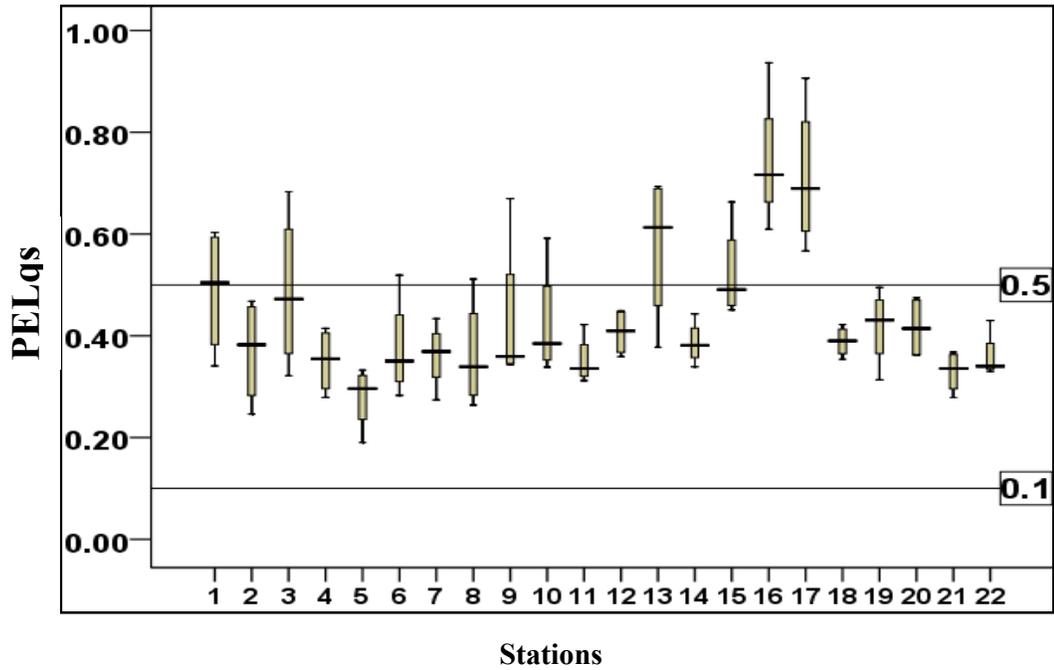


Figure 4.19, Box-Whisker Plots of PELqs values of Heavy metals at 22 stations (the whisker show the minimum and maximum concentration and the line of each plot is the medianvalue).
 PELq<0.1, non-toxic; 0.1<PELq<0.5, slightly toxic; 0.5<PELq<1.5, moderately toxic; PELq>1.5, highly toxic

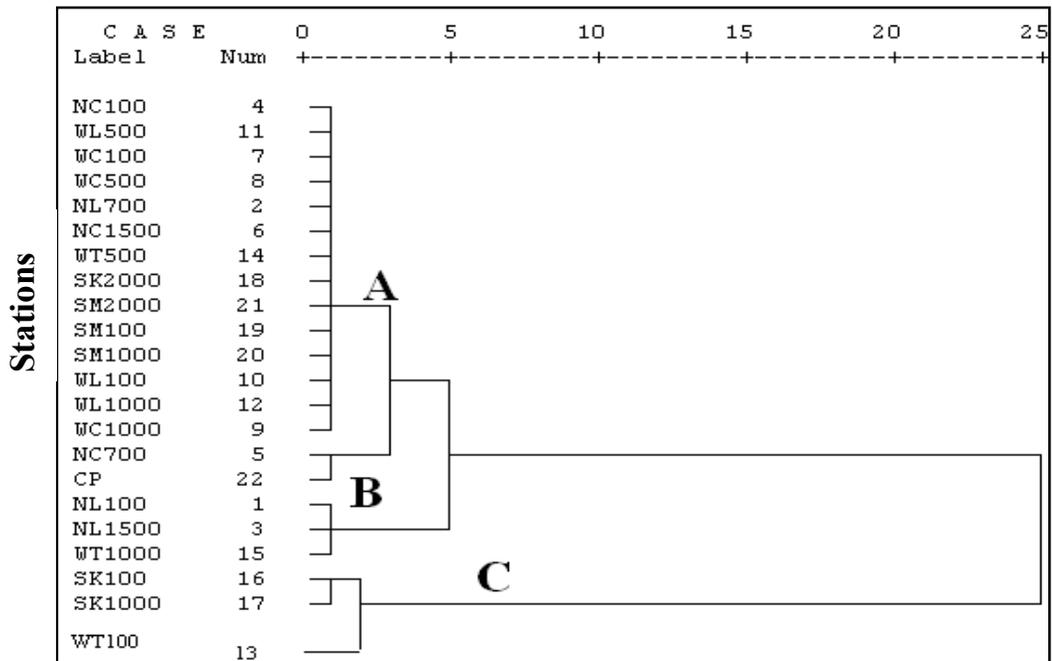


Figure 4.20, Cluster analysis to classify stations based on adverse biological effect of heavy metals in surface sediment

Polyaromatic hydrocarbons (PAHs)

In this study, two sets of sediment quality guidelines, including (a) the ERL/ERM and (b) the TEL/PEL values, were used for an ecological risk assessment of individual PAHs in surface sediments using three classifications of PAH concentrations: adverse biological effects are expected rarely ($<ERL/TEL$), occasionally ($PERL/TEL$ and $<ERM/PEL$), or frequently ($PERM/PEL$) (Long et al., 1995; Liu et al., 2009a).

The comparison of contamination levels with sediment-quality guidelines revealed that the concentrations of naphthalene, acenaphthene, and benzo(g,h,i)perylene were below their respective values (ERL/TEL) of SQGs at all of the stations, indicating that adverse biological effects are likely to occur rarely due to these compounds at all of the stations. Additionally, acenaphthylene and fluoranthene concentrations were below the ERL/TEL values at all of the stations except station 13.

The fluorene concentration at 87% of the stations (except stations 2, 6, 9, 15 and 22) suggested occasional adverse biological effects ($\geq ERL/TEL$ and $<ERM/PEL$). The fluorene concentration was above the ERM/PEL level only at stations 13 and 17, indicating that adverse biological effects are frequently likely to occur due to fluorene at these stations. The fluorene concentrations were below the ERL/TEL levels at the other stations.

For phenanthrene, the levels at stations 1, 7, 13 and 16 were higher than the TEL value, while at the other stations, the levels were below the ERL/TEL levels. These results suggest that adverse biological effects might occasionally occur at these stations.

For anthracene, the concentrations at most of the stations were lower than the PEL and ERM values, while the levels at 48% of the stations (2, 5, 6, 9, 10, 11, 12, 14 and 18) exceeded the TEL value, implying that these stations most likely have an intermediate level of contamination.

Moreover, the PEL level was exceeded at stations 7, 13 and 17, indicating that adverse biological effects may occur frequently at these stations. For pyrene, the levels at 73% of the stations were lower than the ERL/TEL values, while intermediate levels (\geq TEL) were found at the remaining stations (1, 5, 10, 12, 13 and 17).

Benzo(a)anthracene concentrations exceeded the ERM and PEL values only at stations 12,16 and 17, whereas the benzo(a)anthracene levels at 59% of the stations (1,4,7,9,10,11,13,15,16,20 and 21) were in the intermediate level (\geq TEL or \geq ERM), suggesting that these stations were occasionally associated with adverse biological effects in Klang Strait. The chrysene concentration was below the ERL/TEL values at all of the stations except for stations 16, 17 and 7, which contained levels higher than the TEL values. The concentrations of benzo(b)fluoranthene and benzo(k)fluoranthene at all of the stations were below the ERL values except for three stations with levels greater than the ERL values (stations 4 and 16 for benzo(b)fluoranthene and station 11 for benzo(k)fluoranthene). The concentration of benzo(a)pyrene at 64% of the stations was lower than the ERL/TEL levels, but its concentration at stations 8,19 and 20 exceeded the TEL values with occasional adverse biological effects. Additionally, the BaP level at stations 4, 13, 8 and 16 exceeded the PEL value, implying that BaP was likely to cause frequent adverse biological effects at these stations.

The dibenzo(a,h)anthracene concentration at all of the stations was below the ERL and TEL levels, except for at stations 4,9,12,15 and 21, where levels exceeded the ERL or TEL values, and station 4, where the concentration of dibenzo(a,h)anthracene exceeded PEL values and might cause frequent adverse effects on the biological communities at this station.

Therefore, most of the individual PAHs were likely to cause occasional or frequent adverse biological effects in the surface sediment of some of the stations, especially stations 13, 16, 17 and 7.

Apart from these compounds the lowest safe values were not defined for some PAHs with high molecular weights, such as indeno benzo[k]fluoranthene, [1,2,3-c,d]pyrene, benzo[b]fluoranthene and benzo[g,h,i]perylene. These PAHs are likely to cause toxic effects in marine environments (Feng et al. 2007). In Klang Strait, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene were estimated at some stations at levels that can cause mild toxic effects but will not cause serious biological effects in the sedimentary environment in Klang Strait.

The results obtained from the ecological risk assessment of PAHs in the surface sediments of Klang Strait are summarised in **Table 4.14**. These results were arranged based on the concentration of PAHs measured at 22 stations. Most of the PAHs, such as Nap, Ace, Phn, Fla, Pyr, Chy, BbF, BkF and BghiP, had $HQ < 1$ at all of the stations, and other PAHs (Acy, Flr, Ant, BaA, BaP, and DibA) had significantly $HQ > 1$ in some stations, such as 4, 7, 12, 13, 16 and 17, which are highlighted in **Table 4.15**.

In general, the risk assessment revealed that total PAHs are likely to cause slight adverse effects on the biological communities at stations 4, 7, 12, 16 and 17 because these stations showed $0.1 < PELq < 0.5$. Additionally, moderately adverse biological effects were shown for station 13 ($0.5 < PELq < 1.5$), but the rest of the stations showed rare adverse ecological effects due to the PAH exposure in surface sediments ($HQ < 0.1$).

A cluster analysis showed a better view of PAH contaminations and classified the stations into three groups, with station 13 completely separate from the other stations and stations 4, 16 and 17 arranged in the same group (cluster B) with the same range of toxic effects ($0.1 < PELq < 0.5$). The other stations are arranged in cluster A (**Figure 4.21**).

Table 4.14. Toxicity guidelines of PAH compounds for sediment matrices (ng/g dry weight%) and average concentrations in the surface sediments of Klang Strait (E.R Long, Ingersoll, & MacDonald, 2006; E.R. Long et al., 1995)

PAHs	ER-L	ER-M	TEL	PEL
Nap	160	2100	34.6	391
Ace	44	640	5.87	128
Acy	16	500	6.71	88.9
Flu	19	540	21.2	144
Phe	240	1500	86.7	544
Ant	853	1100	46.9	245
Fla	600	5100	113	1494
Pyr	665	26000	153	1398
BaA	261	16000	74.8	693
Chr	384	2800	108	846
BbF	320	1880	-	-
BkF	280	1620	-	-
BaP	430	1600	88.8	763
InP	-	-	-	-
DibA	63.4	260	6.22	135
BghiP	430	1600	-	-
Total PAHs	4022	44792	1684	16770

ERL: effects range-low; ERM: effects range-median;
 TELs: threshold effects level; PELs: probable effects level

Table 4.15, Ecological risk calculated for individual PAHs in surface sediment of different stations

Stations	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BeA	Chy	BbF	BkF	BaP	DibA	BghiP	PELq
1	ND	ND	0.02	0.23	0.08	0.36	ND	0.41	0.8	ND	ND	ND	ND	0.00	ND	0.11
2	ND	ND	0.00	0.07	0.02	0.05	ND	0.09	0.05	ND	ND	ND	ND	0.00	ND	0.02
3	ND	ND	0.06	0.82	0.16	0.24	0.03	0.04	0.00	ND	ND	ND	ND	0.00	ND	0.09
4	ND	ND	ND	0.01	0.02	0.24	0.01	0.01	0.10	0.06	0.45	ND	1.96	1.41	ND	0.28
5	ND	ND	ND	0.12	0.02	0.05	0.01	0.14	ND	ND	0.01	ND	ND	ND	ND	0.02
6	0.01	ND	ND	0.40	0.07	0.15	0.02	0.02	0.26	ND	ND	ND	ND	ND	ND	0.06
7	0.00	ND	ND	0.19	0.23	1.09	0.01	0.01	0.29	ND	ND	0.03	ND	ND	ND	0.12
8	0.01	ND	0.01	0.27	0.01	0.29	0.01	0.01	0.07	ND	ND	ND	0.16	ND	0.04	0.06
9	ND	ND	ND	0.05	0.01	0.03	ND	0.02	0.28	0.23	ND	ND	ND	0.50	ND	0.08
10	ND	ND	ND	0.16	0.01	0.04	ND	0.17	0.40	ND	ND	ND	ND	ND	ND	0.05
11	ND	ND	0.01	0.34	0.03	0.15	0.01	0.02	0.04	ND	ND	0.23	ND	ND	ND	0.06
12	ND	ND	0.01	0.28	0.05	0.95	0.01	0.24	1.12	ND	ND	ND	ND	0.05	ND	0.18
13	0.04	7.26	0.12	4.31	0.41	1.26	0.11	0.17	0.56	ND	0.01	0.02	1.08	ND	0.03	1.03
14	0.01	ND	ND	0.23	0.14	0.74	0.01	0.01	0.21	ND	0.01	ND	0.08	ND	ND	0.10
15	0.01	ND	ND	0.06	0.02	0.02	0.00	0.00	0.11	ND	0.01	ND	0.00	0.96	ND	0.08
16	0.28	ND	0.01	0.84	0.12	0.41	0.06	0.07	1.41	0.14	ND	ND	1.07	ND	ND	0.30
17	0.02	ND	0.03	1.57	0.17	2.45	0.00	0.16	2.15	0.65	ND	ND	0.00	ND	ND	0.48
18	ND	ND	ND	0.14	0.02	0.05	0.00	0.09	0.28	ND	0.20	ND	0.00	ND	ND	0.05
19	0.01	ND	ND	0.25	0.07	0.14	0.01	0.01	0.39	ND	0.01	ND	0.14	ND	ND	0.07
20	0.01	ND	ND	0.26	0.07	0.12	0.01	0.01	0.33	ND	0.00	ND	0.12	ND	ND	0.06
21	0.01	ND	ND	0.25	0.03	0.07	0.01	0.01	0.26	ND	0.01	ND	0.00	0.96	ND	0.1
22	ND	ND	ND	0.09	0.00	0.02	0.00	ND	0.08	ND	0.01	ND	0.00	ND	ND	0.01
Mean	0.02	0.33	0.01	0.50	0.08	0.41	0.01	0.08	0.42	0.05	0.03	0.01	0.21	0.18	ND	0.16

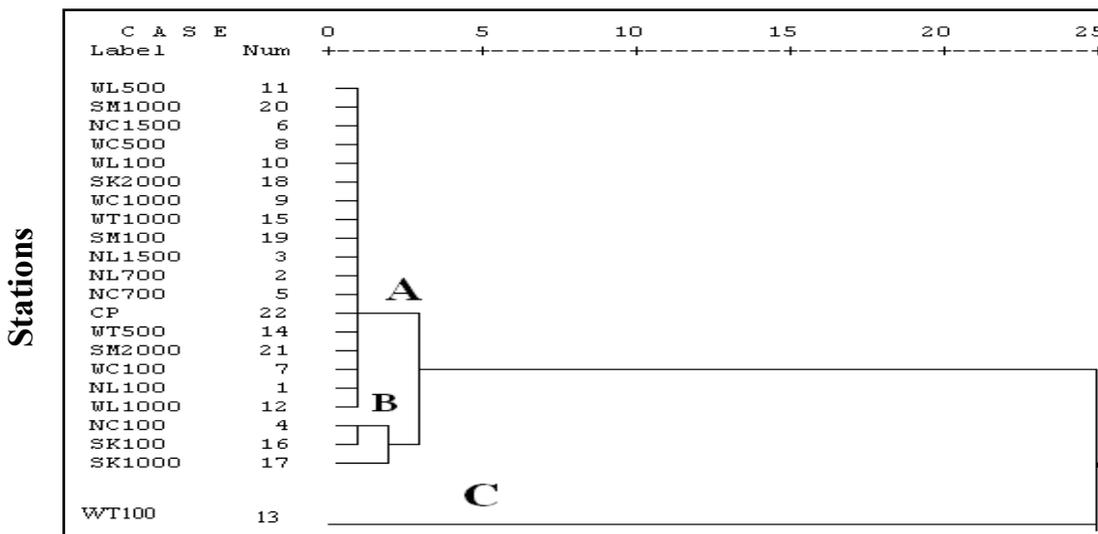


Figure 4.21, Cluster analysis to classify stations based on adverse biological effect of PAHs in surface sediment

4.2.2 Ecological risk assessment based on method of Lars Hakanson

In this section, the sedimentological toxic factor (St^i -value) and the potential ecological risk index Er^i for different heavy metals were determined using several estimations. According to the method in chapter 3, the St^i -value was determined based on the relative-abundance and sink-effect factors, which are the primary effective factors that control the degree of toxicity in sediments. The natural concentrations of metals in several ecological and biological media are given in **Table 4.16**, to review the results provided in this context. The value 1.0 was given to the metal with the highest average concentration, and the results were ranked in **Table 4.18**.

Table 4.17 is useful to compare the concentrations of these seven metals; for example, the average concentration of Cd is 500 times lower than the corresponding value for Cr in igneous rocks. The highest value (marked with **) in Table 4.18 had been omitted for all of the metals to balance the effect of extreme abundance numbers. The abundance number was determined by dividing 4.4 (for Zn) by the sum the remaining abundance numbers.

Table 4.16, Concentration of heavy metals (mg/kg dry weight%) in different medias (Bowen, 1966; Pawlisz, Kent, Schneider, & Jefferson, 1997)

Metals	Igneous rocks	Soil	Sea water	Marine sediment	Mussel
Cd	0.2	0.06	0.00011	1.1	1
Cr	100	100	0.00005	31	1
Cu	55	20	0.003	25	20
Hg	0.08	0.03-0.8	0.00003	0.1	0.5
As	1.8	6	0.003	4.2	1.4
Pb	12.5	10	0.0003	23	2
Zn	70	50	0.01	65	70

Table 4.17, Abundance of heavy metals in different media

Metals	Igneous rocks	Soil	Sea water	Mussel	Marine Sediment	\sum_1^{4*}	Abundance number
Cd	500	1667**	90.90	70	59	719.90	163.61
Cr	1	1	200*	70	2	74	16.8
Cu	1.8	5*	3.33	3.5	3	11.8	2.68
Hg	1250**	240	333	140	650	1363	309.7
As	56**	17	3.33	50	15	85.33	19.39
Pb	8	10	33	35*	3	54	12.27
Zn	1.4	2*	1	1	1	4.4	1

- Highest value- not determined in column marked \sum_1^{4*} .
- ** highest value for each metal

It is necessary, determining the sink factor to assess ecologic risk because this factor can help to evaluate the “fingerprint” of substance in the sediment. For example, according to the **Table 4.18**, Cr and Pb showed the lowest sink factor, which indicates that these elements cause the highest fingerprint in the sediment with high tendency to be deposited in the sediment. Cd shows the highest sink factor which means that Cd gives the lowest fingerprint in sediment and may be it has high concentration in the water compared to the sediment (**Table 4.18**).

Table 4.18, Determination of the sink-factor, sediment-logical toxic factors (St^i) and toxic-respond factor (Tr^i) for metals in the Klang Strait

Metals	Back ground water (mg/l)	Back ground sediment in this study(mg/kg)	*Sink factor	Sink factor × abundance number	** St^i -Value Klang Strait	St^i -Value Hakanson	Tr^i -Value
Cd	0.00	0.19	0.59	163.60	37.00	30.00	$37 \times \sqrt{5} / \sqrt{BPI}$
Cr	0.00	5.71	0.01	0.36	2.00	2.00	$2 \times \sqrt{5} / \sqrt{BPI}$
Cu	0.00	23.21	0.13	0.37	2.00	5.00	$2 \times \sqrt{5} / \sqrt{BPI}$
Hg	0.00	0.08	0.38	112.70	40.00	40.00	$40 \times 5 / BPI$
As	0.00	18.79	0.16	2.82	7.00	10.00	$7 \times \sqrt{5} / \sqrt{BPI}$
Pb	0.00	39.80	0.01	0.07	1.00	5.00	$1 \times \sqrt{5} / \sqrt{BPI}$
Zn	0.01	141.22	0.07	0.07	1.00	1.00	$1 \times \sqrt{5} / \sqrt{BPI}$
PAHs***	-	-	-	-	-	40	$40 \times BPI / 5$

*it is calculated by dividing natural background value for marine water into background value for marine sediment in this study and multiplied in 1000.

** It is calculated by dividing correct abundance number into element with low correct abundance ($Zn=0.07$) and the square-root was taken from these figures and the values also rounded.

**** St^i - Value for PAHs was calculated according to the Hakanson method which was calculated for organic compounds (PCB and PAHs) because there was not any back ground data of PAHs in study area.

In the fourth column in **Table 4.18**, the sink factor was multiplied by the abundance number to correct the abundance number values with a high sink factor and weak fingerprint. Additionally, Cd and Hg had St^i -values that were too high compared to those of the other metals. The BPI value should be determined to evaluate the potential ecological risk factor (Er) for these substances. According to the methodology, BPI is defined as “the N-content on the regression line for IG=10%.” The N-content was given as %ds (dry substance), and the IG content was given in mg/g (ds) (**Figure 4.22**). In this research, the value of BPI was equal to 3.8 based on the linear regression equation.

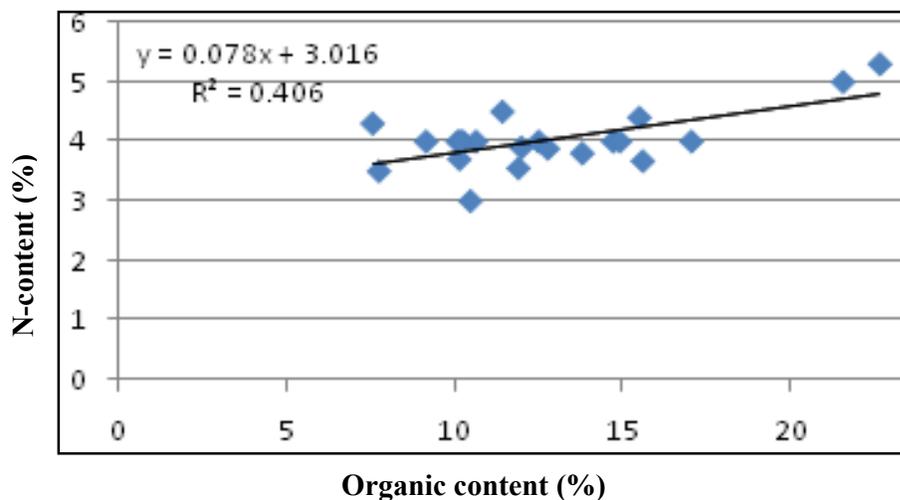


Figure 4.22, Relationship between the organic content and N-content in the Klang Strait

The results of the ecological risk assessment are summarised in **Table 4.19**. The potential ecological risk values for all of the metals except Hg and Cd were estimated as low ($Er^i < 40$) at all of the stations (**Figure 4.22**).

The Er^i -values for Hg and Cd were significantly greater than those of the other metals and varied between moderate levels and high levels of potential ecological risk at all of the stations except the control point. In this study, the potential risk value for all of the contaminants ranked in the following sequence: Cd > Hg > As > Cr > Pb > Cu > Zn (**Figure 4.23**). The values of the risk index (RI) revealed that most of the stations (1-4, 5,6, 9-12, 18 and 21) are at moderate ecological risk, and stations 7, 8, 13, 14, 15, 19 and 20 were at considerable ecological risk. Stations 16 and 17 were in very high risk and only station 22 (the control point) was at low risk. Moreover, the statistical tests showed that there was a significant difference ($p < 0.05$, $df = 21$) in the Er^i -values and RI among the different stations. The cluster analysis was used to categorise stations into 4 different ranges of ecological risk value (**Figure 4.24**). The stations arranged in cluster A is in the same range of ecological risk ($300 < IR < 600$) while cluster B includes stations are in moderate risk ($150 < IR < 300$).

According to the statistical tests, the risk values of stations 22 (cluster C) and 16 and 17 (cluster D) are significantly separated from other stations. Stations 16 and 17 are in very high level of risk ($RI > 600$) and only station 22 (the control point) is in the low range ($IR < 150$) of ecological risk.

Table 4.19, Risk factor (Er^i – value) and risk indices (RI-value) for investigated 22 stations in the Klang Strait

Stations	As $St^i = 6$	Cu $St^i = 2$	Cr $St^i = 2$	Cd $St^i = 48$	Pb $St^i = 1$	Hg $St^i = 40$	Zn $St^i = 1$	PAHs $St^i = 1$	$IR = \sum_{i=1}^8 Er^i$
1	28.18	0.43	1.67	158.17	1.47	91.20	0.37	27.99	294.11
2	22.48	0.42	1.40	113.21	1.2	66.55	0.25	3.62	225.11
3	28.40	0.42	1.68	133.25	1.72	83.23	0.40	7.11	293.82
4	14.17	0.34	1.51	114.51	1.34	68.35	0.33	45.24	299.94
5	12.73	0.31	1.14	112.13	1.19	70.75	0.30	4.23	245.21
6	18.09	0.44	1.42	126.21	1.23	84.53	0.36	7.42	285.6
7	13.34	0.51	2.21	165.75	1.38	272.07	0.35	12.46	448.47
8	19.23	0.40	1.77	131.08	1.32	121.40	0.26	8.33	323.03
9	25.38	0.41	1.84	130.54	1.29	87.55	0.26	9.03	287.8
10	25.14	0.42	1.40	162.50	1.45	107.95	0.27	11.14	201.53
11	17.75	0.47	1.36	197.71	1.36	139.37	0.23	9.64	224.64
12	18.74	0.38	1.77	204.21	1.46	133.15	0.25	25.83	298.59
13	35.11	0.30	2.28	193.38	1.81	150.00	0.35	63.19	446.66
14	22.01	0.34	1.61	138.13	1.34	115.02	0.24	10.22	309.74
15	29.18	0.33	1.73	182.00	1.8	140.83	0.28	10.58	434.50
16	42.03	0.41	2.82	225.33	2.16	213.17	0.90	44.51	631.93
17	39.49	0.40	2.57	206.92	2	189.77	0.90	57.04	611.11
18	15.79	0.29	1.69	140.83	1.88	84.72	0.37	13.02	287.88
19	25.26	0.33	1.88	131.08	1.28	100.83	0.37	9.37	313.90
20	18.73	0.42	1.79	138.67	1.71	108.75	0.38	8.29	324.15
21	14.98	0.36	1.56	123.50	1.32	80.00	0.34	8.61	208.45
22	10.27	0.33	0.70	94.79	0.78	50.70	0.21	1.81	75.40
Mean	22.56	0.38	1.71	151.54	1.48	117.41	0.36	18.35	323.53
SD	11.3	0.12	0.52	50.57	0.48	40.2	0.22	18.2	120.6
Min	10.27	0.31	0.70	94.79	0.78	50.7	0.21	1.81	75.4
Max	42.03	0.51	2.82	206.92	2.16	231.17	0.9	63.19	631.93

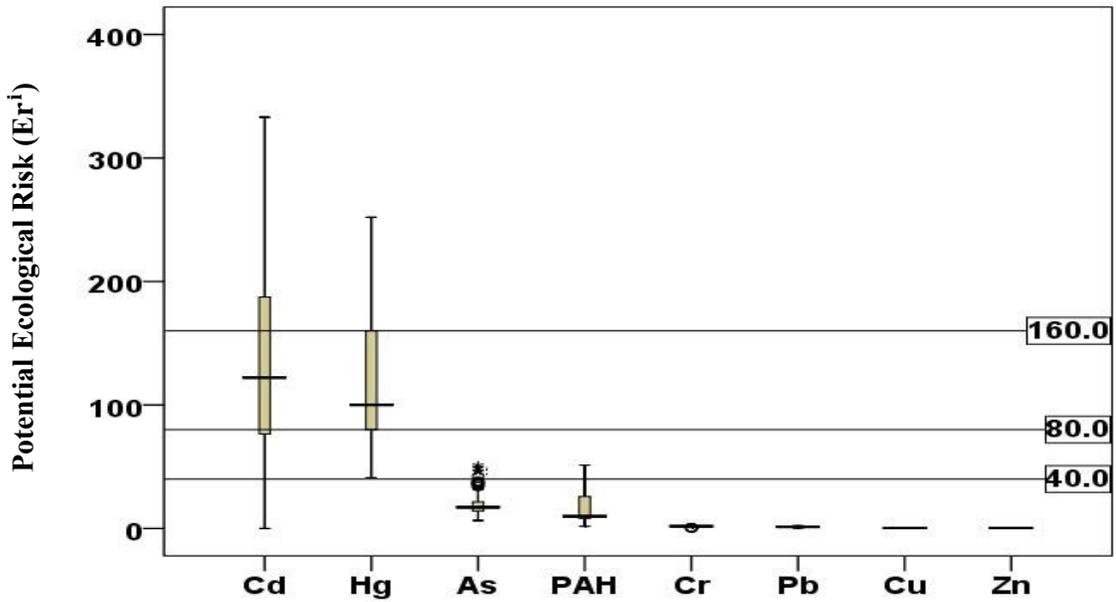


Figure 4.23, Box-Whisker plots of the potential ecological risk (Er^i) variation for metals and PAHs in Klang Strait (The whisker shows the minimum and maximum concentration and the line of each plot is the mean value)

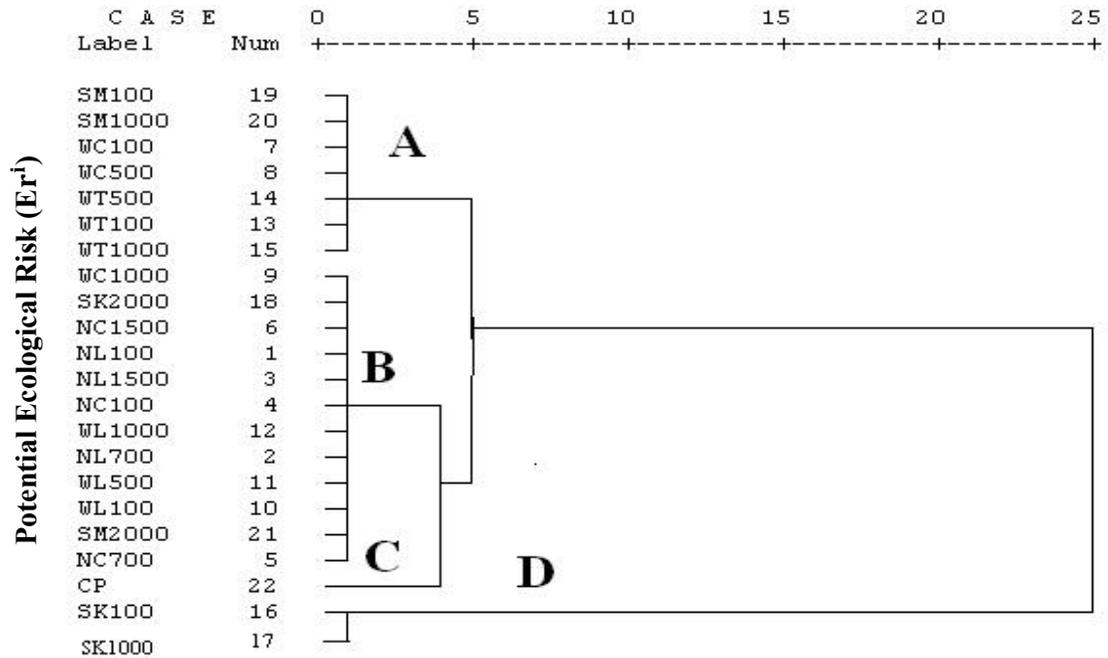


Figure 4.24, Cluster analysis to classify stations based on ecological risk values in Klang Strait

4.3 Water-quality assessment

In the marine environment, a comprehensive assessment of water quality should include the monitoring of hydrological, physicochemical, and biological variables. Information about these properties can provide meaningful and practical conclusions to water-quality monitoring because of the direct effect of the properties on chemical components and biological communities (EPA, October 2001).

4.3.1 Hydrological parameters

All coastal water bodies are influenced by other sources, from atmospheric to marine, via the hydrological cycle, hydrodynamic activities, river discharge, and underground transport; these systems are directly inter-connected. Thus, complete interpretations of water quality assessments are strongly dependent upon knowledge of hydrology and hydrodynamic properties, such as variations of rainfall and river discharge (stream flow), suspended loads, climatic conditions, size of water bodies, and tidal flow (Brooks et al., 2011; Ficklin, Luo, Stewart, & Maurer, 2012; Yahya, Rahman, & Abbasi, 2012).

Tidal circulation is semidiurnal in the Klang Strait; the level of the surface water rises and falls with an average range of 1.4 m to 4.2 m within approximately 12.5 hours, depending on the position of the sun and moon(Yap, 2005). The seasonal alternation between the northeast monsoon (November to March) and southeast monsoon (May to September) causes the main rainfall pattern along the Klang Strait.

In general, the beginning of the northeast monsoon occurs between the 11th and 20th of November, and heavy rainfall usually occurs in the early part of the monsoon season (Cheang, 1988).

The southwest monsoon occurs from May until August and causes a decrease in rainfall. During the monsoon break, which is often between July and September, heavy rainfall occurs because of converging low-level winds from the east or southeast with the south westerly winds from the Bay of Bengal and Sumatra (Yap, 2005). The details of the annual rainfall and river discharges in Klang Strait were described in section 3.1.2.

In the present study, the northeast monsoon (rainy season) started in November 2009 and lasted until March 2010. The southwest monsoon (dry season) started from June 2010 until October 2010, and the monsoon break was observed at the end of the September, with an increase of daily rainfall (280 mm). April and May were considered as the inter-monsoon period with a high amount of daily rainfall.

During the present study, the monthly average rainfall ranged from a minimum of 190 mm in August to a maximum of 410 mm in April and May; the average was 266.91 mm, while the annual rainfall was 236.25 mm. November, April and May were the months with the greatest number of rainy days (**Figure 4.25**).

Other researchers have reported that the river discharge at Klang Strait is highly correlated with rainfall patterns, and as expected, the maximum river discharges were measured in November 2009 and April and May 2010.

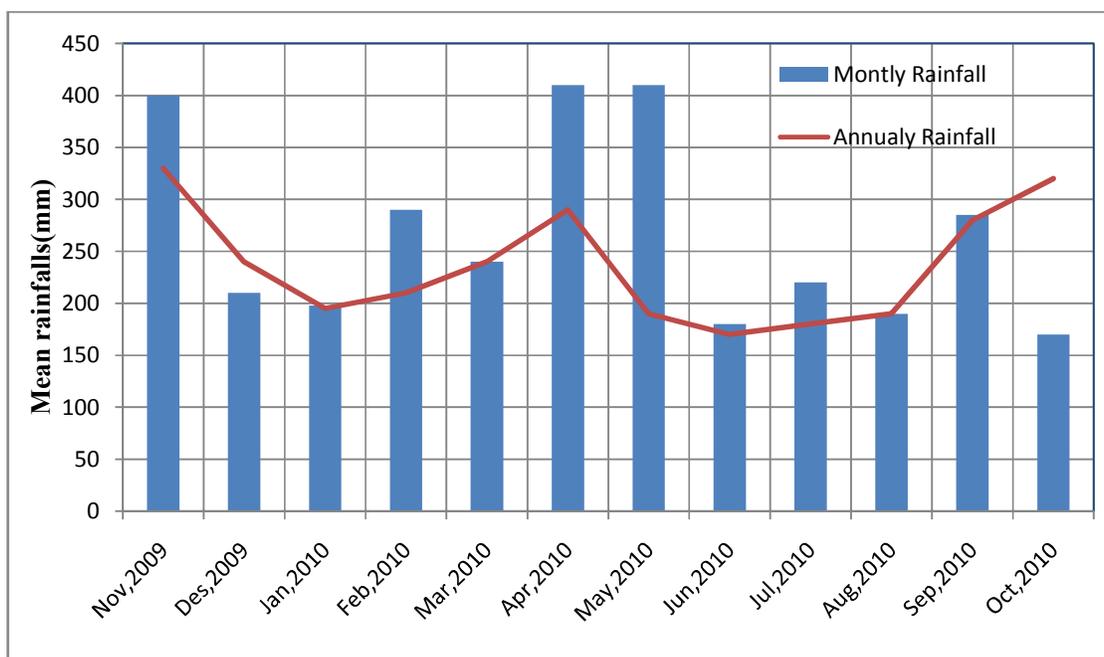


Figure 4.25, Monthly and annual mean rainfalls (mm) from November 2009 until November 2010 in Klang Strait

4.3.2 Physical and chemical parameters

Water quality data from 22 stations during 12 months of sampling are summarised in **Table 4.20** and **Table 4.21**. All of the physicochemical parameters showed significant differences ($P < 0.05$) in the observed spatial and temporal scales based on the Kruskal-Wallis test (**Table 4.22**), and only temperature presented insignificant differences on a spatial scale.

To better understand the temporal and spatial variation, the water quality was described according to the different sites. The coast of Klang Strait was divided into four discrete hydrochemical sites (i.e., North Port, South Port, West Port and the control point), which exhibited specific characteristics of water quality that depended on the relative significance of local/regional marine/land controls as well as the type and intensity of anthropogenic activities conducted at each of the sites.

Generally, on the spatial scale, the water quality parameters significantly different among the different sites, and a Duncan test showed that water quality Parameters (except temperature) at South Port and control point were not homogenous

with those of the other sites (North Port and West Port). There were no clear significant differences of water quality between West Port and North Port, and only nitrite (NO_2^-) and silicate (SiO_4^{4-}) had varied significantly (**Table 4.23**).

The control area was characterised by the lowest concentrations of nutrients, total solids and chlorophyll *a* (*chl-a*) in comparison with other sites, and the range in values of salinity, dissolved oxygen (DO), oxygen saturation (O_2sat) and water transparency (Secchi depth) was higher in other areas. South Port was characterised by the highest concentration of nutrients (except for silicate) and total solids, while the lowest levels of salinity, dissolved oxygen, oxygen saturation and water transparency were found at this site.

Table 4.20, Statistical description of physical parameters

	T (°C)	pH	Salinity (%)	Shecchi depths (m)	TS (mg/l)	DO (mg/l)	O ₂ sat (%)	Current (Knot)
1.Mean	30.27	8.05	30.15	64.50	69.26	6.31	97.58	13.59
SD	0.95	0.13	1.51	24.05	13.12	0.56	11.47	0.29
Min	29.01	7.82	27.29	34.00	49.47	4.98	72.00	13.09
Max	31.67	8.39	32.29	114.00	89.08	7.07	114.00	14.14
2.Mean	30.25	8.00	30.81	74.53	68.78	6.26	99.14	13.50
SD	0.95	0.08	1.52	24.88	13.17	0.56	11.68	0.26
Min	28.99	7.82	27.90	35.00	47.45	5.04	73.00	13.06
Max	31.64	8.15	33.09	118.00	88.51	7.09	115.00	13.94
3.Mean	30.29	8.09	31.24	48.06	72.26	6.14	93.97	13.02
SD	0.98	0.11	1.71	13.71	11.84	0.58	11.38	0.33
Min	28.78	7.91	27.89	30.00	53.56	4.93	71.00	12.53
Max	31.76	8.29	33.79	78.00	89.19	6.98	113.00	13.64
4.Mean	30.09	8.08	30.81	62.08	65.32	6.21	95.86	13.13
SD	0.94	0.17	1.82	25.48	18.19	0.57	12.69	0.41
Min	28.43	7.82	27.10	30.00	39.36	4.99	68.00	12.53
Max	31.51	8.46	33.33	111.00	89.96	7.05	115.00	13.94
5.Mean	30.19	8.02	31.02	72.06	64.23	6.28	98.83	13.26
SD	1.00	0.08	1.61	27.42	19.01	0.57	12.89	0.37
Min	28.64	7.82	27.90	30.00	39.43	5.09	70.00	12.74
Max	31.70	8.16	33.39	123.00	88.65	7.12	117.00	13.94
6.Mean	30.25	8.11	31.36	46.67	71.11	6.03	93.25	13.40
SD	1.01	0.13	1.73	16.54	15.44	0.58	12.73	0.27
Min	28.72	7.96	27.90	29.00	46.87	4.9	66.00	12.88
Max	31.75	8.42	33.83	81.00	92.12	6.92	113.00	13.94
7.Mean	30.08	8.09	30.86	61.81	65.86	6.09	96.08	13.47
SD	0.96	0.10	1.70	28.30	22.18	0.58	14.54	0.25
Min	28.45	7.96	27.79	22.00	37.36	4.69	61.00	13.05
Max	31.53	8.33	33.33	118.00	93.79	6.93	112.00	13.84
8.Mean	30.17	8.01	30.98	71.97	63.73	6.33	98.86	13.47
SD	0.98	0.05	1.64	23.99	20.25	0.53	14.47	0.32
Min	28.57	7.93	27.90	37.00	37.43	5.2	64.00	12.85
Max	31.63	8.09	33.39	119.00	89.57	7.1	115.00	14.04
9.Mean	30.16	8.07	30.86	46.89	71.31	5.8	88.64	13.17
SD	1.03	0.10	1.44	16.55	19.44	0.55	12.94	0.26
Min	28.62	7.95	28.10	23.00	45.87	4.6	59.00	12.77
Max	31.60	8.25	32.83	85.00	93.01	6.7	110.00	13.64
10.Mean	30.06	8.04	30.44	66.78	63.63	6.195	99.25	13.60
SD	0.98	0.10	1.45	20.19	20.86	0.56	13.70	0.29
Min	28.45	7.89	27.68	26.00	36.60	4.96	72.00	13.16
Max	31.53	8.33	32.53	100.00	91.34	7.09	115.00	14.14
11.Mean	30.14	8.00	30.58	68.69	63.93	6.26	100.36	13.54
SD	1.02	0.08	1.47	22.96	20.97	0.65	14.43	0.27
Min	28.58	7.82	27.88	23.00	36.60	5.030	72.00	13.09
Max	31.64	8.14	32.60	106.00	94.37	7.18	116.00	14.04

Table 4.22 (Continued)

	T (°C)	pH	Salinity (‰)	Shecchi depths (m)	TS (mg/l)	DO (mg/l)	O ₂ sat (%)	Current (Knot)
12.Mean	30.06	8.04	30.75	57.81	70.35	6.072	96.06	13.39
SD	1.10	0.09	1.48	16.00	16.30	0.621	12.33	0.25
Min	28.18	7.95	27.90	26.00	48.70	4.82	71.00	13.08
Max	31.68	8.26	32.80	82.00	94.87	7.050	114.00	13.84
13.Mean	29.94	7.97	30.51	63.33	75.88	6.28	100.97	13.22
SD	1.03	0.10	1.48	22.20	9.26	0.59	12.92	0.32
Min	27.80	7.80	27.77	17.00	60.10	5.05	74.00	12.50
Max	31.23	8.20	32.53	94.00	95.37	7.08	115.00	13.74
14.Mean	30.16	7.96	30.63	65.28	74.15	6.37	103.53	13.33
SD	1.03	0.06	1.44	21.07	10.26	0.60	12.28	0.30
Min	28.10	7.85	28.00	24.00	56.15	5.13	77.00	12.79
Max	31.53	8.05	32.63	94.00	88.89	7.17	116.00	13.84
15.Mean	30.15	8.01	30.77	57.33	95.63	6.25	96.83	12.91
SD	1.07	0.04	1.46	20.94	28.81	0.60	11.89	0.24
Min	28.12	7.92	28.10	24.00	66.35	5.03	71.00	12.60
Max	31.54	8.09	32.80	90.00	145.45	7.050	112.00	13.44
16.Mean	29.79	8.02	26.10	27.69	134.97	5.510	81.78	13.17
SD	0.97	0.12	0.77	19.32	11.58	0.47	8.77	0.31
Min	27.69	7.87	24.46	8.00	109.40	4.32	66.00	12.44
Max	31.11	8.50	27.18	90.00	154.00	6.00	93.00	13.61
17.Mean	29.99	8.00	26.12	25.36	117.68	5.49	81.67	13.18
SD	0.97	0.08	0.80	5.67	20.33	0.478	8.53	0.41
Min	28.22	7.89	24.04	10.00	84.40	4.32	68.00	12.37
Max	31.33	8.20	27.34	34.00	144.19	6.00	93.00	14.10
18.Mean	30.02	8.05	30.11	49.51	108.96	6.46	96.86	13.43
SD	0.98	0.05	1.29	15.19	29.63	0.56	13.40	0.28
Min	28.22	7.95	27.40	3.30	50.39	4.80	69.00	12.93
Max	31.44	8.13	31.98	75.00	155.29	6.86	111.00	13.94
19.Mean	30.10	8.09	29.45	39.44	117.62	5.82	92.69	13.12
SD	0.99	0.10	0.63	9.81	19.56	0.45	7.97	0.22
Min	28.36	8.00	28.00	20.00	71.64	4.78	70.00	12.72
Max	31.48	8.37	30.33	60.00	138.70	6.26	105.00	13.37
20.Mean	30.10	8.09	29.54	42.03	118.63	5.834	93.08	13.13
SD	0.99	0.10	0.67	8.77	19.01	0.470	7.79	0.22
Min	28.34	7.98	28.17	22.00	71.86	4.80	78.00	12.72
Max	31.48	8.38	30.53	58.00	136.78	6.35	107.00	13.37
21.Mean	30.26	8.03	30.50	52.67	66.96	6.18	99.97	13.46
SD	0.95	0.05	1.07	10.36	12.83	0.51	10.08	0.27
Min	28.43	7.95	28.04	30.00	53.67	5.17	81.00	13.01
Max	31.58	8.14	31.98	70.00	99.70	7.02	112.00	13.94
22.Mean	30.17	8.03	31.30	159.00	46.41	6.68	105.67	13.39
SD	1.08	0.06	1.62	25.06	4.83	0.42	11.00	0.44
Min	28.07	7.93	28.08	110.00	40.00	5.84	83.00	12.57
Max	31.76	8.13	33.92	212.00	57.89	7.22	118.00	14.14
Average	30.12	8.04	30.22	60.16	80.30	6.10	95.95	13.31
SD	0.99	0.10	1.97	32.16	29.25	0.64	13.17	0.36
Min	27.69	7.80	24.04	3.30	36.60	4.32	59.00	12.37
Max	31.76	8.50	33.92	212.00	155.29	7.22	118.00	14.14

Table 4.21, Statistical description of chemical parameters

	NO_3^- (mg/l)	NO_2^- (mg/l)	NH_3 (mg/l)	NH_4^+ (mg/l)	DIN (mg/l)	PO_4^{3-} (mg/l)	SiO_4^{4-} (mg/l)	$Chl-a$ (μ l)
1.Mean	0.76	0.015	0.055	0.542	1.32	0.108	4.38	8.16
SD	0.16	0.008	0.030	0.131	0.22	0.035	2.19	5.12
Min	0.45	0.004	0.020	0.242	0.87	0.052	1.00	3.65
Max	1.20	0.028	0.140	0.785	1.70	0.157	8.18	19.2
2.Mean	0.51	0.009	0.045	0.467	0.99	0.096	3.99	6.20
SD	0.19	0.004	0.023	0.115	0.29	0.038	1.92	2.88
Min	0.23	0.004	0.019	0.238	0.58	0.037	1.20	3.64
Max	1.10	0.017	0.120	0.792	1.91	0.157	6.98	14.6
3.Mean	0.80	0.014	0.065	0.618	1.43	0.117	3.39	7.64
SD	0.16	0.005	0.034	0.070	0.21	0.041	1.34	3.57
Min	0.53	0.007	0.021	0.496	1.04	0.060	1.20	3.85
Max	1.07	0.023	0.156	0.725	1.75	0.201	5.90	15.60
4.Mean	0.87	0.016	0.061	0.621	1.51	0.142	8.96	7.84
SD	0.42	0.006	0.036	0.160	0.55	0.057	3.46	4.09
Min	0.39	0.005	0.022	0.423	0.83	0.053	2.60	3.80
Max	1.78	0.024	0.166	0.990	2.51	0.280	16.40	14.78
5.Mean	0.53	0.009	0.046	0.500	1.04	0.103	6.10	6.20
SD	0.21	0.004	0.020	0.110	0.32	0.045	2.74	2.86
Min	0.30	0.004	0.019	0.376	0.69	0.037	2.10	3.40
Max	0.98	0.017	0.086	0.730	1.73	0.206	12.00	12.60
6.Mean	0.85	0.016	0.065	0.644	1.51	0.120	5.32	8.81
SD	0.20	0.005	0.034	0.100	0.29	0.046	2.65	4.80
Min	0.56	0.009	0.024	0.511	1.08	0.066	1.90	3.76
Max	1.32	0.023	0.156	0.906	2.24	0.223	12.30	17.20
7.Mean	0.70	0.009	0.068	0.578	1.29	0.110	8.72	7.42
SD	0.16	0.007	0.033	0.089	0.24	0.036	4.02	3.64
Min	0.29	0.001	0.033	0.371	0.68	0.041	1.90	3.36
Max	1.04	0.024	0.176	0.715	1.72	0.168	17.00	14.50
8.Mean	0.45	0.011	0.045	0.448	0.91	0.090	8.36	6.49
SD	0.17	0.006	0.017	0.077	0.23	0.026	3.83	3.17
Min	0.18	0.001	0.021	0.314	0.51	0.037	3.10	2.00
Max	0.82	0.026	0.090	0.544	1.31	0.161	14.50	11.50
9.Mean	0.73	0.012	0.062	0.585	1.32	0.125	7.01	9.92
SD	0.17	0.007	0.031	0.079	0.24	0.066	3.26	5.66
Min	0.40	0.003	0.032	0.428	0.85	0.066	2.20	3.74
Max	1.20	0.025	0.140	0.715	1.87	0.283	12.80	18.90
10.Mean	0.94	0.012	0.061	0.659	1.61	0.114	9.64	4.94
SD	0.44	0.007	0.033	0.116	0.50	0.042	2.65	1.48
Min	0.29	0.002	0.021	0.371	0.69	0.052	4.10	2.10
Max	2.24	0.030	0.160	0.854	2.92	0.213	15.20	8.20
11.Mean	0.57	0.012	0.045	0.475	1.05	0.084	7.22	5.55
SD	0.34	0.006	0.023	0.107	0.39	0.036	2.60	2.75
Min	0.18	0.006	0.011	0.314	0.51	0.041	2.40	3.14
Max	1.54	0.026	0.090	0.683	1.95	0.173	12.30	13.50

Table 4.23 (Continued)

	NO_3^- (mg/l)	NO_2^- (mg/l)	NH_3 (mg/l)	NH_4^+ (mg/l)	<i>DIN</i> (mg/l)	PO_4^{3-} (mg/l)	SiO_4^{4-} (mg/l)	<i>Chl-a</i> (μ l)
12.Mean	0.94	0.012	0.060	0.689	1.64	0.121	8.63	9.22
SD	0.24	0.006	0.036	0.127	0.36	0.037	3.59	4.45
Min	0.40	0.003	0.032	0.428	0.85	0.060	3.80	4.10
Max	1.39	0.024	0.140	0.943	2.35	0.185	16.00	16.97
13.Mean	0.99	0.014	0.034	0.765	1.77	0.118	12.71	7.15
SD	0.36	0.007	0.016	0.234	0.55	0.030	4.75	3.46
Min	0.08	0.007	0.010	0.305	0.43	0.056	5.40	2.20
Max	1.71	0.028	0.069	1.070	2.50	0.200	22.90	14.80
14.Mean	0.62	0.011	0.038	0.537	1.17	0.085	9.22	5.96
SD	0.25	0.005	0.017	0.124	0.35	0.038	2.98	2.42
Min	0.05	0.005	0.019	0.211	0.47	0.037	4.30	1.80
Max	1.04	0.021	0.072	0.761	1.81	0.175	17.00	12.30
15.Mean	1.09	0.015	0.047	0.759	1.86	0.113	9.68	7.70
SD	0.47	0.008	0.015	0.217	0.54	0.035	4.07	3.84
Min	0.54	0.005	0.028	0.400	1.08	0.060	2.70	1.32
Max	2.50	0.031	0.078	1.122	3.24	0.196	14.60	16.50
16.Mean	1.35	0.017	0.122	0.883	2.25	0.171	3.59	11.39
SD	0.55	0.006	0.044	0.247	0.78	0.037	2.18	3.50
Min	0.67	0.010	0.071	0.568	1.25	0.119	1.20	6.17
Max	2.80	0.029	0.230	1.676	4.49	0.267	9.40	17.90
17.Mean	1.07	0.016	0.115	0.835	1.92	0.152	3.87	10.65
SD	0.21	0.006	0.047	0.168	0.33	0.026	2.21	3.83
Min	0.67	0.008	0.061	0.568	1.25	0.106	1.10	4.90
Max	1.60	0.028	0.230	1.224	2.66	0.209	8.50	16.90
18.Mean	0.72	0.015	0.057	0.612	1.34	0.107	7.69	7.91
SD	0.20	0.005	0.015	0.125	0.31	0.035	3.82	3.74
Min	0.41	0.006	0.026	0.433	0.86	0.053	1.90	3.77
Max	1.00	0.024	0.089	0.900	1.76	0.189	18.50	15.60
19.Mean	0.95	0.015	0.091	0.719	1.68	0.148	4.46	8.43
SD	0.37	0.006	0.042	0.211	0.51	0.039	2.47	3.42
Min	0.40	0.007	0.041	0.428	0.84	0.082	0.90	5.18
Max	1.78	0.024	0.200	1.146	2.93	0.226	8.20	16.30
20.Mean	0.91	0.013	0.084	0.704	1.62	0.128	4.16	7.64
SD	0.37	0.005	0.045	0.197	0.51	0.036	2.21	3.17
Min	0.38	0.006	0.034	0.418	0.81	0.074	1.20	4.10
Max	1.73	0.022	0.210	1.120	2.86	0.226	8.00	14.20
21.Mean	0.65	0.013	0.055	0.553	1.21	0.114	7.71	7.40
SD	0.31	0.006	0.020	0.171	0.48	0.031	3.17	4.60
Min	0.35	0.005	0.011	0.355	0.79	0.070	3.50	2.80
Max	1.50	0.024	0.093	1.000	2.52	0.176	15.40	16.00
22.Mean	0.41	0.007	0.029	0.342	0.76	0.073	1.29	4.22
SD	0.09	0.002	0.011	0.076	0.14	0.022	0.48	1.29
Min	0.20	0.004	0.011	0.224	0.43	0.034	0.20	2.67
Max	0.60	0.012	0.063	0.516	1.03	0.126	2.00	7.80
Average	0.79	0.013	0.061	0.615	1.42	0.115	6.64	7.58
SD	0.37	0.006	0.038	0.195	0.54	0.045	4.02	4.02
Min	0.05	0.001	0.010	0.211	0.43	0.034	0.20	1.32
Max	2.80	0.031	0.230	1.676	4.49	0.283	22.90	19.20

Table 4.22, Values of main effects Kurskal Wallis in temporal and spatial scales (p< 0.05)

Station (Spatial)	T	Ph	Salinity	*SD	TS	DO	O ₂ sat	Current	NO ₃ ⁻	NO ₂ ⁻	NH ₃	NH ₄ ⁺	DIN	PO ₄ ³⁻	SiO ₄ ⁴⁻	Chl-a
Chi-Square	19	131	272.8	346	390	162	161	227	337	140	297	357	367	217	382	161
df	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21
P-value	0.54	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
Season (Temporal) Chi-Square	716	253	426	174	227	547	522	384	178	281	241	110	146	289	108	352
df	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
P-value	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001

*Secchi Depth

Table 4.23, Values of main effects Kurskal Wallis between the North Port and West Port (p< 0.05)

Site 1 and 2	T	Ph	Salinity	*SD	TS	DO	O ₂ sat	Current	NO ₃ ⁻	NO ₂ ⁻	NH ₃	NH ₄ ⁺	DIN	PO ₄ ³⁻	SiO ₄ ⁴⁻	Chl-a
Chi-Square	2.25	2.87	1.01	1.31	1.72	0.55	2.65	0.60	3.12	10.71	3.38	7.94	3.43	3.12	118.44	0.29
df	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
P-value	0.13	0.11	0.31	0.25	0.19	0.46	0.10	0.44	0.05	<.001	0.07	0.00	0.07	0.05	<.001	0.59

The mean water temperature oscillated between 27.69°C in October 2010 and 31.76°C from May 2010 until August 2010 (the dry season). Temperature was correlated with salinity ($r= 0.544$; $p<0.001$) (**Figure 4.26**). The minimum pH (7.80) was at station 13, the pH reached 8.50 at station 4, and there were no spatial and temporal trends throughout the year (**Figure 4.27**).

The mean current speed varied from a minimum of 12.37 knots (0.54 m/s) in August 2010 to a maximum of 14.14 knots in November 2009 and February 2010, and this temporal pattern was similar in all of the sampling sites. The maximum current speed was in the North Monsoon period due to the increased movement of surface water, strong winds and wave action. The spatial pattern of the currents was the same from November 2009 until April 2010 with fast currents in the control area and slow currents in South Port, while there was no clear pattern from May 2010 until October 2010 (**Figure 4.28**). Likewise, the current speed was significantly correlated with the total solid NO_3^- , DIN, PO_4^{3-} and chl-*a* levels (**Table 4.24**).

The mean dissolved oxygen and oxygen saturation levels varied between 4.32 mg/l with 59% saturation at station 16 (August 2010) and 7.22 mg/l with 118% saturation at the control point. High values occurred from November 2009 until May 2010 (the North Monsoon and Inter-Monsoon periods), but after this time, there was a decrease until August for all of the sites, and the surface water showed spatial variability with both oversaturation and under-saturation from November 2009 until May 2010 (**Figure 4.29** and **Figure 4.30**). All of the sites except for South Port were oversaturated with oxygen during this period, but after May 2010, all of the sites were on average under-saturated, most likely due to the strong winds and high action of waves during the North monsoon, which caused an increased dissolution of oxygen in the water.

A high correlation was observed between oxygen saturation, and dissolved oxygen moreover had significant negative correlation with NO_3^- , DIN, PO_4^{3-} , chl-*a* and total solids.

Salinity ranged between a minimum of 24.04 ‰ (ppt) at stations 16 and 17 (South Port) to a maximum of 33.92 ‰ at the control station (**Figure 4.31**). Likewise, the salinity showed a seasonal trend, with a high concentration of salinity from June to September 2010 (dry season) at all of the stations when the daily rainfall decreased and a low concentration during the northeast monsoon, especially in November 2009 and December 2010. This seasonal pattern was similar for all of the sites. The spatial variation of salinity was usually the same among the sampling sites. The South Port site had lower salinity, and the difference among the three other sites was more significant. The salinity variation among the other sampling sites was always insignificant. A significant negative correlation was found between salinity and nutrients except for silicate and ammonia.

The levels of mean total solids (TS) and water transparency were strongly seasonal. The total solid levels varied between 36.60 mg/l at the control stations and 146.38 mg/l at station 16 (**Figure 4.33**). The levels of total solids increased for all of the sites from November 2009 to March 2010 (Northeast Monsoon) when rainfall and river discharges were high and the effect of strong winds and waves was greater. Total solids decreased after March 2010, and the lowest value occurred in June 2010, perhaps caused by decreasing marine current speeds, rainfall and river discharges. The levels of total solids were significantly correlated with other parameters, including O_2 sat, DO, NO_3^- , DIN, PO_4^{3-} , chl-*a* and trophic indices. The mean water transparency varied between 30.3 cm at station 16 and 224 cm at the control point, and at all of the sites, the lowest values were observed between November 2009 and May 2010 (Northeast Monsoon and Inter Monsoon), and high values occurred during the dry season (**Figure 4.32**). The water transparency was strongly correlated with DO and O_2 sat.

The mean values of chlorophyll *a* and some of the nutrients usually showed the same spatial pattern, such as NO_3^- , NH_4^+ , NH_3 , PO_4^{3-} and DIN: their high values occurred at stations 16 and 17 at South Port, while the lowest levels were observed at the control point and intermediate stations located in the middle part of Klang Strait, such as stations 2,5,8,11, 13 and 21.

Throughout the year, the dissolved inorganic nitrogen (DIN) concentration ranged between 0.43 at the control station and 4.49 at station 22. There was a seasonal trend over this period, and the highest values occurred during the period of more intense rainfall (northeast monsoon and inter-monsoon) (**Figure 4.36**).

The mean concentration of nitrate ranged from 0.05 at station 14 to 2.8 at station 16. Nitrate was the most abundant nitrogen compound, and its seasonal pattern was similar to DIN variation (**Figure 4.34**). Nitrate exhibited a strong seasonal trend at all of the sites, with decreasing mean concentration from the northeast monsoon to southwest monsoon period. For all of the sites, the highest concentrations were observed between November 2009 and May 2010 except for March 2010, and the lowest levels occurred from July 2010 to October 2010. Nitrate levels significantly correlated with the DIN, PO_4^{3-} , chlorophyll *a* and trophic indices. Ammonium ranged from 0.211 to 1.676 and showed the same pattern as nitrate during the one year of sampling (**Figure 4.38**).

The nitrite contribution to DIN was negligible and varied between 0.001 and 0.031, but its mean concentrations were lower than 0.03 at all of the stations. The highest mean concentration of NO_2^- was in December 2010, and the lowest values were found in November 2009 and January 2010 (**Figure 4.35**). There was no clear spatial pattern throughout the year, but in general, the highest values occurred from May 2010 to October 2010 (during the dry season).

Ammonia concentration varied from 0.21 to 1.67, with the highest concentration observed in July 2010 and the lowest concentration observed in February 2010. The concentration of ammonium was significantly higher at South Port from July 2010 to October 2010 and decreased from November 2009 to Jun 2010 (**Figure 4.38**).

The concentration of orthophosphates was highest in November 2009 and December 2010 and lowest in March 2010 (**Figure 4.40**). Differences among the sites were clearer in this period and were correlated with chlorophyll *a* levels. Throughout the year, the chlorophyll *a* concentration in Klang Strait was under 20 mg/L at all of the sites, ranging from 1.32 mg/l at station 15 to 19.20 mg/l at station 1 (**Figure 4.39**). For all of the sites, the highest values of chlorophyll *a* were observed between January 2010 and June 2010. In present study, the ratio between high dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus was considered to assess the N: P ratio.

The N: P ratio varied between 4.14 and 53.90, and its average value was lower than the normal Redfield ratio (16:1) in all of the months except June, February and March 2010, during which it exceeded the Redfield ratio (**Figure 4.42**). The mean concentration of SiO_4^{4-} ranged from 0.24 mg/l at the control station to 22.90 mg/l at station 13 (close to the container terminal), and there were no significant seasonal trends for any of the sites. The concentration of SiO_4^{4-} was significantly higher at West Port than at the other sites, while the lowest value of SiO_4^{4-} occurred at the control station (**Figure 4.41**). In general, all of the nutrients except for silicate were highly positively correlated with each other and chlorophyll *a*.

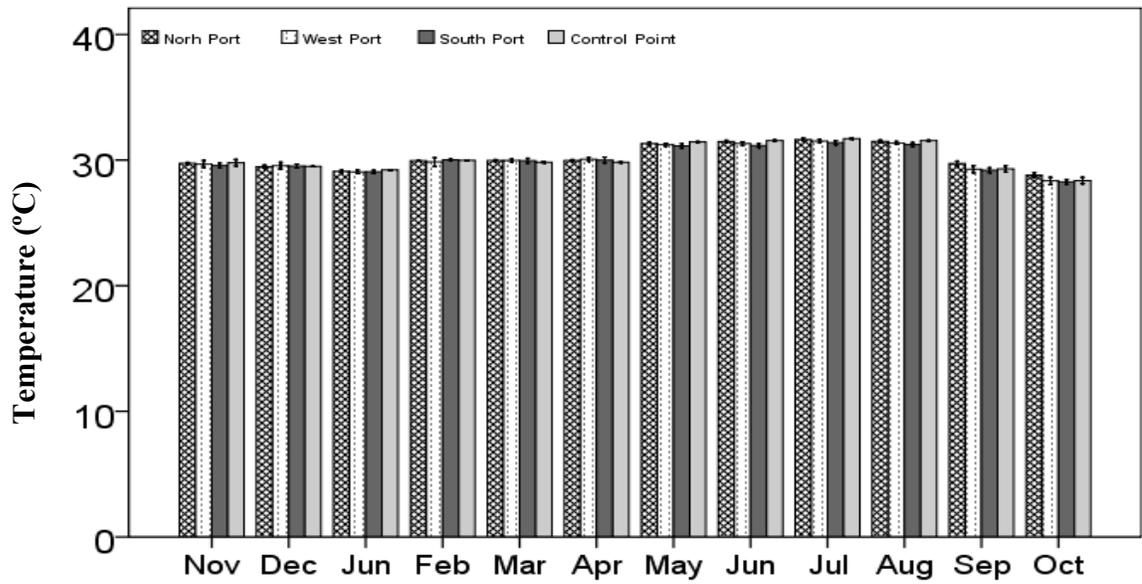


Figure 4.26, Spatial variation of temperature (°C) in water during twelve months of sampling

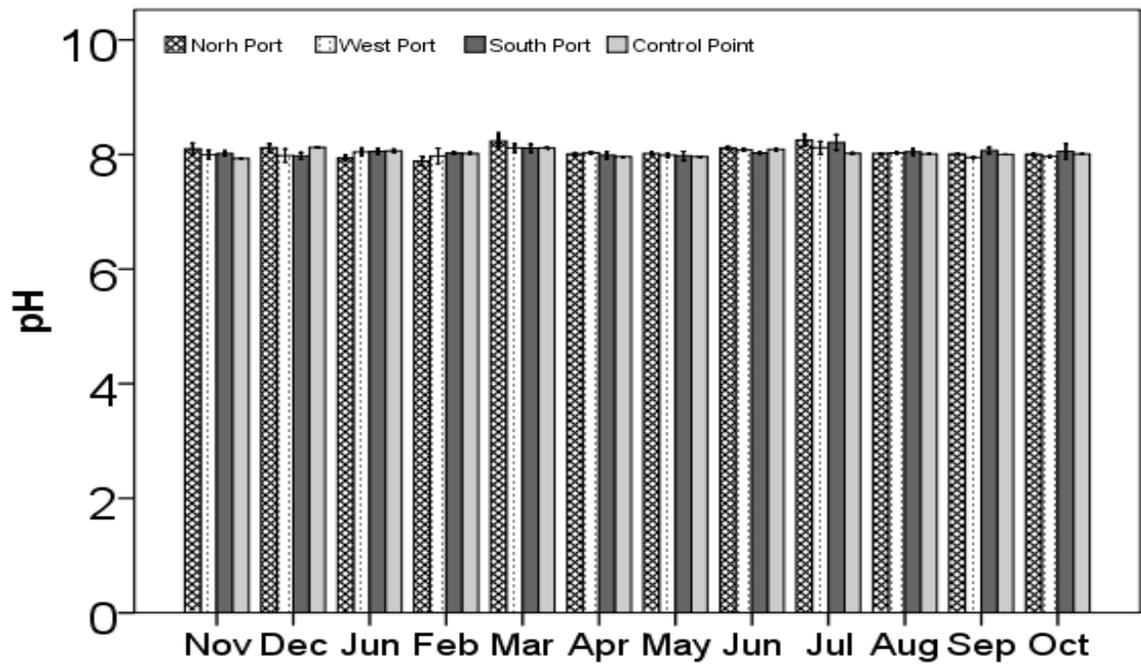


Figure 4.27, Spatial variation of pH in water during twelve months of sampling

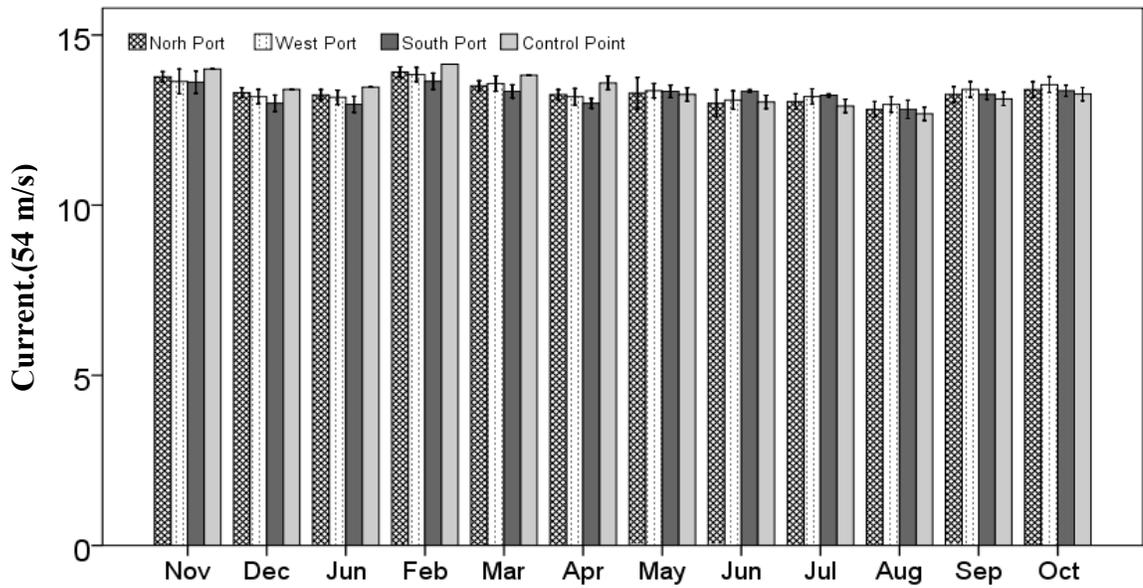


Figure 4.28, Spatial variation of current in water 0.54 m/s during twelve months of sampling

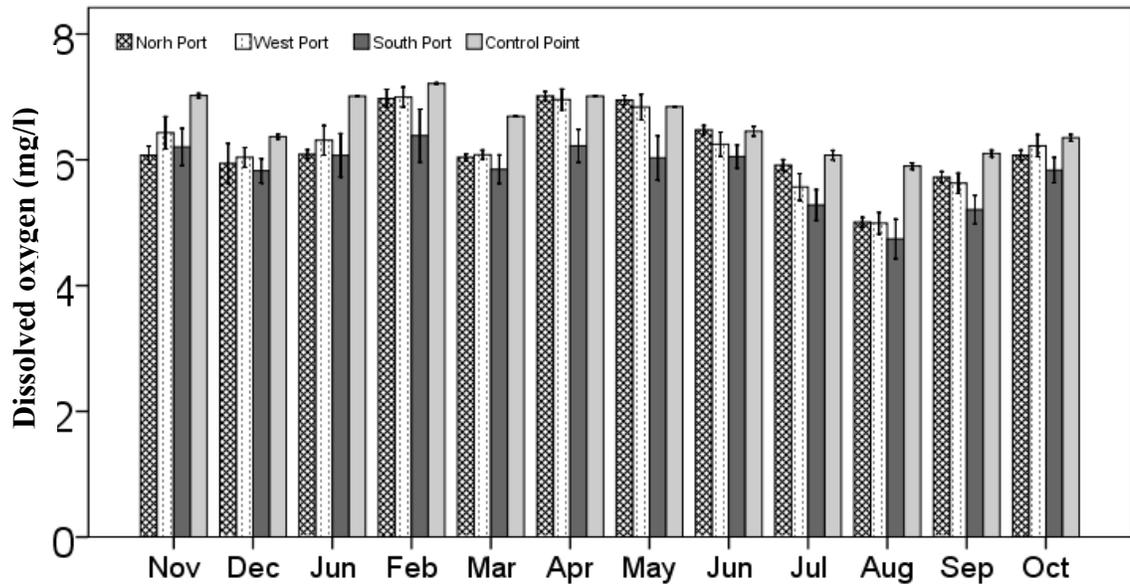


Figure 4.29, Spatial variation of dissolved oxygen (mg/l) in water during twelve months

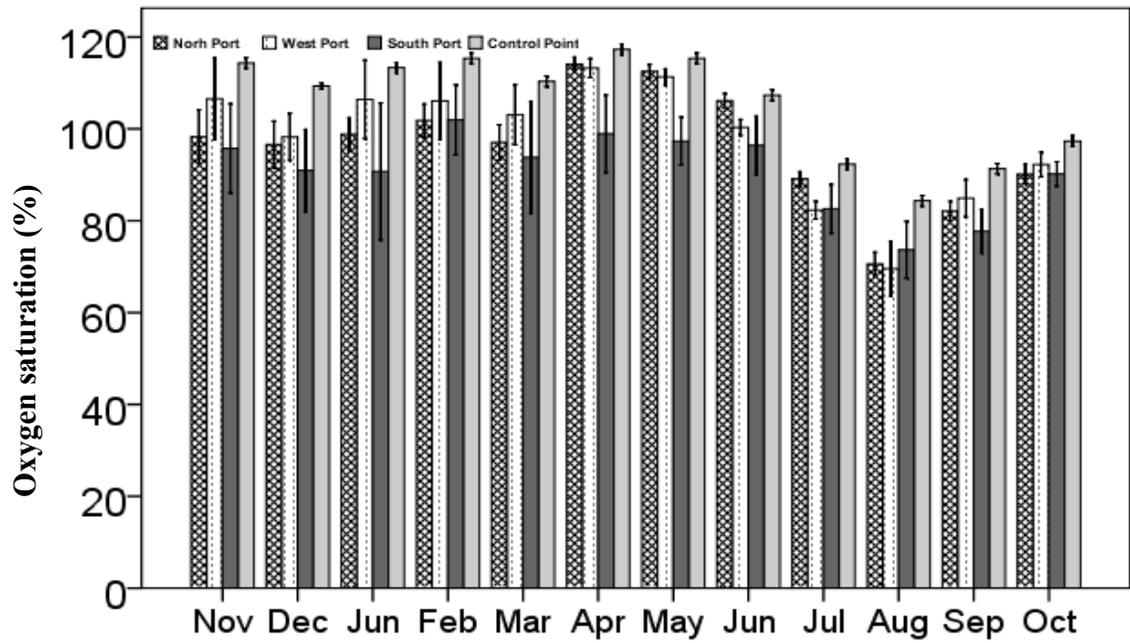


Figure 4.30, Spatial variation of oxygen saturation (%) in water during twelve months of sampling

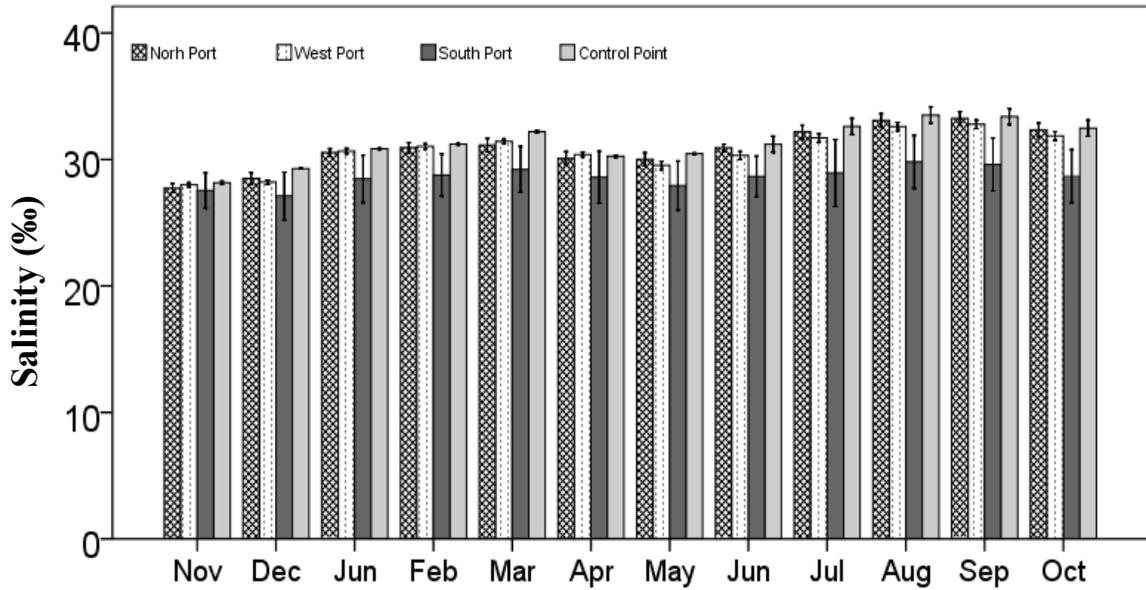


Figure 4.31, Spatial variation of salinity (‰) in water during twelve months of sampling

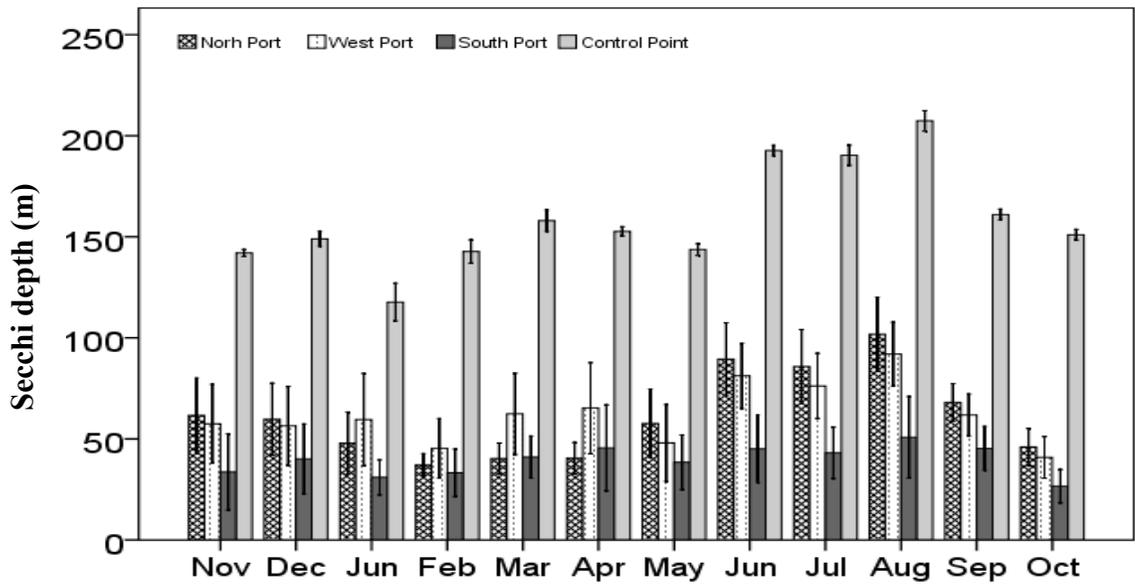


Figure 4.32, Spatial variation of secchi depth (m) in water during twelve months of sampling

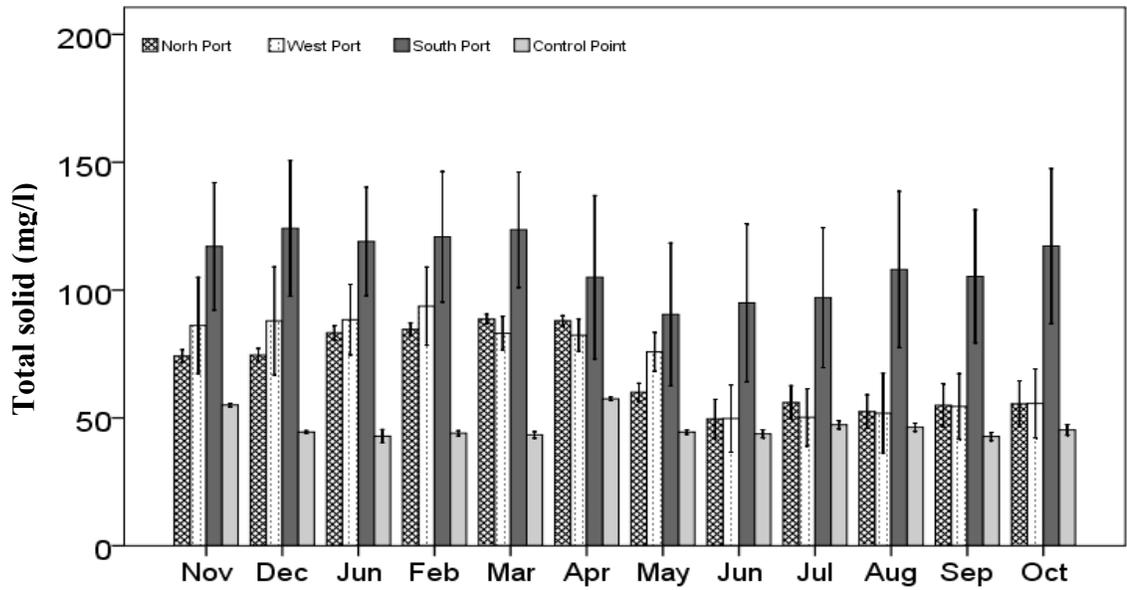


Figure 4.33, Spatial variation of total solid (mg/l) in water during twelve months of sampling

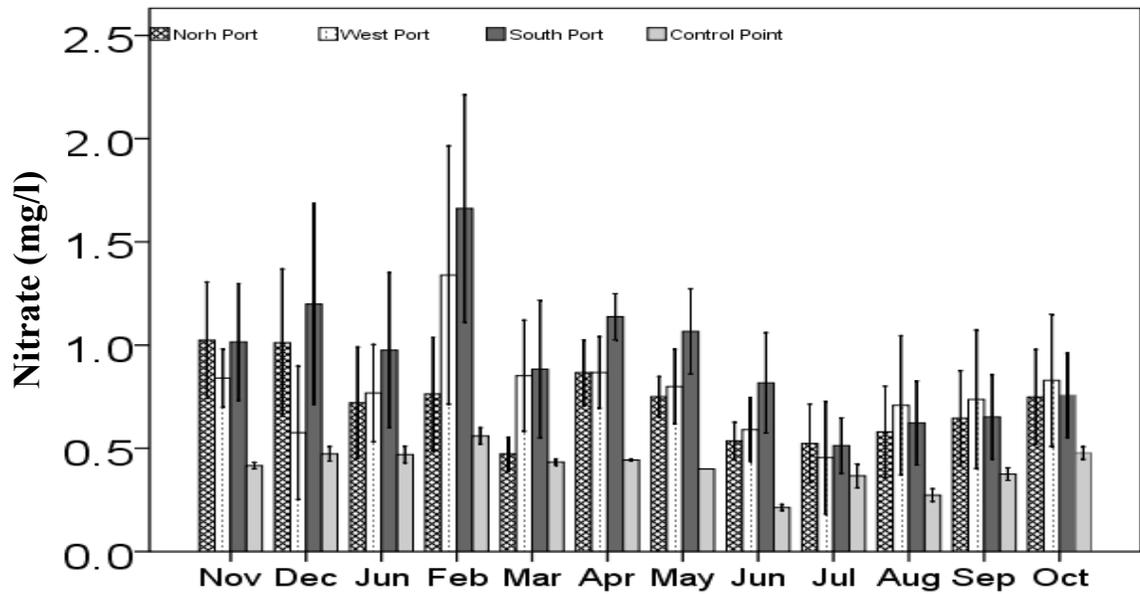


Figure 4.34, Spatial variation of nitrate (mg/l) in water during twelve months of sampling

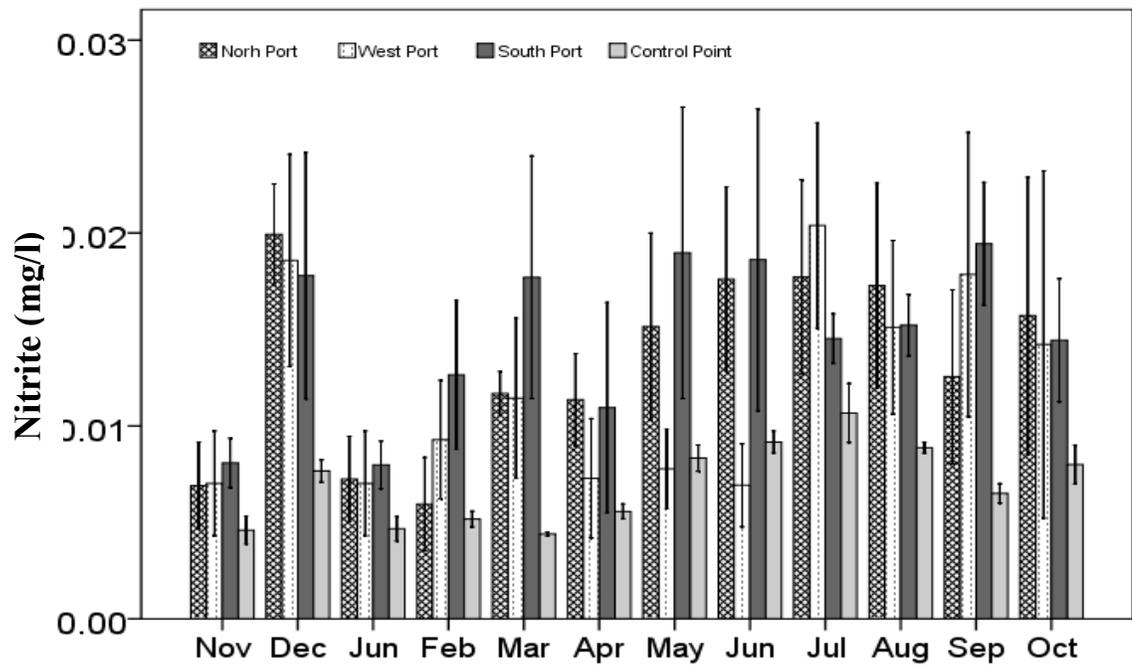


Figure 4.35, Spatial variation of nitrite (mg/l) in water during twelve months of sampling

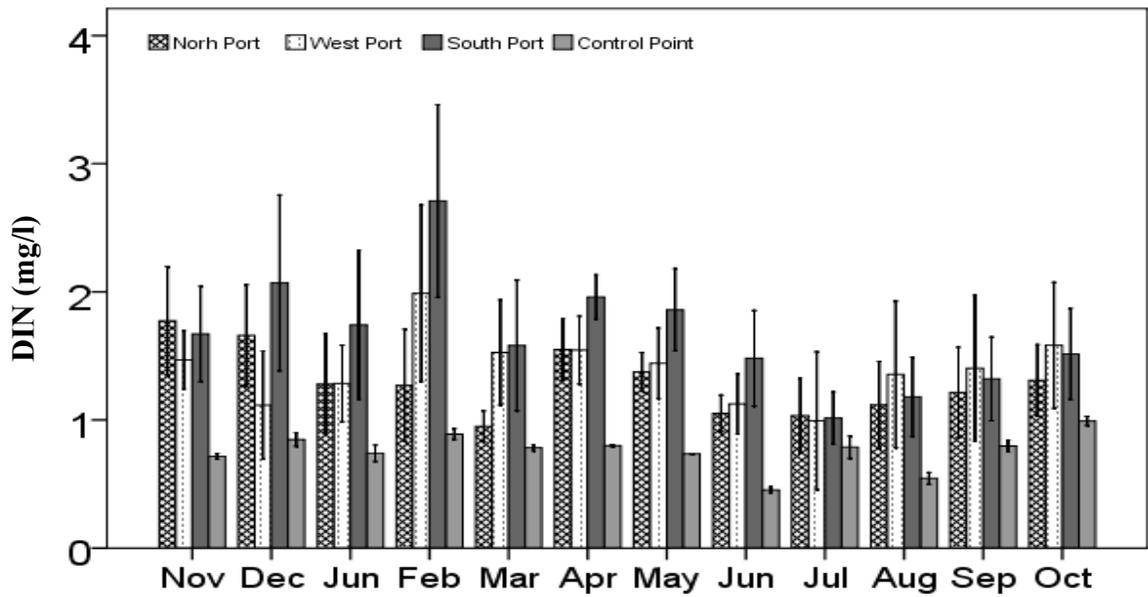


Figure 4.36, Spatial variation of DIN (mg/l) in water during twelve months of sampling

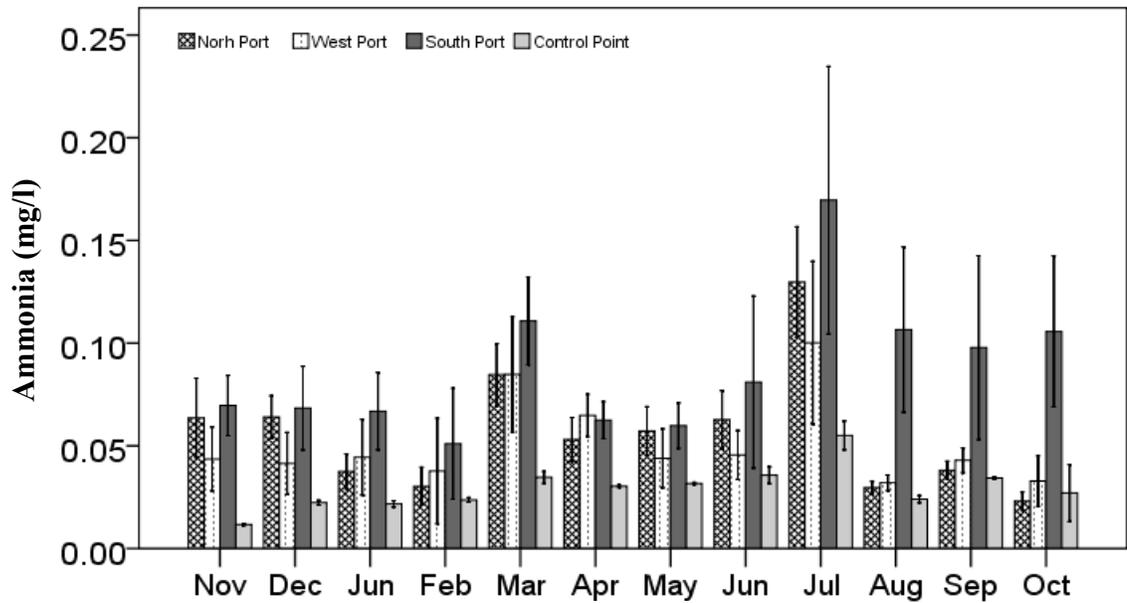


Figure 4.37, Spatial variation of ammonia (mg/l) in water during twelve months of sampling

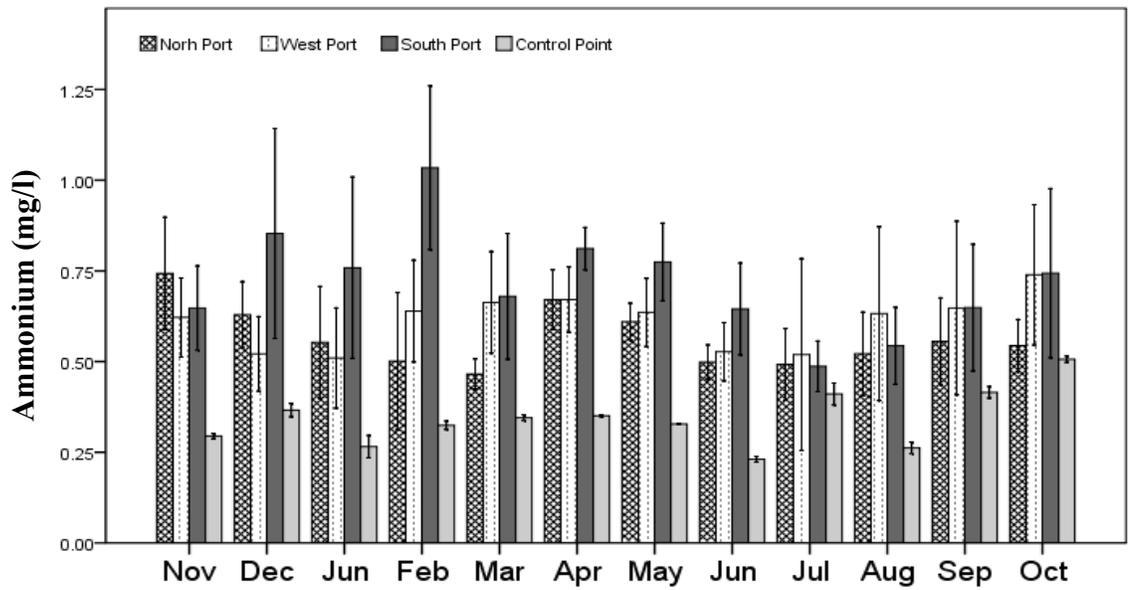


Figure 4.38, Spatial variation of ammonium (mg/l) in water during twelve months sampling

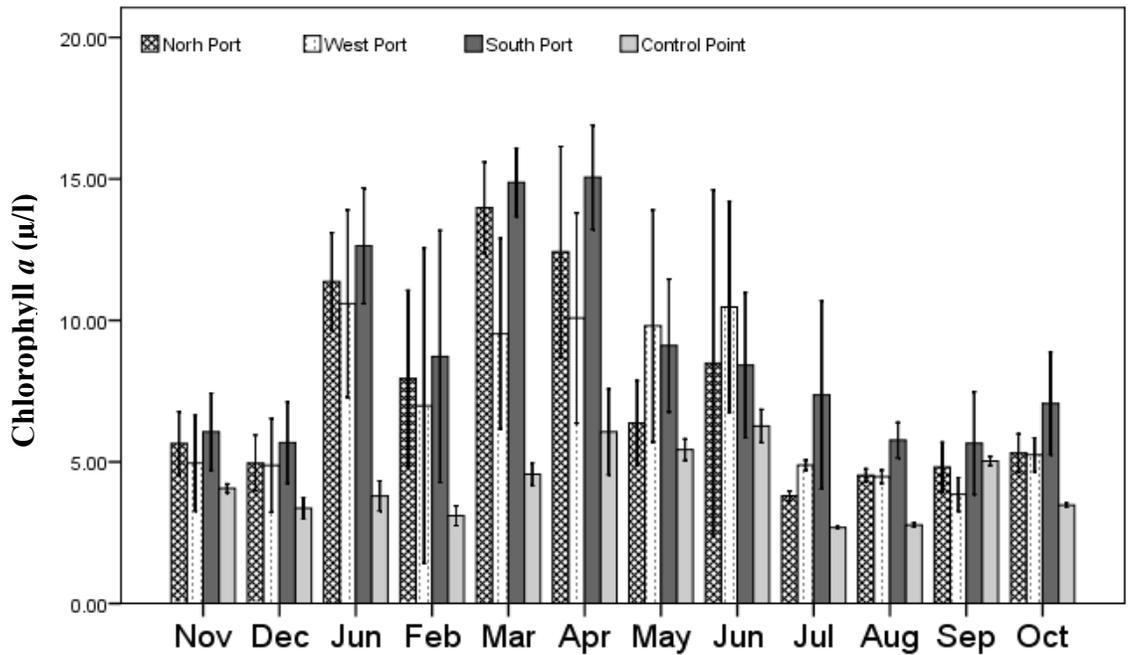


Figure 4.39, Spatial variation of chlorophyll *a* (μ/l) in water during twelve months sampling

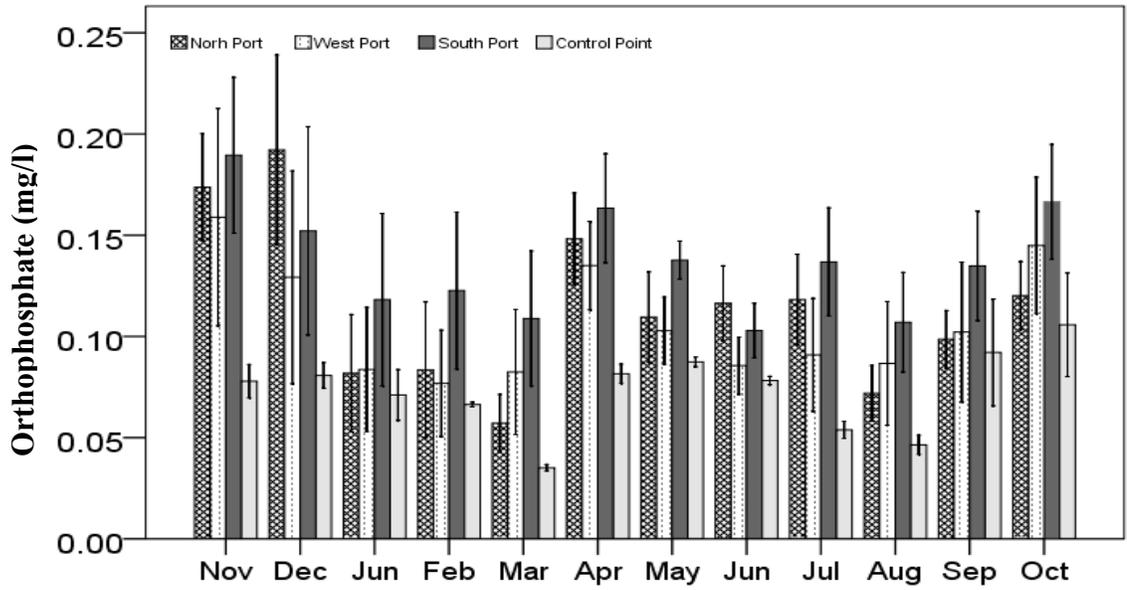


Figure 4.40, Spatial variation of orthophosphate (mg/l) in water during twelve months sampling

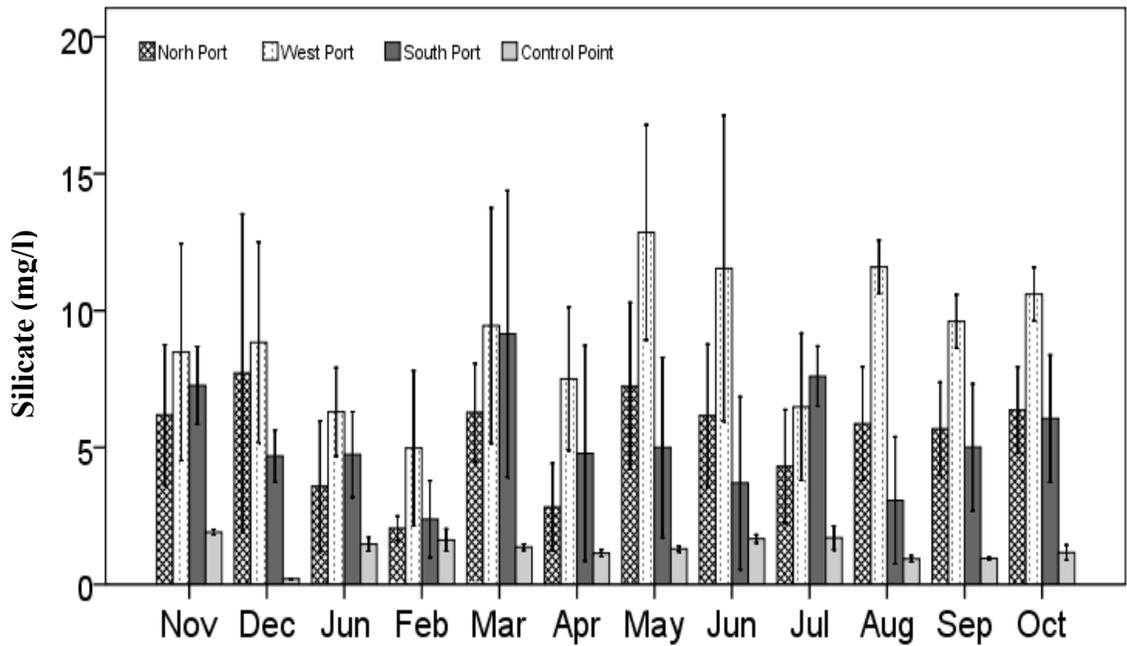


Figure 4.41, Spatial variation of silicate (mg/l) in water during twelve months sampling

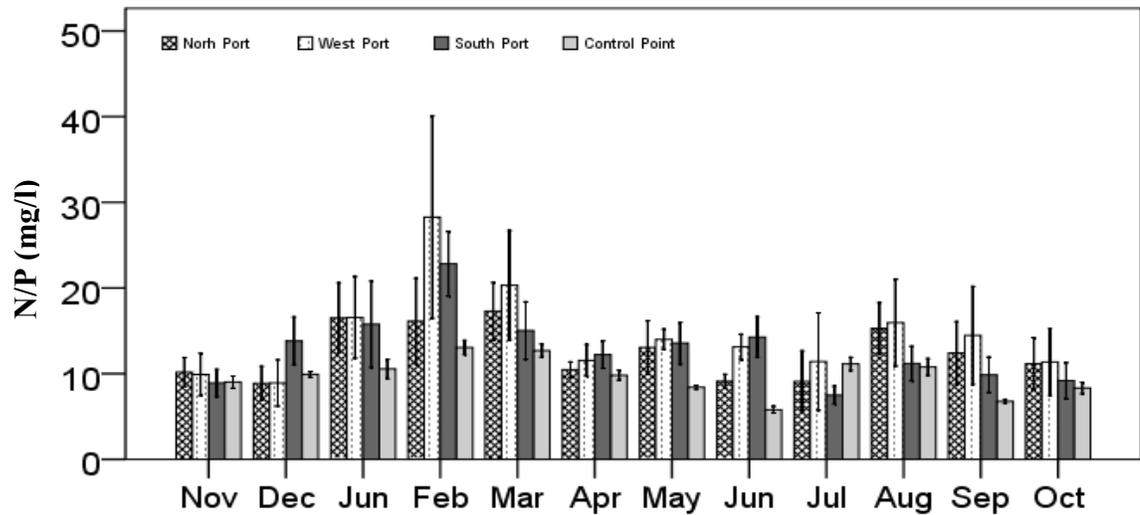


Figure 4.42. Spatial variation of ratio of nitrogen and phosphorus (mg/l) in water during twelve months sampling

Table 4.24. Significant correlation between physicochemical parameters in water

	T	Ph	Current	*SD	TS	Salinity	DO	O ₂ sat	NO ₃ ⁻	NO ₂ ⁻	NH ₄ ⁺	NH ₃	DIN	PO ₄ ³⁻	SiO ₄ ²⁻	Chl- <i>a</i>
T	1.00															
Ph	0.14	1.00														
Current	0.13	-0.15	1.00													
SD	0.25	-0.33	0.17	1.00												
TS	-0.26	0.08	0.44	-0.62	1.00											
SALINI	0.45	0.10	0.03	0.45	-0.45	1.00										
DO	0.15	-0.43	0.34	0.66	-0.47	0.37	1.00									
DO	0.26	-0.42	0.23	0.77	-0.52	0.37	0.73	1.00								
NO ₃	-0.41	0.11	0.46	-0.57	0.50	-0.42	-0.44	-0.49	1.00							
NO ₂	-0.26	0.19	0.29	-0.59	0.48	-0.42	-0.44	-0.47	0.59	1.00						
NH ₄	-0.44	0.14	0.41	-0.62	0.57	-0.41	-0.50	-0.54	0.83	0.57	1.00					
NH ₃	-0.19	0.54	0.23	-0.67	0.41	-0.27	-0.78	-0.80	0.48	0.44	0.55	1.00				
DIN	-0.43	0.11	0.46	-0.60	0.55	-0.44	-0.47	-0.52	0.96	0.62	0.95	0.51	1.00			
PO ₄	-0.29	0.35	0.43	-0.70	0.53	-0.44	-0.73	-0.73	0.66	0.58	0.69	0.52	0.67	1.00		
SiO ₂	-0.23	-0.17	0.10	0.21	-0.16	-0.04	0.26	0.28	0.08	-0.06	0.08	-0.26	0.07	-0.13	1.00	
Chl- <i>a</i>	-0.18	0.25	0.33	-0.63	0.52	-0.25	-0.67	-0.64	0.48	0.58	0.47	0.45	0.49	0.69	-0.17	1.00

*Secchi Depth

The cluster analysis of the sites produced three clusters based on their hydrological similarities: group A as formed by North and West Port, group B was composed of South Port stations (except of station 18 and 21), and the third cluster included the control area, which was completely separate from the other clusters (**Figure 4.43**).

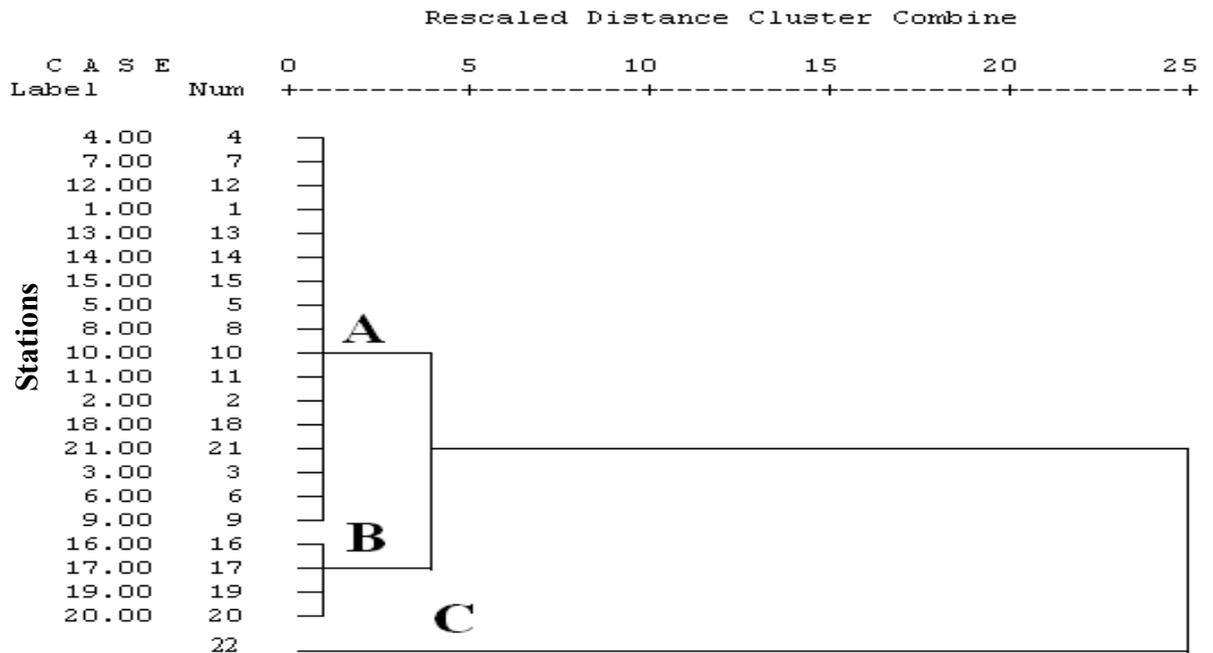


Figure 4.43. Cluster analyses to classify the different stations based on physicochemical parameters Of water quality

A principal component analysis (PCA) was used to assess the variability of the water quality data and quantify the contributions (percentages) of the individual physicochemical parameters. As shown in **Table 4.25**, the PCA analysis classified data into 3 major principal components (PCs) at North Port, which accounted for 96.3% of the variability in this area. The first component accounted for 63.5% of the variation of the data. This component was strongly controlled by pH, chl-*a* and nutrients (except for silicate) with a highly significant correlation with the first component. Silicate and salinity were significantly correlated with components two and three, respectively. At West Port, the data were classified into 3 principal components (PCs). The first component accounted for 40.11% of the total variance, with high loading from pH, NH₃, PO₄³⁻ and chlorophyll *a* levels. The second component accounted for 33.0% of the total variation, with strong loading from NH₄⁺, NO₃⁻, DIN, SiO₄⁴⁻ and chl*a*, which were strongly correlated with

component two (PC2), while NO_2^- and total solids were significantly correlated with the third component.

The PCA analysis classified data into two main principal components at South Port. The first component accounted for 81.12% of the total variability, with a significant correlation with levels of NH_4^+ , NO_3^- , PO_4^{3-} , DIN and total solids, while NO_2^- and chl-*a* levels were significantly correlated with the second component (PC2) and accounted for 11.75% of the total variation. At the control area, the water quality data were classified into three main groups that explained 70.31% of the variability in this area. The first component included oxygen saturation, DO, transparency, total solids, nitrate, Ammonium, DIN and current speed, which accounted for 43.09% of the variation. PC2 accounted for 16.21% and was strongly correlated to SiO_4^{4-} , while PC3 account for 17.36% with high loading from levels of chl-*a*.

Table 4.25, Rotated component loadings of three principal components (PCs) for physicochemical parameters in the water of Klang Strait

	North Port			West Port			South Port		Control area		
	1	2	3	1	2	3	1	2	1	2	3
T	-.021	-.987	-.051	.021	-.898	.147	-.559	-.663	-.429	-.564	.442
PH	.956	-.018	.282	.878	-.013	-.359	.259	-.923	-.678	.450	.358
Current	-.194	-.338	-.806	-.162	-.050	-.970	-.682	.048	.795	.315	.348
Secchi depths	-.840	.322	-.429	-.798	-.055	-.496	-.634	-.646	.713	-.590	.083
TS	.484	-.832	.111	.034	.180	.935	.854	.257	.740	.416	-.299
Salinity	.113	.145	.228	-.434	-.779	.172	-.566	-.811	.637	-.174	.149
DO	-.863	.190	-.464	-.939	.181	-.176	-.682	-.717	.844	-.012	.483
O2 sat	-.766	.437	-.418	-.966	-.004	.033	-.681	-.601	.895	.104	.363
NO_3^-	.982	.150	.059	.217	.816	.472	.790	.569	.716	-.246	.065
NO_2^-	.986	.114	-.115	-.178	.428	.762	.423	.789	-.383	-.427	.058
NH_4^+	.926	.093	.362	.190	.829	.512	.799	.600	.757	-.227	-.050
NH_3	.941	-.071	.315	.846	.002	-.403	.808	.570	-.842	.382	.164
DIN	.977	.133	.154	.207	.823	.490	.798	.584	.722	-.248	.029
PO_4^{3-}	.741	.618	.219	.748	.587	.246	.793	.514	.362	.461	-.333
SiO_4^{4-}	.184	.960	.035	-.404	.774	.235	-.653	-.212	.245	.772	.388
chl <i>a</i>	.970	-.106	-.142	.781	.075	.448	.721	.850	.262	.011	.569

4.3.3 Trophic indexes

The trophic state index (TRIX) ranged from 5.80 (June 2010 at the control station) to 8 (April 2010). Throughout the year, the majority of the water samples (99.36%) varied between 6 and 8 and suggested a highly productive system with a high trophic level, characteristic of a low-quality system (**Figure 4.44**). The eutrophication index (EI) varied from 0.65 to 5. Throughout the year, most of the samples had a bad (49%) or poor (45.5%) water quality, and only 5.3% of the water samples were at mediocre levels, typical of poor to bad productive systems with a high trophic level (**Figure 4.45**). The highest levels of the eutrophication index ($EI < 1.5$) were observed between January 2010 and June 2010 for all of the sites except the control station. The lowest levels ($EI < 1.5$) were observed in November 2009, December 2010 and from July to October 2010 for all of the sites except South Port, where EI was greater than 1.5 throughout the sampling period.

In **Table 4.26**, the average annual concentration of operational indicators and trophic indices are compared with the characteristic trophic categories of coastal and marine areas (salinity $< 20\text{‰}$). All of the sites except for the control area were at a eutrophic to hypertrophic level according to the value of the Secchi depth, chl-*a* level, nitrogen concentration, and trophic indices. The control point showed different results and was at a eutrophic to hypertrophic level according to trophic categories based on Secchi depth, nitrogen, phosphorus and trophic indices, while it had a mesotrophic condition based on comparison with the chlorophyll *a* values.

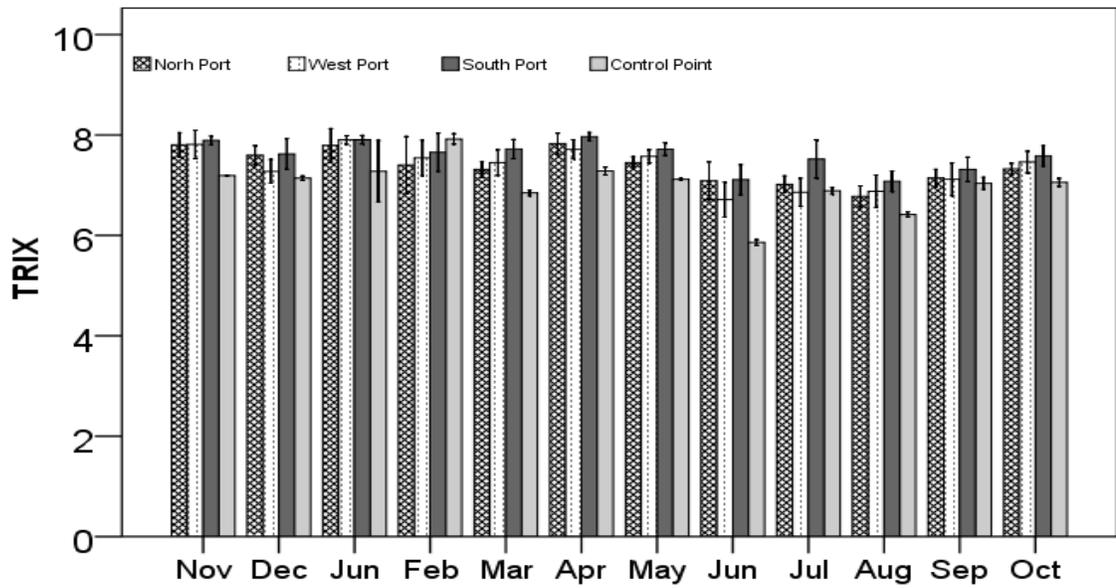


Figure 4.44, Spatial variation of TRIX index during twelve months of sampling

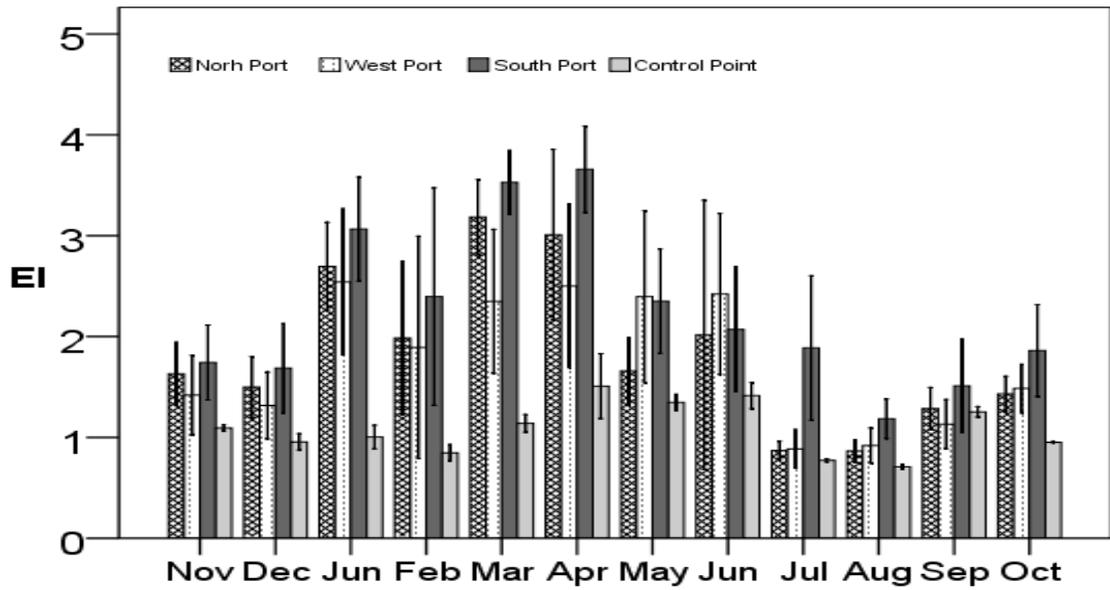


Figure 4.45, Spatial variation of eutrophic index (EI) during twelve months of sampling

Table 4.26, The average annual concentration of operational indicators and trophic indices are compared with the characteristic trophic categories of coastal and marine areas

Operational indicator and indices	Secchi depth(cm)	Chl-a (µg/l)	Total-N (mg/l)	Total-P (mg/l)	TRIX	EI
This study North Port	61.315±24.77	7.475±3.054	1.299±0.293	0.114±0.036	7.37±0.41	1.84±0.72
West Port	62.21±22.5	7.150±2.891	1.403±0.402	0.107±0.032	7.35±0.45	1.77±0.67
South Port	39.490±16.0	8.867±3.020	1.673±0.517	0.137±0.041	7.58±0.36	2.24±0.73
Control area	159±25.05	4.22±1.289	0.757±0.144	0.073±0.022	7.03±0.51	1.08±0.16
Trophic status and Oligotrophic (high quality)	>1100	<2	<0.110	<0.015	2-4	<0.38
Mesotrophic (good quality)	600-1100	2-6	.011-0.29	0.015-0.04	4-5	0.38-085
Eutrophic (Bad quality)	200-600	6-20	0.29-0.94	0.04-0.130	5-6	0.85-1.51
Hypertrophic (Poor quality)	<200	>20	>0.94	>0.13	6-8	>1.51

CHAPTER V: DISCUSSION AND CONCLUSIONS

5.1 Sediment quality assessment

Assessment of sediment quality is essential because sediment acts as a reservoir for many types of contaminants in marine ecosystems. Thus, despite sediment contamination, the dynamics of contaminants vary extensively based on fluxes in physicochemical and biological variables that affect the movement of contaminants into or out of the sediment, although these contaminants may be stable in the sediment over the long term. These dynamics may alter the quality of pore water and the distribution of biological communities. In general, in a comprehensive assessment of sediment quality, the following tenets should be followed: the use of suitable sampling strategies at different spatial and temporal scales, analysis of physicochemical and biological variables through laboratory testing, and evaluation of ecological indicators such as the structure of benthic communities (GIPME, 2003; U.S.EPA, 2004). In the present study, a combination of biological and physicochemical variables was monitored over multiple spatial and temporal scales because the distribution and effects of contaminants are influenced by water bodies, specific chemical contaminants, the natural properties of the sediment, and the indigenous biological communities (flora and fauna).

5.1.1 Variation in the concentration of physicochemical variables

Some physicochemical parameters of water and surface sediment were estimated to evaluate the possible relationship between these parameters and the distribution of contaminants. The pH is a primary indicator used to assess water quality and pollution in marine and coastal systems. According to the guideline suggested by (WHO, 1993), the acceptable range for pH is 6.5–8.5.

In this study, the measured pH ranged is 7.80–8.50, which indicates an alkaline nature for Klang Strait coastal water. The measured temperature and dissolved oxygen values ranged between 27.69–31.76°C and 4.32 -7.22 mg/L, respectively (**Figure 4.27 and Figure 4.26**). There were no significant differences in temperature or dissolved oxygen among the stations. Salinity values ranged between 24.04 - 31.92‰, and the lowest salinity values were recorded at stations 16 and 17 because these stations are greatly influenced by the fresh water from the Klang River.

All organic and inorganic pollutants exist in aquatic systems in dissolved, particulate and colloidal forms, but the proportion of the dissolved form is generally low (Connell & Miller, 1984). The physicochemical parameters of an aquatic system control the deposition, adsorption and desorption rates of the pollutants in the water and sediment (Nduka & Orisakwe, 2011). For example, desorption rate of a specific concentration of a metal may be increased by an increasing salinity or a decrease in redox potential or pH (Connell & Miller, 1984; Nduka & Orisakwe, 2011). In this study, pH, salinity and temperature appeared to have no effect on the distributions of metals and PAHs, because the variations in these parameters were not significant between stations and remained within the acceptable standard range for marine and coastal water.

The analysis of particle size and total organic carbon is the first step in assessing sediment quality, and this information is practical for describing variation in contaminants and the structure of biological communities (C. & Szava-Kovats, 2008; U.S.EPA, 2004).

In the Klang Strait, fine-grained sediments predominated in almost all stations, with the highest amount of fine sediment in the vicinity of stations near the mangrove edge and the mouth of the Klang River (**Table 4.1 and Figure 4.2**).

Sediment grain size variation is controlled by several factors in marine environments, including sedimentary processes, sediment transportation, distance from material sources and dredging (He et al., 2009; Kumar, Solanki, & Kumar, 2012; Qin et al., 1989).

The stations with a high percentage of fine sediment along the mangrove edge (stations 3, 6, 9, 12 and 15) reflected the effect of mangrove forest on increasing the rates of sedimentary processes. The mangrove forest acts as a sediment trap, providing a mechanism that sinks suspended solids by decreasing hydrodynamic energy (tidal current and baroclinic circulation), which provides time for the sinking and re-deposition of fine grain sizes (Cunha-Lignon et al., 2009; Furukawa, Wolanski, & Mueller, 1997; Kathiresan, 2003; Wolanski, Mazda, & Ridd, 1992; Woodroffe, 1992), otherwise sediment in mangrove shores and mudflats in Klang Strait should largely consist of fine sediment like clay and silt. Moreover, sediments with fine grain sizes along the mangrove edge were likely to be transported by land-based runoff.

Other stations (16, 17, 18, 19, 20 and 21) with a high percentage of fine grain sizes were located close to the Klang River in the South Port, which indicates the effect of river transportation (Qin et al., 1989). The Klang River contributed significantly to the distribution of sediment particles, and the weak hydrodynamic energy increased the sedimentation rate of fine-grain-sized sediment.

Some stations such as 2, 5, 8, 11, 13 and 22 with high percentage (> 48%) of sand sized sediment (**Table 4.1**) to compare other stations, which indicates the effect of regular dredging of shipping channels in vicinity on the sea bottom. The shipping lanes (**Figure 3.8**) are annually dredged to deepen to at least 15 meters depth to facilitate approach of large tanker and ship. Thus, dredging of Klang Strait may be the reason for the occurrence of coarse or sand sized sediment recorded in these stations.

Sediment grain size plays a significant role in the concentration and distribution of heavy metals in coastal and estuarine sediments. The concentration of heavy metals is higher in fine particles compared to sand-sized particles because fine-grained sediment significantly adsorbs heavy metals from water. In addition, the fine fraction of sediment also has a high capacity to retain heavy metals compared to other fractions (Abraham, Parker, & Nichol, 2007; He et al., 2009; Lim, Jung, Choi, Yang, & Ahn, 2006; Nobil, Dilipan, Thangaradjou, Sivakumar, & Kannan, 2010; Ye, Li, Zhang, Tong, & Zhang, 2012). Thus, the fine fraction of sediment is frequently used to assess contaminant variation and for toxicity tests in environmental research.

In the present study, TOC and the concentrations of some metals such as Al, Cd, Cu, Fe, Ni, V and Zn exhibited significant correlations with percentage fine particles (**Table 4.2**).

The distribution of TOC revealed a peak value at the South Port near the mouth of the Klang River and lower concentrations at stations 8 (near the cement outlet in West Port) and 11 (liquid berth in the West Port) (**Table 4.1 and Figure 4.1**). Its distribution was synchronous with that of fine-grain-sized sediment in most parts of the study areas (except stations 9 and 12), with high values for both parameters along the mangrove edge and the mouth of the Klang River.

Generally, the fine-grain-sized sediment, specifically the clay colloid, exhibits a significant trend towards the adsorption of TOC, and TOC increases as the average grain size decreases (He et al., 2009). Some heavy metals exhibited significant positive correlations with TOC, such as Al, Cd, Cu, Fe, Ni, V and Zn (**Table 4.2**).

TOC and humic material have a high adsorption and complex influence on the re-deposition of heavy metals (Nduka & Orisakwe, 2011). Furthermore, anthropogenic heavy metals are widely absorbed on the surface of the sediment or combined with TOC in suspended solids and deposited on bottom sediments (Ghadeer & Macquaker, 2012; Ingelmo Sánchez, Molina, Soriano, & Gallardo, 2012; Zhang, she, & Zhang, 1996).

5.1.2 Concentration and distribution of heavy metals and PAHs

In this study, the Klang Strait was divided into three specific geochemical sites (the North, West and South Ports) to describe the distribution and concentration of contaminants.

Considerable variations were observed in the concentrations of all heavy metals (except for Cu, Ni, Hg and Fe) and PAHs among different stations and sites, which were evidenced by a nonparametric Kruskal-Wallis test. The highest concentrations of all metals (except for Mn), PAHs, TOC and fine-grain-sized sediment were observed in the South Port relative to the other sites. These results indicate that the concentrations of these variables were affected by several sources of contamination in the Klang Strait.

Studies elsewhere have indicated that several factors such as erosion, sedimentation, sediment type, water dynamics, urbanisation, industrialisation, river discharge, and geochemical reactions affect the distribution and constitution of heavy metals and PAHs in coastal and estuarine waters (Naji, Ismail, & Ismail, 2010; Nobi et al., 2010; Pan & Wang, 2011; Siddique et al., 2009).

Distribution maps were used to provide a better visualisation of the distribution of contamination at the spatial scales described in Appendix 2; the details of the data are described in section 4.2.1.

At the South Port, the distributions of all metals and PAH compound (*PAH_{Combust}* and *PAH_{toxic}*) sediments exhibited a homogenous pattern of decreasing concentration in the north to south direction, and concentrations were high at the 16 and 17 stations, which are parallel to the mouth of the Klang River. This pattern supports the view that the Klang River may be the primary source of contamination in the Klang Strait and influence the concentration and distribution of metals and PAHs because water and suspended solids were easily exchanged between the South Port and the polluted Klang River, which contains industrial effluents and untreated municipal waste (Balamurugan, 1991; Greenwood & Jr., 2007; Naji et al., 2010).

The water currents in the vicinity of the South Port are weak (Ibrahim, 1988); therefore, there is enough time for the deposit of organic components and absorption of heavy metals by suspended solids for deposition onto surface sediments. Heavy metals are not easily deposited onto bottom sediments where there are strong water currents (He et al., 2009). According to the correlation analysis, there was no correlation between Mn and other metals, and Mn exhibited a different spatial distribution relative to the other metals. These results are most likely due to the low concentration of biogenic carbonates in South Port sediments. The dissolved concentration of Mn controls absorption and substitution in calcite. Most particulate Mn is easily bound to seawater carbonates (Wartel, Skiker, Auger, & Boughriet, 1990; Wartel et al., 1991). A study has also reported a strong correlation between the concentration of biogenic carbonates and Mn in the coastal sediments of Taiwan and the East China Sea (He et al., 2009).

In the North Port, the distributions of As, Cr, Hg, and Zn generally exhibited a bimodal pattern that varied from a high to a low concentration moving from north to south, as well as a trend towards high values in the east (along the berth line).

High concentrations of Cu and Pb also occurred in the east and the northwest. These areas adjoin regions of land-based runoff and industrial outlets, which can directly release organic and inorganic pollutants. The distribution of Al, Fe, Mn, V and Cd showed the highest trend in the western part of the strait with the mangrove forest, which had the same distribution pattern of TOC and fine-grained sediment.

The highest concentrations of Al, Fe, Mn, V and Cd occurred in the western part of the strait and along the fringes of the mangrove forest, which was related to the higher concentration of TOC and fine grain size in mangrove sediment.

In this study, there were significant correlations ($0.4 < r$; $P < 0.01$) between fine particle size and the following metals: Al, Cd, Fe, V, Cu and TOC (**Table 4.2**).

The results indicate that these metals were more highly concentrated in finer particles compared to sand-sized particles; therefore, high concentrations were estimated near the mangrove edge. The distribution of Ni was unique because it was high along the mangrove edge. Generally, the lowest concentration of metals (except for Al and As) was found close to stations 2 and 5 (along the middle transect) in the North Port. This may be due to the strong water currents in this area, which decrease the rates of chemical reactions between metals and sediments. Moreover, these stations had substrates with a high percentage of sand-grain-sized sediments compared to other stations.

In the West Port, the spatial distributions of As, Pb, V, Al, Fe, Hg and Ni were generally homogenous, with a low to high concentration gradient on moving from the north to the south. This distribution may be related to the large container terminal and the inflow of land-based runoff in the southern part of the West Port, which may have caused an increase in metal concentrations. The concentrations of Hg and Ni peaked at the 11 and 12 stations and were significantly different from the concentrations at other stations.

These stations were probably influenced by both the high-sedimentation area (mangrove coast) and the industrial waste from the industrial outlets that are located along the coastline. The concentrations of Zn and Cr exhibited a trend towards higher values both southeast and northeast of the strait (along the coastline). The concentrations of Cd, Mn and Cu decreased from the mangrove edge to the coastline, which was similar to the distribution patterns observed at the North Port.

At both the West Port and North Port, the spatial distribution of PAHs exhibited an east-west gradient that decreased from east to west. These stations were located close to the near shore area and thus are strongly influenced by port activities, especially stations 4 and 13, which are close to the terminal containers (Near-shore area) in the North and West Port (**Table 4.6**). Additionally, land-based runoff directly releases organic compounds in the vicinity of these stations.

More research revealed significant differences in the sources and concentration of PAHs in sediment samples of near-shore vs .Offshore areas. PAH concentrations in sediment samples collected from near-shore sites (city hinterland) were greater than PAH concentrations in offshore areas. This implies that PAH concentrations in near-shore areas are influenced by lateral transport such as run-off and the transportation of water due to daily rainfall (Sakaria et al., 2010). Ikaneka (2005) indicated that heavy rainfall and flood contribute significantly to the pollution of marine sediments. Moreover, the results of their research indicate that near-shore areas received both burnt material (pyrogenic) and oil products (petrogenic), whereas offshore stations were primarily influenced by burned material (Boonyatumanond, Wattayakorn, Togo, & Takada, 2006; Farrington, Goldberg, Risebrough, Martin, & Bowen, 1983; Ikenaka, Eun, Watanabe, Kumon, & Miyabara, 2005; Kumar et al., 2012; Sakaria et al., 2010).

Overall, the distinct pattern in the distributions of measured parameters revealed that multiple sources contributed significantly to the heavy metal and PAH loads in the Klang Strait. These sources include the large-scale inflow from industries such as the palm oil, cement and food manufacturers that are located along the coastline of the North and West Ports, vessel-based discharges, Klang River outflow, land-based runoff, sedimentation, and siltation.

The concentration of metals in the sediment showed wide variations over time (**Figure 4.3**). This may be due to differential loading of these contaminants from lithogenic sources and untreated effluent discharges (anthropogenic sources), and can result in seasonal fluctuations.

The results also indicated that the concentrations of metals (except of Cr and Mn) in surface sediments changed significantly over the studied temporal scale, which was evidenced by statistical testing (**Figure 4.4**).

The significant temporal variation of heavy metal concentrations is most likely due to seasonal fluctuations. This significant difference in metal concentration is unusual, considering the short duration of the sampling period. However, several studies have indicated that changes in the chemical properties of metal, water, and sediment, which are associated with other environmental factors such as atmospheric deposition, the dynamics of marine water, tidal and seasonal currents, and changes in anthropogenic pollution loads, can cause this temporal variation in the mobility and bioavailability of heavy metals over a short time. For example, several studies have reported that in the rainy season, the concentrations of heavy metals in sediment are lower than in the dry season because rainwater causes increased mobility and dilution, which decrease the heavy metal concentrations in the sediment (Olubunmi & Olorunsola, 2010; Aydin Onen, Kucuksezgin, & Kocak, 2011; Zhang, Cui, Xiao, & Zhao, 2010).

According to, **Figure 4.4**, some metals (Al, Fe, Ni, Cd, Ni, and Hg) showed significant reductions in their concentrations in the sediment with the increasing rainfall that occurred in November 2009 and May 2010. This pattern implies that these metals are bound to the exchangeable phase of the minerals in the sediment and are likely to be more easily influenced by dilution due to heavy rainfall and strong marine currents, which occur in the North Monsoon and Inter Monsoon periods.

5.1.3 Sources of contaminants in sediment

The concentrations of metals and PAHs are influenced by two major sources: lithogenic (natural) and anthropogenic. It is not easy to determine which source is most significant for specific pollutants at specific locations. Thus, an assessment of sediment quality should be able to discriminate between the contributions of naturally-occurring contaminants (heavy metals and hydrocarbons) and anthropogenic sources. The natural concentration of chemical compounds is characterized with base and background levels for identifying the sources of anthropogenic additions (GIPME, 2003; Lehr & Keeley, 2005).

5.1.3.1 Heavy metals

The metal enrichment factor (EF) was also applied to evaluate the anthropogenic contribution of heavy metals in surface sediments. The results indicated that variations in the enrichment factor were significantly different for heavy metals. The Fe in the sediment may have originated entirely from natural processes or crustal materials. The enrichment values of Cu, Cr, Mn, Ni, V and Zn were between 2 and 5, indicating that the sediments of the Klang Strait were subject to moderate anthropogenic inputs of these heavy metals.

Significant enrichment of Pb, As and Hg was observed in the sediments, and only Cd originated from a high proportion of anthropogenic sources (**Figure 4.8**). In general, the sediments of all stations are in the same class of enrichment factor ($5 < EF < 20$) or have moderate anthropogenic inputs of metals (**Figure 4.9**), but cluster analysis revealed a better view of the enrichment factor at different stations.

According to the cluster analysis, stations 1, 2, 4 (close to the berth line in the North Port), 7, 8, 9 (vicinity of a cement outlet), 10,11, 12 (vicinity of a liquid berth and food and oil factories in the West Port), 13,14 and 15 (near a container terminal in the West Port) are included in the same group because the enrichment factor (9-11) was higher in these stations in comparison with other stations (5.2-8.87) (**Figure 4.10**).

Based on the enrichment factor, the heavy metal contamination of marine sediments in the Klang Strait was attributable to both natural processes and mineralogy and human (anthropogenic) activities. Furthermore, the marine sediments of Klang Strait had high anthropogenic inputs of Cd, Pb, Hg and As, especially in stations close to the berth line.

These metals (Cd, Pb, Hg and As) originate primarily from industrial processes including mining, the burning of fossil fuels, waste recycling and cement manufacturing, as well as paper and glass production (Cossa et al., 2010; Davis, Marjorie Aelion, McDermott, & Lawson, 2009; Jennings & Rainbow, 1979; Pan & Wang, 2011; Yasar, Aksu, & Uslu, 2001). There are several industries in Port Klang involved in cement manufacturing, palm oil processing and oil/electrical based power generation. Other sources of these metals might include atmospheric deposition, river inflows and terrestrial runoffs, which are the primary routes for release of metals into marine environments. Additionally, As, Cd and Hg are able to build up in the sediment through plant cycling because these metals are easily absorbed by plants, thus entering into the biological cycle (Zhang et al., 2010).

In the South Port, the high proportion of anthropogenic origins of these elements around the mouth of the Klang River is consistent with observations that the river is a primary route for the release of heavy metals.

Several studies have indicated that organic herbicides, insecticides (Lead-Arsenate), pesticides and fertilisers applied in agriculture activities as well as industrial discharges are the land-based anthropogenic sources of metals that are transported into rivers, where they can pollute coastal and estuarine areas (Kumar et al., 2012; Ye et al., 2012).

Moreover, the high concentrations of Cd and As could have originated from tsunami-related sediment deposition, ship waste, embarkation activities and/or the anticorrosive paints used on marine vessels (Pan & Wang, 2011; Liu et al., 2010).

5.1.3.2 Poly aromatic hydrocarbons (PAHs)

Like to other contaminants, the sources of PAHs are divided into two major groups, anthropogenic and lithogenic. Anthropogenic sources of PAHs include pyrogenic and petrogenic sources. Pyrogenic PAHs primarily include those with more than three aromatic rings (4-6 rings), and their original source is the incomplete combustion of organic compounds, which form very rapidly at high temperatures (approximately 700°C). These contaminants originate from activities involving the combustion of fossil fuels (heating oil, cooking, burning coal, vehicle emissions) and biomass burning (fireplaces, controlled burns) (Beyer et al., 2010; Khairy et al., 2009; Pies et al., 2008). Petrogenic compounds are normally related to PAHs with lower molecular weights (Naf, Acy, Ace, Flr, Phn and Ant) that have undergone various weathering processes (dissolution, evaporation and photo-oxidation) rather than PAHs with high molecular weights (Fla, Pyr, BaA, Chy, BaP, BkF, InP, Bghip and DibA) (Beyer et al., 2010; Zakaria, Okuda, & Takada, 2001; Pies et al.,

2008). Petrogenic PAHs involve unburned fossil fuels, including oil spills and the in concentration of petroleum products that originated from coal, crude oil and refined products. Petrogenic PAHs can enter into a marine environment through land-based runoff, discharges from ships and accidental spills (Beyer et al., 2010; Neff, 2002; Robertson, 1998).

Lithogenic sources of PAHs originate from biogenic and diagenic sources (Beyer et al., 2010). Diagenic PAHs in sediments originate from organic material (natural oil, coal erosion, forest and grass) and form rapidly over days or years. Biogenic PAHs are formed during the biosynthesis process by organisms such as fungi and bacteria (Beyer et al., 2010; Nahla, 2009; Neff, 1979, 2002; Whitehouse, 1983). The concentration and distribution of PAHs observed in the sediment reflect the PAHs' source characteristics, which are influenced by the physicochemical properties of individual PAHs. PAHs in a harbour area such as Klang Strait could originate from a variety of sources (pyrogenic and petrogenic).

The results showed that the anthropogenic sources of PAHs consisted of a mix of pyrogenic and petrogenic sources in all stations except stations 4, 14 and 21, where most of the PAHs were found to have originated from the combustion of materials such as kerosene, wood, coal and grass (**Figure 4.11 and Figure 4.12**). Some stations (3, 6, 7, 8, 11, 13, 16, 19 and 20) showed a mixed pattern of petroleum combustion sources (liquid fossil fuel due to vehicle and crude oil). At other stations (1, 2, 5, 9, 10, 12, 15, 17, 18 and 22), the PAHs in the sediment originated primarily from combustion, although petroleum-derived contamination cannot be ignored.

In general, source analysis revealed that the PAHs in the sediment in the Klang Strait are derived primarily from liquid fossil fuels related to vehicle use, crude oil and coal (petroleum combustion sources), which can originate from industry discharges such as effluent from cement, food and oil factories. A minor amount of PAHs may be related to direct petroleum discharges and land-based runoff.

The results of the PCA analysis are concordant with the evidence from the pair isomer ratio of PAHs, which revealed a mixture of pyrogenic- and petrogenic-derived PAHs in the Klang Strait.

The PCA analysis described 63.65 % of the total variance (PC1, PC2 and PC3) in the PAH load, including individual PAHs that are known to originate from incomplete combustion, the pyrolysis of fuel and tracers for oil spills. Only 19.42% of the total variance (PC4 and PC5) in PAHs with a high load of NaPs was explained, and the variance in PAHs was not related to unknown and biogenic sources (**Table 4.9**).

Moreover, a correlation analysis revealed a significant correlation between some individual PAHs related to pyrogenic and petrogenic compounds, such as Nap, Acy, Ace, Flr, Phn, Ant, Fla BaP, and Bghip. This implied that the sediment samples are polluted by anthropogenic sources of PAHs because unpolluted sediment samples do not exhibit an oil fingerprint and only some PAH compounds may be found in this sediment (**Table 4.7**).

Mahyar et al, (2010) studied the characteristics and possible origins of PAHs in the developed and developing areas around the coastal waters of peninsular Malaysia. They collected sediment core samples to assess the historical profile of PAHs from 1875 to 2007. Their research agrees well with our results because they revealed that older sediment samples (1875-1899) did not exhibit an oil fingerprint and that only some PAH compounds were found (Sakaria et al., 2010).

Sediment samples that are polluted by oil products generally exhibit high concentrations of phenanthrene and its methylated derivation.

Thus, there is a high correlation between crude oil and petrogenic and pyrogenic compounds, whereas this correlation in old sediment samples with natural inputs (with no oil fingerprints) ranges from low to negative values.

Similarly, they indicated that in near-shore and offshore areas near Klang, high levels of PAHs originated from pyrogenic sources such as the combustion of fossil fuel and the burning of biomass and wood. The dominance of pyrogenic sources in this area is due to the discharge of by products of combusted petroleum from industries and automobiles (Krauss et al., 2005; Sakaria et al., 2010).

In addition, other studies have reported that various sea and land-based sources of contamination contribute to increasing petrogenic pollution in the coastal waters of west coast Peninsular Malaysia. For example, in 1999, Abdullah revealed that land-based runoff and contamination from an offshore oil field near Sumatra Island contribute to petroleum contamination in the Malacca Strait, a narrow channel of marine water located between Sumatra Island, Indonesia and peninsular Malaysia. This strait is vulnerable to contamination caused by tanker operation and oil spills (Mirsadeghi, Zakaria, Yap, & Shahbazi, 2011). The Strait of Malacca also plays an important role in transporting pollution into Klang Strait. Pauzi Zakaria in 2001 used a biomarker compound to identify the source of tar-balls off the coast of Malaysia. They identified several petrogenic sources of contamination in the western coastal waters of Peninsula Malaysia, such as accidental oil spills and tanker-derived sources in the Strait of Malacca and crude oils originating from land-based runoff from human activities. Additionally, they clearly showed that the western coastal waters of Malaysia have received approximately 30% of their petroleum pollution from Middle East crude oil (MECO) and South-East Asian crude oil (SEACO), which was

probably transported to Malaysia via marine currents, tankers, and shipping discharges, including ballast water and tank-washing water (Pauzi, Okuda, & Takada, 2001).

5.1.4 Degree of contamination of the sediment and adverse biological effects

5.1.4.1 Heavy metals

In the present study, the degree of contamination of the sediments and related adverse biological effects were estimated based on the contamination factor (CF) and a comparison between the contamination concentration at the study stations and specific values (TEL and PEL) given in the sediment quality guidelines described in the methodology. The contamination factors for Al, Fe, Mn, Cu, Cr, Ni, V and Zn were lower than 1 at all stations (**Figure 4.7**), implying that the marine sediments of the Klang Strait have not yet been polluted with these metals. Most of the stations were considered to be moderately polluted with Pb, As and Hg, and Cd exhibited a high degree of pollution in all stations except stations 10 and 11, which were moderately polluted (**Figure 4.6**).

Additionally, the results indicated that Cu, Cr, Ni and Zn have rare adverse effects on the biological community because their concentrations were lower than the TEL, background and igneous rock values at all stations. Cd, Pb and Hg were found to have occasional adverse effects and As exceeded the PEL value, indicating likely significant adverse effects on biological organisms. Moreover, the concentrations of these metals were significantly greater than the background and igneous rock values (**Table 4.15**).

The variation in the estimated PEL_q factor and contamination degree (C_d) value revealed that the sediments collected from stations 13 and 15 (around the container terminal in the West Port) and stations 16 and 17 (close to the mouth of the Klang River in the South

Port) were highly polluted with heavy metals and were considered to exhibit moderate adverse effects. The rest of the stations were considered to be moderately polluted with slight adverse biological effects, and the control station was unpolluted (**Figure 4.19**).

This study clearly shows that the Cd, Pb, Hg and As concentrations in the Klang Strait were influenced by disturbances, which changed the associated geochemical concentration ratios, and that the metal concentrations increased from their standard range. The relative concentration ratio of the metals exceeds standard variation levels in the sediment when geochemical metal concentrations experience disturbances due to environmental change.

These disturbances may be related to differential derivation and can be due to lithogenic sources and the multiple anthropogenic sources described in section 5.1.3.

5.1.4.2 PAHs

In this study, sediment quality guidelines (SQGs) are applied as a practical tool to evaluate PAH contamination and adverse biological effects (Long et al., 1995, 2006; Qiao et al., 2006; Quiroz et al., 2010).

Based on a comparison with the sediment quality guidelines, contamination factors for individual PAHs such as Nap, Ace, Phn, Fla, Pyr, Chy, BbF, BkF and BghiP were lower than 1 at all stations. This implies that these PAHs have rare adverse effects on the biological community; only Acy, Flr, Ant, BaA, BaP and DibA were associated with adverse biological effects, only at stations 4 (close to the container terminal in the North Port), 7 (cement outlet), 13 (container terminal in the West Port), 12 (around the mangrove forest in the West Port) 16 and 17 (vicinity of the mouth of the Klang River) (**Table 4.17**).

The variation in the estimated PEL_q factor for total PAHs revealed that the sediments collected from stations 4, 7, 12, 16 and 17 around the berth line and mouth of the Klang River were slightly polluted, and PAHs were likely to have slight adverse effects on the biological communities at these stations.

Only station 13 (close to the container terminal in the West Port) was moderately polluted, and the rest of stations were subject to rare adverse ecological effect due to the PAHs exposure in the surface sediment. The present study shows that, generally, the average concentration of total PAHs is 994.02 ± 918.1 in the Klang Strait and that the sediment is slightly polluted with PAHs (PEL_q = 0.16).

According to the above discussion, it may be concluded that PAHs are not a primary pollution concern in the Klang Strait and that only station 13 can be considered to be a vulnerable station.

In this research, our hypothesis was defined based on the serious threat posed by petroleum contamination to the Klang Strait because of its specific strategic importance: this strait serves as a major, high-traffic gateway for shipping activities in peninsular Malaysia is coastal waters and is also influenced by various environmental stresses from land-based sources of contamination such as domestic waste, transportation activities, and industrial and agriculture inputs. Moreover, in 1982, the coastal area of the Klang Strait was categorized as moderately polluted with petroleum hydrocarbons according to the standard classification of the FAO (the Food and Agriculture Organization), which also indicated that the petrogenic pollutants in the Klang Strait originated from oil spill events and ship ballasting or bilge pumping due to tanker and non-tanker operations (Marchand, Bodennec, Caprais, & Pignet, 1982; Yap, 2005).

According to the present study, this hypothesis was rejected because at most of the stations, the average PAH concentration was significantly lower than the background value and rarely reached a level likely to cause adverse biological effects.

Recently, some studies recorded a significant decline in PAHs discharges around the near-shore zone of the Klang Strait between 2000 and 2007. The highest value for PAHs contamination was estimated at 1700 ng/g d.w (Wang et al., 2011).

In near-shore Klang sediment samples from 1976 to 1999, with a predominant input of burnt materials such as oil and petroleum products. The dominance of pyrogenic sources was due to combusted petroleum discharges from industries and automobiles. From 1976 to 1999, several international and national events affected Malaysia's environmental history and caused an increase in the levels of PAHs and other organic hydrocarbons in the near-shore area of the western coastal waters of peninsular Malaysia. This region underwent many development activities related to marine transportation, urbanization, industrialization and motorizations along the shore. Additionally, rapid development occurred in the Klang Strait, such as the construction of the West Port and maritime-related industries that caused greater numbers of ocean-going ships to enter the strait from the South China Sea and the Far East to transport goods. Moreover, in 1997, a collision between two tankers in the straits of Singapore caused 25,000 tons of heavy fuels oil to be released into the marine environment, of which 700 tons of oil were released into the Malacca strait, negatively affecting the coastal area of the Klang Strait (Yap, 2005).

There were several reasons for the subsequent decline of the concentrations of petroleum hydrocarbons from 2000 until 2007, including the establishment of an integrated management programme, meteorological conditions and weathering.

An integrated management programme was established in 1996 in which several responsible organizations (the weather forecast department, maritime department, DOE, Navy, Coastal Guards, emergency response, and NGOs) contributed to solve the environment problems in Malaysia's marine environments. For example, urban management defined an integrated approach to prevent oil derivatives from entering marine and coastal waters.

Similarly, the DOE and other organizations should take part in wastewater treatment and runoff control. Beside from this collaboration involving various organizations, specific regulations relating to marine pollution were ratified in 1990 and 1997 to control petroleum and chemical contaminants in the Klang Strait.

These regulations focused on strategies that were based on international agreements to prevent and control pollution from ships, platform draining and industrial inputs such as MARPOL 1997, CLC convention, UNCLOS IN 1996 and OPRC 1990 (Zakaria et al., 2001).

The weathering processes can greatly deplete PAH concentrations in a marine environment. The list of compositional indices of PAHs is presented in **Table 4.8**. The L/H-PAH ratio is accepted as a practical method for assessing weathering based on the differences between the low molecular weight and high molecular weight of PAH compounds. These results show that the concentration of high-molecular-weight PAHs is significantly greater than that of low-molecular-weight PAHs in most stations. Thus, the L/H-PAH ratio was below 1 at most of the stations and above 1 only at stations 3, 7, 13 and 14.

In general, a low ratio of L/H-PAHs is probably due to high resistances of the high-molecular-weight PAHs to microbial degradation, which is consistent with other studies. Such a low ratio could also be due to the high solubility and volatility of the low-molecular-weight PAHs, which would lead to their depletion (Chandru et al., 2008; Pauzi Zakaria et al., 2001; Rocher, Garnaud, Moilleron, & Chebbo, 2004).

In addition, there is also evidence of a greater depletion of low-molecular-weight PAHs by the weathering process, which is clearly indicated by Pauzi Zakaria (2001).

He compared the ratio of L/H-PAHs in crude oil (Middle East crude oil and South-East Asian crude oil) with tar-ball samples that were collected from the western and eastern coastal waters of Malaysia. Their results revealed that the tar-ball samples from west coast Peninsular Malaysia coastal waters had undergone significant weathering because their L/H-PAH ratios were much lower (0.23-1.48) than the ratios of crude oil samples (8-44 for SEACO and 12.13-20.3 for MECO) (Zakaria et al., 2001).

In the present study, this ratio ranged from 0.02-2.61, which was significantly lower than that of the crude oil in this region. Several possibilities have been described to explain why the PAH compositions had a lower ratio of L/H in the west coastal waters of Peninsular Malaysia, such as wandering due to long-haul transportation, ballast water and tank washings. Sea currents distribute petroleum as water-in-oil emulsions and transport them many kilometres away from the spill site in eastern coastal platforms. The emulsion compounds normally form viscous pancake-like masses with slow degradation and high stability in marine water, which will persist for several months at sea. These currents are controlled by the southward and northwest ward flows of the South China Sea.

The long distance transport from the eastern to the western coastal waters of Peninsular Malaysia could increase the weathering process and lead to the formation of petroleum samples with low molecular weights in west coastal waters (Neff, 1979; Zakaria et al., 2001; Sakari et al., 2008).

Tank washing and accidental spills from tankers are other mechanisms that could also play important roles in increasing low L/H ratios of PAH compounds because tank-washing discharges are rich in paraffin wax. Waxy crude oil covers the tanks during long-range transport and is discharged to the sea during delivery and loading port transits.

This compound includes specific features characterized by a low ratio between high-molecular-weight n-alkane and low-molecular-weight alkane (Low L/H-alkane), a low concentration of PAHs (Low PAH/n-alkane ratio) and a low ratio of L/H-PAHs (Blumer, Erhardt, & Jones, 1973). Pauzi Zakaria indicated that most of the tar-ball samples that were collected from the western coastal waters had all of these characteristics and that their ratios (L/H-alkane, PAH/n-alkane and PAH L/H) were lower than those of crude oil. Thus, these results indicated that PAH compounds are to some extent derived from tank-washing discharges (Pauzi et al., 2001; Yap, 2005).

Additional research has indicated that meteorological conditions play a major role in controlling PAH concentrations over spatial and temporal scales, and a significant negative linear relationship was found between wind speed, temperature and PAH concentration because atmospheric turbulence causes a dilution of contaminant concentrations and speeds the weathering process, especially if the wind speed is greater than 5.8 Km h⁻¹ and the temperature is greater than 20 °C (Guitart, García-Flor, Miquel, Fowler, & Albaigés, 2010; Montuori & Triassi, 2012; Rocher et al., 2004).

Thus, the higher temperature (approximately 30 °C) of the Klang Strait as a tropical area could increase the depletion of PAHs.

5.1.5 Biological response

More recently, efforts have been made to explore the correlation between sediment and the distributions of benthic communities, leading to the belief that a complex interaction of multiple parameters can either directly or indirectly control the distribution of a benthic community.

These parameters include concentrations of organic compounds, salinity, oxygen levels, sediment type, hydrodynamic environment, food availability and anthropogenic stress, which is the primary parameter constraining the structure of a benthic community (Leonardsson, Blomqvist, & Rosenberg, 2009; Pacheco, Laudien, Thiel, Oliva, & Arntz, 2010; Rosenberg, 1976; Rosenberg et al., 2009). The benthic community's response to these multiple parameters is complicated by spatial and temporal changes in community composition. In this research, there were no temporal changes in species richness or the abundance of dominant species, but a larger effect on the benthic composition of sensitive species was found on the spatial scale.

In this study, every sampling site (the North Port, West Port and South Port) had a unique configuration of these parameters. In the North and West Ports, data indicated that TOC, particle size and depth controlled the spatial distribution of benthic species because the abundance, diversity and richness of the macro-benthic community were strongly correlated with TOC, fine particle size and depth (**Table 4.16**). Over a one year study period, stations near the berth line supported relatively lower abundance, diversity and richness than stations near the mangrove edge.

Every sampling location along the mangrove edge had a similar configuration, with shallow water (6.8-11.2 m) and high organic content (11.98-17.04%) in a soft and muddy

substratum (63.42-73.77) suitable for settlement by diverse species, factors that may cause species abundance to increase. Data revealed that the high TOC along the mangrove edge could not suppress the colonization of benthic species in this area because this organic enrichment is not strong enough to result in serious oxygen depletion and is only sufficient to provide a rich food source for the benthic community. Additionally, the locations along the mangroves are located far (1500 -2000 m) from point sources of anthropogenic discharges, another potential reason for their higher species diversity.

Other studies have frequently indicated that some metal ions, such as Na, K, Ca, Fe, Mn, Co, Cu, Zn and Mo, are essential for biological systems when their concentration levels do not exceed those required for correct nutrition (Rékási, Gilkes, & Prakongkep, 2010; Varol & Şen, 2012).

Most of the sampling stations along the berth line and in the middle of the strait are in deeper water (12.5-21.60 m) with coarser and sandy sediments (40.21-50.3%), to cause reduce of species diversity, especially at stations in the vicinity of the cement outlets and the container terminal berth. Additionally, Fe and Mn showed significant positive correlations with benthic abundance, implying that Fe and Mn are linked to an increase in benthic abundance.

Anthropogenic stress can be another cause of reduced benthic community because the stations along the berth line are close to anthropogenic discharges from port activities and industrial outlets, which may suppress benthic community development. The results of our correlation analysis supported a negative effect of anthropogenic stress (heavy metals and PAHs) on benthic composition.

According to this results, As, Cd and Cu exhibited significant negative correlations with the abundance of the benthic community, implying that increases in these metals probably cause decreases in the abundance of benthic species but that changes in diversity

and richness were independent of the As, Cd, and Cu concentrations. Similarly, the total concentration of PAHs exhibited a significant negative correlation with the diversity and richness of benthic species.

The effect of PAHs on the benthic community has been frequently examined in several studies, which indicate that opportunistic species (ecological groups V and IV) with high abundances are replaced with other ecological groups when the benthic communities are exposed to PAH contamination (Rosenberg, 1976; Schafer, Hearn, Kefford, Mueller, & Nugegoda, 2010; Veiga, Rubal, & Besteiro, 2009).

The results of our analysis of spatial distribution indicated that the abundances of common opportunistic species (*Lumbriculus sp* and *Glycera alba*) increased greatly at stations 7, 8, 13 and 14, where *Lumbriculus sp* was a dominant species, and diversity and richness were significantly decreased (**Table 4.10** and **Figure 4.13**).

Similarly, the AMBA analysis revealed that the benthic community is moderately exposed to anthropogenic stress at these stations (**Table 4.13**). A high proportion of the sediment samples that were collected in the vicinity of the cement outlet (stations 7 and 8) were polluted with cement (more than 50%); this may hinder the development of benthic fauna.

According to the comparison results of the sediment quality assessment, stations 13 and 14, in the vicinity of the container terminal, were significantly polluted by heavy metals and PAHs and were considered to exhibit moderate to high adverse effects, whereas the rest of the stations were considered to be moderately polluted with slight/moderate adverse biological effects, and the control station was unpolluted. These results are completely synchronous with those of the AMBA analysis described above.

In the South Port, the sampling stations are in shallow water (7.5-12.40 m) with high organic content (11.89-22.65%) and muddy sediments (57.73-95.39%) (**Table 4.1**).

Spatial differences in the benthic community showed a strong negative correlation with TOC, fine particle size and heavy metals (except Ni and Mn) (**Table 4.15**). In fact, the abundance, diversity and richness of benthic communities decreased along gradients of increasing organic materials in the South Port. Sediment samples that were collected in the vicinity of the Klang River (stations 16 and 17) were completely devoid of fauna species, but moving away from the mouth of the Klang River, species abundance and diversity increased slowly at the other stations in the South Port. *Lumbriculus sp* and *Glycera alba* were the dominant taxa at these stations (**Table 4.10** and **Figure 4.13**).

Decreased salinity and dissolved oxygen probably caused the reduction in species diversity near the Klang River, although no significant correlation was observed between these parameters and the benthic community in the Klang Strait. The results of the AMBA and the sediment quality assessment revealed that stations 16 and 17 are highly polluted by heavy metals and organic content, with strong adverse biological effects.

Several studies have indicated that sediments near discharge point with high concentrations of organic compounds are devoid of benthic species and that the number of species will slowly increase further away from a discharge area.

A high concentration of organic compounds can increase oxygen depletion, and well-oxygenated sediments are essential for protecting the benthic population (Rhoads & Boyer, 1982; Rosenberg, 1976; Rosenberg et al., 2009; Shin, Lam, Wu, Qian, & Cheung, 2008).

In 1978, Pearson, Rosenberg, and Rhoads presented succession models of benthic communities over temporal and spatial scales, which showed that the biomass, abundance, and diversity of benthic communities vary in predictable patterns in response to organic compounds (**Figure 2.1**). They indicated that the abundance of benthic communities increases along decreasing gradients of organic materials. Moreover, they indicated that in

the part of an estuary closest to the river mouth, the diversity is low due to the low salinity and the high percentage of silt and clay (Rhoads & Boyer, 1982; Rosenberg, 1976; Rosenberg et al., 2009).

The present data showed that in the North and West Ports, the variation of the macrobenthic community was primarily related to sediment characteristics (TOC and fine particles size) and that releases of anthropogenic pollution are secondary disturbances that hinder benthic development, especially in the South Port where heavy metal contamination plays a major role in hindering the development of benthic communities.

5.1.5.1 Succession stages

In 1978, Pearson and Rosenberg exemplified the acceptable model (P-R) to clarify the effects of eutrophication on benthic composition, which is applicable for coastal and estuary waters worldwide because of its extensive usage in the literature (Calabretta & Oviatt, 2008; Kennish, 1997; Montuori & Triassi, 2012; Shin et al., 2008). This model shows that variation in the concentration of organic compounds from low- to high-input leads to frequent succession stages in the macro-benthos from the normal structure of the benthic community, with diverse species, to a transitional community structure with a high abundance of opportunistic species, and finally to azoic sediment devoid of fauna. The P-R model logically described a recovery pattern for an impacted macro-benthic community. First, a few opportunistic species increase in abundance in azoic sediments, which is considered as pioneer community'.

This community undergoes several successions to create an 'intermediate community' and reaches a stable final point, the 'climax community'(Rosenberg & Blomqvist, 2004). The climax community was recorded at a control point that is free of contamination. Several factors affect the succession and recovery process in aquatic areas,

such as water circulation, rapid fluctuations of salinity, temperature, releases of toxic substances from the sediment, topography, hydrodynamic conditions, water turbidity and water exchange patterns (Calabretta & Oviatt, 2008; Pacheco et al., 2010).

Benthic data collected during this research identified the presence of distinct benthic structural assemblages at each of the 22 stations in the Klang Strait, presenting a progression in the community of benthic assemblages from early successional stages to the azoic stage.

Most stations in the Klang Strait are in the early stage of succession, including all stations in the North Port (1-6), stations 9, 10, 11, 12, 15 in the West Port and stations 18 and 21 in the South Port. AMBA analysis confirms these results because all of the above stations were slightly polluted, with a high abundance and diversity of ecological groups I and II (sensitive species) (**Table 4.13** and **Figure 4.17**). Stations 7, 8, 13, 14 in the West Port and stations 19 and 20 in the South Port were in the transitional stages of succession, with high abundances of ecological groups IV and V (opportunistic species), and were moderately polluted. Stations 16 and 17 were in the azoic stage, whereas only station 22 (control point) exhibited a normal benthic community composition, with high diversity and without opportunistic species. In the South Port, changes in the benthic structure along a gradient of anthropogenic disturbances clearly followed those expected according to the P-R model of benthic succession.

In the West Port, stations near the cement outlet (7, 8 and 9) and container terminal (13,14,15) also closely follow this model, which is evidence that anthropogenic discharges from the cement factory and container terminal likely affect the benthic community in this area. All stations in the North Port were in the early stages of succession, which indicates that this port is less influenced by anthropogenic sources to comparison with the West and South Ports in the Klang Strait.

In this study, evidence is presented that the benthic community in the Klang Straits generally in the earlier stages of succession and is less diverse than benthic communities observed in a more pristine area (control point). The results indicate that the distribution of the benthic community is controlled by several factors between different sites (Appendix 2).

In the South Port, there is a north-south gradient of increasing benthic diversity and decreasing opportunistic species that closely follows a similar pattern that had previously been identified with the P-R model to describe the variation in benthic structure along a decreasing gradient of organic compound concentration and sediment pollution by heavy metals and organic pollutants. Similarly, correlation analysis clearly indicated an effect of anthropogenic stress (total organic compounds, heavy metals and PAHs) on the distribution of the benthic community in the South Port.

In the West and North Ports, the distribution of the benthic community does not follow the gradient of organic compounds (1978). In this area, there is an east-west gradient (from the coastline to the mangrove edge) of increasing benthic diversity and decreasing opportunistic species, implying that this pattern of benthic distribution is influenced more by sediment pollution, sediment type and food availability rather than by organic compounds because from the east to the west side of the strait, there is a gradient of decreasing sediment pollution (heavy metals and PAHs) and increasing fine-grain-sized particles, total organic compounds and food availability. The increase in total organic compound from east to west did not hinder the increase in benthic diversity.

The model of benthic faunal succession in the West and North Ports can be considered to represent changes in the structure of macro-benthic communities along a gradient of natural and anthropogenic impacts because the relationship between the general characteristics of these port benthic communities and the mangrove system as a natural

habitat is clear. From a management point of view, an understanding of the composition of Klang Strait benthic communities is valuable for the development of management policy.

5.2 Ecological risk assessment:

According to our results, the potential ecological risk values for all metals except Hg and Cd were estimated to fall into the low potential risk value category ($Er^i < 40$) at all stations. The Er^i -values for Hg and Cd were significantly greater than those of the other metal and varied between moderate and high levels of potential ecological risk among the different stations. In this study, the potential risk value for all metals was ranked in the following sequence: $Cd > Hg > As > Cr, Pb > Cu > Zn$ (Figure 4.24).

Regarding the ecological risk assessment, Er - values and RI - values constitute one method for assessing the adverse effects of metal contamination on biological communities and human health. Cd and Hg represent high and significant potential risks to biological communities, whereas the rest of the investigated metals represent only low risks.

The sequence of C_f^i – values and Er^i – value revealed some differences among metals in the contamination profile of the Klang Strait.

The result of the sediment contamination factor analysis indicated that surface sediments are moderately polluted ($1 \leq C_f^i < 3$), with Hg and Pb, and are highly polluted ($3 \leq C_f^i < 6$) with As and Cd in most of the stations.

Moreover, the results of a comparison between the contaminant concentrations and the specific values (TEL and PEL) from the sediment quality guidelines indicated that the concentrations of Cd, Pb and Hg were associated with occasional adverse effects. The value for As exceeded the PEL value, indicating a high likelihood of adverse effects for biological organisms. Other metals and PAHs were rated as causing rare adverse biological

effects in the surface sediment because their concentrations were lower than the TEL values.

In contrast, the risk analysis that evaluated differences among metals based on the Er^i -value implied that not only Cd but also Hg pose high potential risks for biological communities ($80 \leq Er^i < 160$) whereas other parameters represent low risks ($Er^i < 40$). The reason for this difference is related to the low sediment-logical toxic factor (St-value = 7) of As in comparison with Cd and Hg (37 and 40).

In 1980, Hakanson indicated that in a risk index, the toxin factor provides complex information about the potential transport roads of toxic factors to man and aquatic ecological systems and also provides information about the threat posed by a toxic factor to an aquatic ecological system. As matter of fact, the toxic factor acts as the “main road in this model that goes from contamination of water-sediment-biota–fish-man.”

Thus, sometimes the risk factor (RI) provides a different picture of contamination in comparison with the contamination factor and contamination degree because in the risk model, the toxicity of elements and the sink effect of coastal water sensitivity are considered, but the contamination factor and contamination degree is an earlier models that are estimated based only on the concentrations of elements.

According to these results, the highest potential risk is posed not by As, as might have been anticipated, but rather by Cd and Hg in the Klang Strait. The results of present study implies large contamination factor for As, Cd, Hg and Pb which indicates the source of contaminates, but not necessarily the ecological significance of pollution. The potential risk factor analysis applied to distinguish which metals should be given more attention in West Port. Hg and Cd should be given high priority while other metals low priority.

A risk index (RI) analysis was performed to rank stations based on the ecological risk to the biological communities in the Klang Strait. This analysis revealed that stations 16 and 17 (mouth of the Klang River) are at very high ecological risk and that most of the stations along the berth line (except for stations 1 and 10) are at high ecological risk, and these stations at moderate risk. The control station was found to be subject to rare adverse effects due to contamination.

There is a disagreement between the results of the RI analysis and PELq, which is related to the levels of risk at different stations. The variation in estimated PELq values for heavy metals showed that only the sediment samples collected in stations 16, 17 and 13 were considered to exhibit moderate adverse effects, and the rest of the sediment samples were considered to represent slight adverse effects. For PAHs, PELq values were moderate only at station 13 and were slight or rare at the other stations. This difference is related to the toxin factor and sink factor included in the RI analysis because these factors are independently estimated for each contaminant (except for PAHs) and are relevant to the individual background value and BPI for the Klang Strait. In this method, regional variation was also considered to some extent.

As no sediment quality guidelines were available for the west coast of Peninsular Malaysia or even for other areas around this country, the results of a risk analysis based on the guidelines alone cannot provide an accurate view of the risk level in this area.

In addition, the results of the benthic response to exposure in the sediment confirm Hakanson's method in this study because Hakanson's risk levels were completely synchronous with the level of response of the benthic communities to changes in contaminants at the stations 16 and 17, Whereas the rest of the stations (except of station 40) were one level up than the level of response of the benthic communities to changes in contaminants.

For example, the AMBA analysis revealed that the benthic community is moderately exposed to anthropogenic stress at stations 19, 20, 7, 8, 13, 14 (**Table 4.13**) while the high risk level was estimated for these stations.

Likewise, in other stations (except of 16, 17) benthic community was slightly exposed to anthropogenic stress, but the risk level was moderate for these stations.

The first basic study on the straits was initiated by several research organisations in 1981, including the ASEAN (Association of Southeast Asian Nations) and DOE–Selangor (Department of Environment)(Ho, Tahir, & Tong, 1986-1988).

Ten specific pollutants (bacteria, phenol, oil and grease contamination and Cd, Hg, As, Pb, Cu, Cr and nutrient concentrations) were estimated to assess environmental quality. That study recorded high concentrations of chemical pollution in the form of heavy metals in the water, sediments and organisms in the Klang Strait. In particular, the levels of iron and lead were high compared to the standard levels for coastal water as a result of navigation and transportation, land-based pollutants and industrial activities (Law & Singh, 1986).

Moreover, the study initiated in 1981 recorded moderate pollution levels of polyaromatic hydrocarbons in this area. The Malaysian government has put regulations, guidelines and international agreements into place to decrease the concentrations of chemical contaminants in harbours and to require treatment of waste water flowing out of ships (Yap, 2005). However, previous studies did not provide enough information to estimate the degree of contamination or toxicity levels in the sediment.

There are no existing data on the distribution of heavy metals in Klang Strait, and therefore, a thorough ecological risk assessment cannot be performed. The results of this research support the idea that the sediment quality of the Klang Strait area has to some extent recovered. In the present study, the contamination levels of most metals (except for

Hg, As and Cd) and polyaromatic hydrocarbons in the sediment were classified as unpolluted or slightly polluted at most stations except for station 13, which is close to the container terminal in the West Port, and stations 16 and 17, in the vicinity of the Klang River.

These results were most likely due to the wastewater management regulations that were ratified in 1990 and 1997 to control petrogenic and chemical contaminants in the Klang Strait. These regulations focused on strategies that were based on international agreements to prevent and control pollution from ships, platform draining and industrial inputs (MARPOL 73/78 and OPRC 1990) (Sasekumar and Chang, 2005).

It is clear that these regulations have controlled contamination to some extent but have not been adequate for complete recovery from toxic metal contamination, because the contamination levels of some very toxic elements such as Hg, As and Cd were categorized as moderately to highly polluting in most sediment samples. Thus, sediment from the most polluted stations was a significant source of toxic metals.

These stations are influenced by the Klang River runoff and the terminal container and cement outlet in the West Port, which may not be covered under the protective regulations.

In addition, this research collected comprehensive experimental data over a one year period to identify vulnerable and high-risk areas for contaminants based on ecological risk and biological response and provided distribution patterns for heavy metals and PAHs. This research is an initial step forward from earlier studies which only considered metal concentrations in sediments based on experimental analysis, scientific model and indices. As a matter of fact contamination factor and degree of contamination means that a first step towards a diagnostic tool to assess the level of anthropogenic sources, risk factors and risk index were used as a second step to establish ecological adverse effects. Due to lack of

consumption rate and body level measurements for metals, human risk assessment was not carried out in this study.

5.3 Water quality assessment

The trophic condition in Klang Strait exhibited a significant spatial and temporal variation despite a similar tropical climate throughout this study area. These differences are most likely related to variation in nutrient concentrations due to anthropogenic activities that change coastal dynamics or nutrient balances as well as river discharges in South Port, which affect the variation of inorganic particular material.

5.3.1 Water quality trends

There several sources in marine systems that affect water quality, such as river discharges, upwelling, remineralisation/sediment, re-suspension, industrial waste and effluents; thus, it is difficult to quantify the relative contributions of nutrient sources to marine and coastal systems (Coelho, Gamito, & Pérez-Ruzafa, 2007; Kitsiou & Karydis, 2011).

In the Klang Strait, the water temperature and current speed at the different sites were usually related to the climatic condition of the west coast of peninsular Malaysia. The temperature gradually increased from the north monsoon to the south monsoon, while the current speed decreased during this period. This seasonal variation matches the seasonal pattern of water masses in Malacca and the west coastal water of peninsular Malaysia (Amiruddin, Ibrahim, & Ismail, 2011).

In the case of salinity, although the climatic patterns were the same at all of the sites, there were significant differences among sites and months. The variation of salinity in

coastal and marine systems usually results from the hydrological variation due to evaporation water loss and freshwater inputs, such as rainfall and river discharges (Amiruddin et al., 2011; Hakanson & Blenckner, 2008; Lars Håkanson & Eklund, 2010). The spatial variation of salinity was usually the same among the sampling sites (**Figure 4.31**). The lower value observed in South Port. It is unlikely that an area near the mouth of Klang River or in South Port would show no water circulation especially with the river flow and tidal current. Consequently, the South Port stations had lower salinity, and the difference from the three other locations was more significant. Salinity variation among the other sampling sites was always insignificant. The seasonal pattern of salinity was similar for all of the sites: salinity was low during the northeast monsoon (rainy season) because of salinity dilution and high during the southwest monsoon because of evaporation water loss. In the present study, salinity was significantly negatively correlated with the levels of total solids, DIN and PO_4^{3-} , (**Table 4.26**) and these correlations have also been discussed in other studies. Salinity is the main physical variable that affects the diversity and abundance of biologic communities. Salinity also influences the mass transfer of suspended particles and water clarity in coastal water because increasing salinity increases the flocculation of suspended particles.

In fact, the higher the salinity, the clearer the water (Coelho et al., 2007; Hakanson & Blenckner, 2008). In general, research has shown that in areas with high anthropogenic loads of nutrients, there is a negative correlation between salinity and nutrient levels, especially in estuaries and coastal waters, where high river discharges and land-based runoff occur and mix freshwater and seawater (Campbell, Yarbrow, & Fourqurean, 2012; Lars Håkanson & Eklund, 2010; Iwata et al., 2005). Likewise, the salinity value can be negatively correlated with the ratio of DIN and PO_4^{3-} . This ratio reduces as salinity increases, and a sudden shift between phosphorus and nitrogen limitation due to different

anthropogenic and lithogenic discharges is generally a result of limiting nutrient variation (Håkanson et al., 2007; Lui & Arthur Chen, 2011).

The spatial and temporal differences in dissolved oxygen concentration and periods of saturation, result from turbulence, diffusion and solubility of oxygen, and biogeochemical processes (remineralisation, consumption, and production) (Alvarez-Gongora & Herrera-Silveira, 2006; Kitsiou & Karydis, 2011). The highest values for both oxygen concentration and saturation occurred during the northeast monsoon (**Figure 4.29 and Figure 4.30**). This season is characterised by strong winds and high action of waves that increase turbulence, and thus, the rate of oxygen diffusion was varied between the atmosphere and surface water; likewise, the lower temperature in this period caused increased oxygen solubility. Lower oxygen levels were found during the southwest monsoon (dry season), perhaps due to warmer water temperatures that stimulate respiration and decrease the solubility of oxygen (Amiruddin et al., 2011).

In Klang Strait, significant negative correlations were found between oxygen values and nutrients and chl-a. Empirical and dynamic models were created based on this negative correlation to predict average oxygen saturations related to nutrient loading rates and the morphometry of the coastal area.

These models showed that higher loads of nutrients (nitrogen and phosphorus) reduced oxygen saturation, and the deeper coastal areas have lower oxygen saturations (Ferreira et al., 2011; Hakanson & Blenckner, 2008; Kitsiou & Karydis, 2011).

Secchi depth is a key component in empirical and dynamic models to express water clarity and turbidity because it directly reflects the amount of suspended materials that scatter light in water bodies (Gallegos, Werdell, & McClain, 2011; Huo et al., 2011). Recently, researchers have noticed a significant negative relationship between Secchi

depths and levels of nutrients, chlorophylla and total suspended solids, and total solids are positively correlated with levels of nutrients (except for silicate) and chlorophyll *a*.

These results were also frequently found in other studies. Moreover, the levels of total solids and transparency at four of the sites were strongly related to rainfall, river discharges, hydrodynamic turbulence and water production. These factors lead to high quantities of resuspendable materials that increase the internal loading of nutrients and increase production and levels of total solids; a high amount of coloured materials in estuaries and coastal water creates a lower photic zone and decreased water transparency (Banerjee & Choudhury, 2011; Coelho et al., 2007; Hakanson & Blenckner, 2008; Intxausti, Villate, Uriarte, Iriarte, & Ameztoy, 2011).

In Klang Strait, a significant difference was observed on spatial and temporal scales. During the northeast monsoon, storms produce strong waves, leading to re-suspension of previously deposited particles that contain carbon and major nutrients as well as mineral particles and pollutants, which re-enter the aquatic system.

Additionally, during this period, high daily rainfall increases river discharges and land-based runoff, which increase the levels of suspended solids and decrease water transparency (**Figure 4.32** and **Figure 4.31**).

Total solids includes total suspended solids and total dissolved solids, which are directly related to several parameters of overall use for coastal water management as indicators of water clarity, but in ecological research, the major focus may not be on total solids but on indicators influenced by total solids, like the Secchi depth and oxygen saturation. In aquatic areas, suspended particles widely influence bacterial decomposition, oxygen concentrations in sediment, and primary and secondary production (Crump, Baross, & Simenstad, 1998).

Suspended particles settle on the bottom sediment, and the organic portion of these particles is decomposed by bacteria during the mineralisation process; hence, this process leads to the recycling of major nutrients, organic matter and pollutants and reduces the concentration of oxygen in a given aquatic ecosystem.

Likewise, many pollutants (e.g., heavy metals, nutrients and radio nuclides) can be removed from the water column by sinking to the bottom sediments with suspended solids and burial in sediments (Kawasaki, Sohrin, Ogawa, Nagata, & Benner, 2011; März, 2010).

In Klang Strait, there were spatial and temporal differences of nutrient concentrations due to mutual interaction between anthropogenically generated wastewater at the coast and biogeochemical processes (re-mineralisation and biodegradation process around the mangrove line).

In addition, land-based runoff and Klang River discharges contributed to the variation among sites. Importantly, Klang River discharges can act as a point-source at South Port, which was extremely polluted by nutrients except for SiO_4^{4-} . In the North and West Port sites, the high concentration of nutrients and chlorophyll *a* as a consequence of human activities (industrial discharges and berth platform washing) and natural processes of remineralisation, resuspension, and turbulence led to increase nutrient concentrations in the water column and stimulated phytoplankton biomass.

The inverse relationship between silicate and salinity indicates that the silicate is largely derived from anthropogenic sources (**Table 4.26**). The concentration of silicate in West Port was significantly higher than at the other sites. This result was related to discharges from a cement factory because silicate is a primary ingredient of cement products. Additionally, 87% of the sediment samples of West Port were completely mixed with cement, especially in the vicinity of cement-factory outlets.

In South Port and North Port, the concentrations of silicate were low at stations that were far from the cement factory (1-3, 16, 17, 19 and 20), while the concentrations of silicate increased at stations 4,5,18 and 21, which were close to the cement factory. Additionally, the concentration of silicate at the control point is good evidence because silicate levels were significantly lower at the control point than at the other sites, with low standard deviation.

Natural processes can be another source of silicate. Most geological studies show that much of the bedrock in peninsular Malaysia consists of limestone, and the Klang Valley is one of the major areas widely covered by limestone rock (Boon-Kong, 2000; Ismail, Mansor, Rodsi, & Bujang, 2011; Samy, Shattri, Bujang, Ahmed, & Sharharin, 2012). Limestone is a type of sedimentary rock that includes the minerals calcite, dolomite, microcrystalline and amorphous silica, SiO_2 , clay, organic matter and iron oxides. Limestone has a unique property of easy dissolution in slightly acidic waters (Ogle & Walsh, 2010). In the Klang valley, major parts of the limestone formations have been metamorphosed into marble, which has the same composition as limestone (Samy et al., 2012). In addition, land-based runoff and river discharges can be considered as other sources of silicate in this region because high variation based on standard deviation of silicate level occurred during the rainy season at all of the sites except the control area, while this variation was low in the dry season.

The chlorophyll *a* concentration is a major abiotic variable used to estimate phytoplankton biomass in aquatic sciences (Ferreira et al., 2011; Hakanson & Blenckner, 2008; Kitsiou & Karydis, 2011).

Several empirical models predicted chlorophyll *a* concentrations from nutrient concentrations, water temperature and light conditions, and these models showed a very strong correlation ($r = 0.88$) between nutrients (TP and TN) and concentrations of chlorophyll *a* (Håkanson & Eklund, 2010).

Chlorophyll *a* levels changed seasonally and spatially in Klang Strait due to the different processes that control the abundance of phytoplankton throughout this region. The highest concentrations of chl-*a* occurred during the north monsoon (rainy season) and inter-monsoon, while the lowest levels occurred during the south monsoon.

The high concentrations of chl-*a* are mainly related to gradual nutrient increases during the rainy season and to sediment re-suspension due to strong water turbulence during the north monsoon (Philippart et al., 2000). In 1984, the mean concentration of chl-*a* in the Klang coastal area was between 5.10 and 21.20 $\mu\text{g/l}$ (Yap, 2005). In this research, however, the mean chl-*a* concentration at the sites inside the strait were higher than in the control area, indicating early-stage eutrophication at these sites.

At North Port and West Port, the chl-*a* levels were likely due to nutrient discharges from the harbour and mangrove re-sustentation caused by benthic or microbial communities that occurred along mangrove line or due to strong winds and high wave action during the north monsoon.

Multivariate statistical (classification and ordination) methods were applied to describe associations among the environmental parameters or sites and to explore the importance of hierarchy among the parameters. These methods facilitate better ecological descriptions of field data and the generation of new hypotheses. The cluster-classification analysis based on hydrological parameters revealed that North and West Port clustered together, which might represent the strong effects on both of the Ports from harbour activities and re-sustentation and re-mineralisation processes.

The clustering of South Port separate from the other groups was most likely due to the high nutrient and total solid levels, low transparency and distinct salinity profiles. The control point was completely separated from the other clusters, likely due to its lowest concentration of nutrients and highest water transparency (**Figure 4.43**).

At south port, a significant relationship was found between NH_4^+ , NO_3^- , PO_4^{3-} , NH_3 , DIN, chl-*a* and total solids and the first component, which explained 81.12% of the variability (**Table 4.28**). The association with this component suggests the influence of the Klang River, which has high total solid and nutrient loads, especially PO_4^{3-} derived from urban and industrial effluents and agriculture fertilisers (Rustam, Karim, Ajward, & Jaafar, 2000; Tan, Goh, Vijayaletchumy, Loong, & Ang, 1990). Many researchers have shown that more than 70% of the dissolved inorganic nitrogen, especially NO_3^- , in marine systems is discharged into estuarine and coastal waters by rivers that might be polluted by anthropogenic activities (especially waste and fertiliser run-off) with old nutrients, while NH_3 is indicative of new nutrients due to human effluents and is very toxic for phytoplankton in high concentrations (Hakanson & Blenckner, 2008; Suthers & Rissik, 2009).

Additionally, there is scientific evidence to confirm that in aquatic areas, NH_3 and PO_4^{3-} can naturally originate from the decomposition of organic and inorganic matter, nitrogen reduction by microorganisms, and biotic excretion. These compounds are also loaded into aquatic areas by industrial outlets, fertiliser runoff, and urban waste (Ferreira et al., 2011; Harrison, Bouwman, Mayorga, & Seitzinger, 2010). Likewise, the high inverse association between salinity and chlorophyll *a*, total solids and all nutrients except SiO_4^{4-} suggests discharges from the Klang River, while the direct relationship with the other parameters is likely related to natural processes in this Strait.

At North Port and West Port, the association of all of the nutrients and chlorophyll *a* suggest the effect of nutrient loads and organic material derived from both industrial wastewater and natural interactions of mangrove forests, such as resuspension processes, biotic decomposition and nitrogen reduction.

In West port, the high inverse relationship observed between salinity and the levels of all nutrients, total solids and chlorophyll *a* implies the effect of anthropogenic discharges, likely industrial discharges and harbour activities, while in North port, a low direct relationship was found between salinity and nutrients, likely a result of natural processes, such as re-sustentation and re-mineralisation.

The results imply that the mean concentration and standard division of nutrients at the control point are significantly lower than at other sites inside Klang Strait. This difference is good evidence that these sites are influenced by their internal load of nutrients. At the control point, Dissolved Oxygen, Oxygen Saturation, transparency, total solids, currentspeed, DIN and SiO_4^{4-} accounted for 55.4% of the water quality variability.

This result implies that the low effects of nutrient discharges are due to the location of this area far from coastline-oceanic interactions and anthropogenic discharges.

In contrast, nutrients were significantly correlated with salinity in these sites, suggesting internal nutrient loading by natural sources. Based on the multivariate analyses, we suggest that the water quality at North Port and West Port are related to the levels of nutrients and biomass of phytoplankton (chlorophyll *a*), which result from industrial discharges, harbour activities, natural processes around mangrove forests and coastline-oceanic interactions. At south Port, the water quality was greatly influenced by Klang River discharges, while at the control point, most of the water-quality variation resulted from physical parameters and water turbulence.

5.3.2 Water-quality zoning

There are several sources in marine systems that affect water quality, such as river discharges, upwelling, remineralisation or sediment resuspension, industrial waste and effluents; thus, it is difficult to quantify the relative contributions of nutrient sources to marine and coastal systems (Kitsiou & Karydis, 2011). In the present study, the water quality parameters at each site and their relationship with anthropogenic activities revealed that the coastal waters of South Port are strongly affected by Klang River and Langet River discharges, with characteristic low salinity, water transparency and dissolved oxygen levels and relatively high levels of nutrients (except silicate), chlorophyll *a* and total solids. These rivers input change physicochemical parameters that are related to coastal water and flow rates.

Several researchers have reported that these river contains high concentrations of nutrients resulting from urbanisation and agriculture fertilisers (Boon-Kong, 2000; Tan et al., 1990). The discharges of these river containing high amounts of nutrients enter the coastal system of south Port and stimulate phytoplankton growth, with characteristically high concentrations of chlorophyll *a* at these sites in comparison to other sites.

All of the physicochemical parameters (except NO_2^- and SiO_4^{4-}) showed similar spatial and temporal patterns, with insignificant differences between North Port and West Port (**Table 4.26**). The high concentrations of nutrients indicate that the trophic condition at these sites is influenced by industrial waste, land-based run-off and remineralisation/sediment re-suspension in mangrove forests. These sites are located between the berth line and mangrove line in a region that receives the greatest impact from anthropogenic and lithogenic sources, resulting in highly eutrophic conditions in the North Port and West Port.

The results in **Table 4.23** showed that the highest concentrations of nutrients were found at stations in the vicinity of the berth line and mangrove line, and the lowest concentrations were at intermediate stations. Around the berth line, several anthropogenic sources have been reported that increase nutrient concentrations, leading to eutrophic conditions. These sources include wastewater from industrial discharges (food and oil factories and a cement factory) and port activities, such as discharges from berth-platform washing and wastes related to the shipping of goods related to fertilisers, detergents and food products. Moreover, the concentration of silicate in West Port was significantly higher than at the other sites (**Figure 4.41**), likely related to the discharges of the cement factory, which greatly influenced the water quality.

The higher levels of nutrient and chlorophyll *a* in the vicinity of the mangrove forests might be related to the impact of mangrove-derived organic matter. Coastal lagoons and mangrove forests are natural sources of nutrients to the marine coastal area, and their discharges occur seasonally through pulses due to natural climatic events (hurricanes and storms) (Coelho et al., 2007). The dissolved inorganic nutrients are effectively re-suspended in mangrove sediments by the microbial degradation of organic matter, denitrification processes and re-mineralisation. Sediment re-suspension increases nutrient availability in water bodies, stimulate phytoplankton biomass and macroalgae, which exacerbate eutrophication in coastal systems (Feller, Whigham, O'Neill, & McKee, 1999; Smith, Burford, Revill, Haese, & Fortune, 2012; Sweetman et al., 2010).

At the control area, low concentrations of nutrients and chlorophyll *a* characterised this region because this area was selected in a remote area far from the coastal area of Klang Strait; therefore, this area is less affected by anthropogenic activities than the other sites.

5.3.3 Trophic level:

Several multimetric indices have been proposed to evaluate and classify coastal and marine systems based on eutrophication conditions or trophic status, which are commonly described according to the productivity, such as a state of low productivity (oligotrophic), intermediate productivity (mesotrophic), or high productivity (eutrophic) (Suthers & Rissik, 2009). In this research, the eutrophication index (EI) and trophic index (TRIX) were applied to assess the trophic level.

Based on the trophic index described by Vollenweider (1998) and Penna et al. (2004), the water quality of Klang Strait can be considered eutrophic at all of the sites (**Figure 4.44**), which corresponds to highly productive waters, and the condition of the coastal study area ranged from 6 to 8. The levels of dissolved inorganic nitrogen, chlorophyll *a*, and total phosphorus were the variables responsible for this water classification.

Although TRIX has been used as a water quality index to assess trophic levels in different coastal areas, namely in coastal areas of the Black Sea, Caspian Sea, Persian Sea, Montego Estuary, southeast Mexico, and Helsinki Sea (Kitsiou & Karydis, 2011; Vollenweider et al., 1998), there are drawbacks to TRIX. TRIX cannot meet some of the requirements of the European water framework (WFD, 2000/60/EC), and TRIX does not conform to natural reference conditions used to normalise the scale (Kitsiou & Karydis, 2011). The European Environmental Agency (EEA) recommends that the specific scale of TRIX should be described for different areas or regions to increase the sensitivity of this index.

It is also important to select which data are applied for the TRIX estimation (seasonal averages, seasonal averages over several years or annual averages) to make the index less sensitive to natural meteorologically forced variations (Commission, 2000).

Despite these drawbacks, the EEA indicates that the general approach using TRIX can be a comparable and practicable method to monitor and assess trophic levels, and TRIX can also be used to identify eutrophication trends of marine and coastal waters (Kitsiou & Karydis, 2011). Likewise, researchers in recent studies do not recommend this index for shallow aquatic areas that are dominated by macroalgae and seagrasses and instead apply benthic indices, which are more effective because the biomass of phytoplankton is not appropriate for defining the nutrient effects (Giordani et al., 2009; Primpas & Karydis, 2010).

In 2010, Primpas proposed another multimetric index to assess trophic status. This index tests three standard sets of water types (oligotrophic, mesotrophic, and eutrophic) and historical data of Rhodes coastal water. Their results showed that the EI is effective and valid index to assess water quality. The results of testing this index correspond to previously published data from the Rhodes coastal area and demonstrate the adaptability of this index to the requirement of the European water framework (Primpas & Karydis, 2010). Therefore, in this research, the EI index was used to better characterise the trophic level of Klang Strait.

The values for the eutrophication index (EI) of water quality ranged from mesotrophic to hypertrophic in terms of the condition of the coastal system of Klang Strait. The water quality at the control area was categorised as eutrophic (0.85-1.51) and was moderate (0.38-0.85) only in February, August and July 2010 (**Figure 4.45**). This finding might have been a result of natural nutrients entering from mudflats and runoff of the mangrove fringe area. In the other sites, the water quality was generally classified as hypertrophic ($EI > 1.5$), but in November 2009 and December, July, August and September 2010, the water quality of North Port and West Port was estimated as eutrophic.

Generally, the poorest water quality conditions were observed at sites with the highest influence from anthropogenic activities, such as West port, North port and South port, while good quality water conditions were located at the control area, far from the coastal areas. This finding indicates that the water health status is threatened in the Klang Strait.

During this study, seasonal variation affected trophic variation. During the north monsoon (rainy season), hurricanes reduced the water quality by increasing land-based runoff and river discharges, suggesting an important connection between the coastal area and the sea; moreover, reduced transparency and increasing nutrient and sediment concentrations occurred in the coastal waters. The impact of hurricanes was short-term for salinity and water transparency reduction, while the nutrient values increased due to land-based runoff, river discharges and remineralisation (Steward et al., 2006).

Several researchers have shown that integrated indicators are more appropriate to assess eutrophication levels. These researchers have developed different criteria of trophic trends for the classification of marine and coastal waters based on operational variables, such as DO, chlorophyll *a*, nutrients, macroalgae, SAV, HAB and macrobenthic indicators (Borja et al., 2012; Devlin et al., 2011; Ferreira et al., 2011). Recently, researchers have begun to consider water transparency, oxygen budget and chlorophyll levels as effective parameters, while nutrients in coastal systems must be preferably applied as pressure indicators, generally according to nitrogen and phosphorus compounds (Ferreira et al., 2011; Ferreira et al., 2010). The use of pigment measurements as phytoplankton indicators and the coupling of these measurements with other physicochemical variables (e.g., transparency and oxygen budget) as well as the use of multimetric indexes has been proposed to improve coastal water quality monitoring.

The different indicators used to assess the eutrophication of coastal aquatic ecosystems described above result from a number of reasons: (a) different types of aquatic systems require particular field information related to physicochemical, biological and geological parameters and likely require specific indices, and (b) several multimetric indices have become famous over the last decade because they are practical in coastal environmental management research, for which integrated information is required (Borja et al., 2012; Campbell et al., 2012; Ferreira et al., 2011; Paerl et al., 2011).

To introduce an occurrence level of trophic conditions, operational indicators were applied. Among the physicochemical variables used to guide values based on the United States National Estuarine Eutrophication Assessment, only the dissolved oxygen concentration (>5 mg/l) and pH (5 - 9) had levels in the range of the recommended intervals.

The average water transparency in all of the sites showed the hypertrophic level category (< 200 cm), this might have been caused by high discharges of particulate matter from land-based runoff and river discharge into the coastal area. The average DIN concentrations at the South Port, North port and West port were in the hypertrophic category ($\text{DIN} \geq 0.94$ mg/l), while the control area was in the eutrophic category ($0.94 > \text{DIN} \geq 0.29$ mg/l) during the year of sampling (**Table 4.23**). The average phosphorus concentration at all of the sites was at the eutrophic level ($0.13 > \text{P} \geq 0.04$ mg) in most of the months, and in some of the months, such as November 2009, December, April, May, July, September and October 2010, the concentration of phosphorus was in the hypertrophic category ($\text{P} > 0.13$ mg/l) (**Table 4.23** and **Figure 4.40**).

The average concentration of chlorophyll *a* in the control area showed mesotrophic conditions throughout the sampled year. The average chlorophyll *a* concentrations in North port, South Port and West Port were in the eutrophic range ($20 > \text{chl } a \geq 6$) from January

2010 to July 2010, and in the other months, the mean concentration of chlorophyll *a* showed the mesotrophic ($6 > \text{chl } a \geq 2$) level in North Port and West Port.

In the present study, the overall water quality was described based on the annual average of operational indicators and trophic indices. According to these results, the trophic level of Klang Strait coastal water (South port, North Port and West Port) can be considered eutrophic to hypertrophic based on the dissolved inorganic nitrogen, phosphorus, water transparency, chlorophyll *a* and trophic indices (EI and TRIX).

The trophic level of the control area ranged from mesotrophic to eutrophic based on the phosphorus concentration, DIN, chlorophyll *a* and eutrophication index (EI). The values of water transparency and the TRIX index were not used to classify the trophic level in the control area because their range was far from the range of other key indicators, especially chlorophyll *a*.

The indicators and indices used to classify the trophic level of Klang Strait did not always lead to the same trophic classification because of the differences between the categories of chlorophyll *a* and nutrient concentrations (N and P).

Several methods have been described to assess eutrophication trends to protect estuarine and coastal waters from degradation. Most of these eutrophication assessments imply that increased chlorophyll *a* is the primary symptom or direct effect of the first stage of eutrophication. Increased chl-*a* is considered as a biological response to increase primary production (Ferreira et al., 2011; HELCOM, 2009). Changes in dissolved oxygen levels, toxic blooms and losses of SAV are secondary symptoms and indirect effects that indicate the advanced development of eutrophic conditions in an aquatic system (S. Bricker, Ferreira, & Simas, 2003; HELCOM, 2009; OSPAR, 1998).

We concluded that nutrient concentrations, when applied jointly with chlorophyll *a* assessments, are a closer step toward an accurate eutrophication evaluation. However,

nutrient concentrations may not be a practical indicator in all coastal waters because although P and N generally seem to be important to predict the trophic level and chlorophyll *a* levels in coastal systems, the use of nutrients faces a problem: several bio-available dissolved forms of nutrients and their seasonal trends have been shown to have high coefficients of variation or standard deviation in aquatic systems.

This means that many water samples should be analysed at different spatial and temporal scales to collect reliable empirical data. Likewise, high standard deviations lead to overlap among the nutrient datasets used to distinguish among oligotrophic, mesotrophic and eutrophic conditions (Håkanson & Blenckner, 2008; Kitsiou & Karydis, 2011).

Thus, the results of chl-*a* are more reliable than other parameters because chl-*a* is applied as a proxy for phytoplankton biomass, is typical to all models and methods, and there is wide research on its use as a bio-indicator in estuarine and coastal waters (Borja et al., 2012; Bricker et al., 2003; Bricker et al., 2008; Bricker et al., 2007; Friedland et al., 2012; Håkanson & Eklund, 2010; Kitsiou & Karydis, 2011; Peng, Gitelson, Keydan, Rundquist, & Moses, 2011; Zaldívar et al., 2008).

In the present study, the results of chl-*a* concentration suggest a eutrophic condition in sites inside Klang Strait and mesotrophic conditions in the control area, and the results of the Redfield ratio support the eutrophic categorisation.

The Redfield ratios of dissolved nutrients are used to describe primary production in water bodies and reflect the limiting variables. Research has shown that in coastal and estuarine systems, if this ratio is greater than 16, P limitation of primary production is occurring, indicating that a lack of phosphorus is preventing increased primary production. Ratios lower than 16 suggest nitrogen limitation of primary production. Phosphorus is known as a crucial limiting nutrient for freshwater primary production, but estuarine and ocean environments are typically nitrogen limited. However, Guildford and Hecky in 2000

indicated that phosphorus is a major nutrient regulating primary production in freshwater as well as coastal and marine systems (Håkanson & Blenckner, 2008; Håkanson & Eklund, 2010).

Several investigations have shown that the trophic status of estuarine and coastal waters based on the Redfield ratio range from oligotrophic (Redfield ratio of N:P close to 7:1) to eutrophic systems (Redfield ratio close to 14:1)(Guildford & Hecky, 2000; S. M. Smith & Lee, 2006; Suthers & Rissik, 2009).

Moreover, in some coastal environments, such as the equatorial Pacific, primary producers (phytoplankton) have access to high values of nitrogen and phosphorus, but their biomass is low (generally estimated based on the chlorophyll *a* concentration) (Guildford & Hecky, 2000; Suthers & Rissik, 2009).

During the research period (Håkanson et al., 1986), the N:P ratio in most of the months was close to or greater than the Redfield ratio (16:1, 14:1) inside Klang Strait, suggesting a eutrophic condition, and the ratio was significantly lower than the Redfield ratio (from 7 to 14) only in November 2009 and December, July and October 2010, implying mesotrophic conditions in these months.

According to the trophic indices, the high concentration of exogenous nutrient sources changed the trophic status to eutrophic. Klang Strait is most likely in an early stage of eutrophication, and the chlorophyll *a* concentration seems to reflect this result, but no eutrophication events or secondary symptoms, such as phytoplankton blooms or oxygen depletion, occurred during the research period. This result might be related to hydrodynamic turbulence and water exchange, which prevent the development of eutrophic conditions in Klang Strait.

Hydrodynamic turbulence is a major characteristic of coastal areas and includes Coriolis-driven coastal jet-zone, up-welling, tidal effects and waves. These hydrodynamic processes are generally very complex and dynamic in marine coastal waters and cause exchanges of coastal water with the outside seawater over only a few days.

Therefore, it is easy to understand why the retention time of surface water is approximately 2-6 days for coastal areas. This result implies that coastal water is in close contact with conditions in the outside sea, especially in small, open coastal areas (Håkanson & Blenckner, 2008; Håkanson et al., 1986).

In these types of coastal areas, the coastal nutrient or contaminant concentrations are similar to the concentrations off shore water because the coastal water is exchanged several times each month. Hence, the concentrations of nutrients and organic material greatly vary during these water exchanges, making it difficult to predict the trophic level based on the nutrient concentrations in the coastal water (Fang et al., 2011; Håkanson & Blenckner, 2008; Karlsson, Malmaeus, Josefsson, Wiberg, & Håkanson, 2010; Pilesjö, Persson, & Håkanson, 1991).

Klang Strait is typical of the small, open coastal waters of west coast peninsular Malaysia that are extremely influenced by hydrodynamic actions, such as shipping movements, strong waves and winds during the north monsoon. These actions increase the hydrodynamic turbulence and advection of primary producers (phytoplankton). Both of these parameters reduce the nutrient assimilation by phytoplankton and likely prevent the development of bloom conditions and other secondary symptoms, such as oxygen depletion.

In addition, the frequency of water renewal or exchange through the semidiurnal tidal current of the strait could have contributed to the reduction of the effects caused by nutrient accumulation.

The diagnosis based on water quality and chlorophyll *a* used in this research has helped to describe differences in the values of the measured parameters within each of the sites and to characterise the individual response of each metric according to site-specific combinations of regional conditions.

However, the variation found in the data for the metrics applied at the studied spatial and temporal scales (within stations and months) implies that, to improve the quality of future analyses for resulting management strategies, this assessment must be conducted on a longer temporal scale. The present study is the first attempt to assess the ecological condition of a marine coastal system in Klang Strait based on the water quality and chlorophyll *a*.

The results of this study will be useful and practical as baseline data for future monitoring programs to assess whether the condition of the ecological system at each site improves or worsens after the recommended actions in marine coastal management are implemented.

5.4 Conclusion

There is a need to critically assess the present quality of the marine ecosystem, especially the connection between ecosystem changes and ecological risks. The conclusions are described in the context of the objective and scope of the present research. Additionally, the conclusions for the ecological risk assessment have been drawn. The following are the conclusions of this study:

1. Variations in total organic carbon (TOC) content and sediment grain size are generally more important than variations of the physical parameters of water for predicting the distribution and variation of heavy metals, polyaromatic hydrocarbons (PAHs) and benthic communities in sediments. TOC and sediment grain size were significantly correlated with some metals (Al, Cd, Cu, Fe, Ni, V and Zn) and PAHs in sediment.

2. A significant variation was found in the distribution and concentration of all of the heavy metals and PAH compounds on both spatial and temporal scales. The highest concentrations of all of the metals (except for Mn) were determined at South Port at stations 16 and 17, which are parallel to the mouth of the Klang River, and at station 13 around the container terminal in West Port. On a temporal scale, the concentrations of metals, except for Cr and Mn, in surface sediments significantly varied, most likely due to seasonal fluctuations. Likewise, the highest concentration of PAHs was determined at stations close to shore (at the berth line), especially at stations 4, 13 and 14, which were close to a container terminal in North and West Port, and at stations 16 and 17 in South Port.

3. As a result, the significant distribution patterns and correlation analyses showed that multiple sources greatly contributed to the contaminant loads in Klang Strait. These sources included industrial inflow, such as the palm oil, cement and food manufacturers

that are located along the coastline of North and West Ports, vessel-based discharges, Klang River and land-based runoff, and mangrove sedimentation processes. The enrichment factor (EF) also indicated that all of the metal concentrations, except for Fein sediment, were influenced by anthropogenic inputs, especially very toxic elements, such as As, Cd, Hg and Pb, which were enriched at high levels at stations close to the berth line and the mouth of the Klang River. In general, all of the stations had the same classification based on the enrichment factor, which indicated moderate anthropogenic discharges of heavy metals. Thus, both natural processes or local mineralogy and human activities (anthropogenic) contributed to heavy metal loads in Klang Strait. The PCA analysis is concordant with evidence from paired isomer ratios of PAHs, which revealed that the anthropogenic sources of PAHs are influenced by mixed sources of pyrogenic and petrogenic PAH pollution at all of the stations except stations 4, 14 and 21, where combustion was a more important source. A source analysis revealed that PAHs are primarily derived from liquid fossil fuels due to vehicle, crude oil and coal (petroleum combustion) sources, which might originate from industrial discharges, such as those from cement, food and oil factories. A minor amount of the PAHs may be related to direct petroleum discharge and land-based runoff.

4. The contamination degree of the sediment contamination was estimated based on the contamination factor (CF) and a comparison between the contaminant concentrations and the specific value (TEL and PEL) of sediment-quality guidelines. The data revealed that the sediment condition is in a pristine state with respect to metal contamination except for Cd, As, Hg and Pb. The surface sediment is moderately polluted with Hg, Pb and As, and only Cd was estimated at a high level of contamination.

Regarding the PEL_q estimation for total PAHs, only station 13 (close to the container terminal in West Port) was moderately polluted, and the rest of the stations were at risk of rare or slight adverse biological effects due to PAH exposure in surface sediments.

5. The ecological risk was estimated according to the potential ecological risk and toxic factor of heavy metals and PAHs. The potential ecological risks of Cd and Hg were high and signified potential risks for biological communities at all of the stations, and the rest of the investigated metals and PAHs had low risk factors.

6. Our hypothesis indicates there is a high threat of petroleum and heavy metal contamination on the biological community in Klang Strait; according to the above discussion. This hypothesis was rejected and only considered for Cd and Hg as primary stressors that cause adverse effects on biological communities in Klang Strait. Several factors cause the decline of these contaminants, such as an integrated management programme and regulation, meteorological conditions and weathering.

7. According to the risk index (RI) classification, only the sediment from stations 16 and 17 (at the mouth of the Klang River) can be considered as causing very high ecological risk. The vulnerable stations and all of the stations along the berth line (except stations 1 and 10) are at high ecological risk, and the rest of the stations are at moderate risk. The control station was found to have low adverse effects with normal responses.

8. In this research, there were no temporal changes in the species richness and abundance of benthic communities (based on exposure), but the greatest effects on benthic composition were found on the spatial scale. The biological indices (AMBI, M-AMBI and BI) and correlation analyses are in good agreement, confirming the response of benthic communities to changes of contaminant levels at the different stations.

9. According to the P-R model of benthic succession, most of the stations are in an early stage of succession in Klang Strait, including all of the stations in North port (1-6), stations 9, 10, 11, 12, 15 in West Port and stations 18 and 21 in South Port. The AMBI analysis confirmed these results: all of the above-mentioned stations were slightly polluted with high abundance and diversity of ecological groups I and II (sensitive species). Stations 7, 8, 13, and 14 in West Port and stations 19 and 20 in South Port were in transitional stages of succession, with high abundances of ecological groups IV and V (opportunistic species), and were moderately polluted. Stations 16 and 17 were in azoic stages, while only station 22 (the control point) had a normal composition of the benthic community with high diversity and without opportunistic species.

10. The variations of water-quality parameters (except temperature) were significantly different on spatial and temporal scales due to seasonal fluctuations, anthropogenically generated wastewater at the coast and biogeochemical processes (re-mineralisation and biodegradation processes around the mangrove line) and Klang River discharges. Multivariate statistical methods (cluster, PCA and nonparametric analyses) revealed that nutrients (especially DIN and PO_4^{3-}), chlorophyll *a* and total solids are major variables that contributed to the variability in Klang Strait coastal water, while at the control point, most of the water quality variation resulted from physical parameters and water turbulence. Statistical analyses revealed that there was no significant variation in hydrological parameters (except NO_2^- and SiO_4^{4-}) between North and West Port, and these sites were in the same cluster. The clustering of South Port separate from the other sites was most likely due to its high nutrient and total solid levels, low transparency and salinity profile, while the control site was completely separated from the other clusters, likely due to its low concentration of nutrients and high water transparency.

Moreover, the concentration of silica at West Port was significantly higher than at the other sites, and this result was related to discharges from the cement factory, which greatly influenced the water quality.

11. Multimetric indices (Eland TRIX) and operational indicator have been proposed to evaluate and classify coastal and marine systems based on eutrophication conditions or trophic status. According to these results, the trophic level of Klang Strait coastal water (South Port, North Port and West Port) can be considered to range from eutrophic to hypertrophic based on levels of dissolved inorganic nitrogen, phosphorus, water transparency, chlorophyll *a* and trophic indices. The chl-*a* concentration was used as a biological response of phytoplankton biomass and showed a eutrophic condition in Klang Strait and mesotrophic condition in the control area. Klang Strait is most likely in an early stage of eutrophication, and the chlorophyll *a* concentration seems to reflect this result, but no eutrophication events or secondary symptoms, such as bloom conditions or oxygen depletion, occurred during the study period, this may be related to hydrodynamic turbulence and water exchange, which prevent the development of eutrophic conditions in Klang Strait.

12. Wastewater-management regulations were ratified in 1990 and 1997 to recover the sediment from most of the metal and poly-aromatic hydrocarbon pollution, but these regulations are not adequate to control Hg, As and Cd, and this area can be considered as a hot spot for these elements.

5.5 Recommendation

The present study recommended further investigations, including the following tasks:

- 1- Study the concentrations of heavy metals and PAHs in the wastewater of the factories that are located along the coastline of Westport and the Klang River to distinguish the major contribution of each factory to the pollution load.
- 2- Conduct toxicity tests and bioaccumulation tests on biological communities on a laboratory scale to provide adequate data for human health risk assessments.
- 3- Study the spatiotemporal variations of heavy metal and PAH concentrations in the sediment of the mangrove Islands that surround Klang Strait.
- 4- Modify the trophic assessment by estimating water parameters in small-scale temporal variations, such as hourly or daily, to better understand the relationship between water-quality variables and hydrodynamic turbulence due to the semi-diurnal tides and monsoon current.

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APPENDIX

APPENDIX 1

A: Information of layout plan of berth

South Port

Table 1, Berth Information of the South Port

Berth	Max Disp (Tones)	Length (m)	Depth (m)	Ht. of wharf above Chart Datum (m)
1(Liquid Bulk)	40000	177	10.5	6.53
2 (Liquid bulk)	40000	177	10.5	6.53
3	23000	177	10.0	6.53
4	20000	146	9.0	6.52
5	6000	107	6.0	6.52
6	6000	107	6.0	6.51
7	6000	94	5.0	6.51
7A	6000	94	5.0	6.51
P7A		43	2.2	Pontoon

South Port includes the liquid berth and dry berth. Liquid bulk exports handled here are coconut oil, palm oil and latex. Berths No. 1 & 2 is the main berths for export loading purposes. Its length is 177m with the 10.5 meters depth, and caters to ships of up to 40,000 displacements. Dry bulk exports wheat, feed, maize and meal that are handled through berth No.3 and 4, which can receive ships of up to 23,000 and 20,000 tones displacement respectively.



Figure1, Berth layout plan- South Port

North Port

The main goods in Liquid berth are including refined vegetable oils, petroleum and chemicals products. These Products are arranged by major oil companies such as PETRONAS which are located here are, industrial fuel, diesel and oil and unleaded gasoline.

At berth No. 24 and No. 25 the importing of bulk fertilizer is handled. The terminal area were developed on 13.2 hectares of land and is equipped with two bulk handling cranes, a conveyor system and warehouses onshore. Also the exporting of palm kernel expellers and importing of maize, sugar, feed meal and cement are being also performed.

Table 2, Berth Information of the North Port

	Berth	Max Displacement (T)	Length (m)	Depth (m)	Ht. of Wharf above Chart Datum (m)
Container	8	40000	213	11.0	6.53
	9	60000	320	13.2	6.53
	10	120000	320	13.2	6.54
	11	100000	226	13.2	6.55
	12	120000	178	15.0	6.55
	13	120000	178	15.0	6.55
	14	120000	178	15.0	6.55
Break Bulk	15	60000	244	13.0	6.56
Container	16	60000	213	12.5	6.56
	17	80000	213	12.5	6.56
	18	80000	213	13.0	6.57
	19	80000	213	13.0	6.57
	20	80000	213	13.0	6.57
	21	80000	213	12.6	6.57
Liquid Bulk	22	60000	213	11.6	6.57
	23	60000	213	11.6	6.57
Bulk	24	80000	213	12.0	6.58
	25	80000	213	12.0	6.58

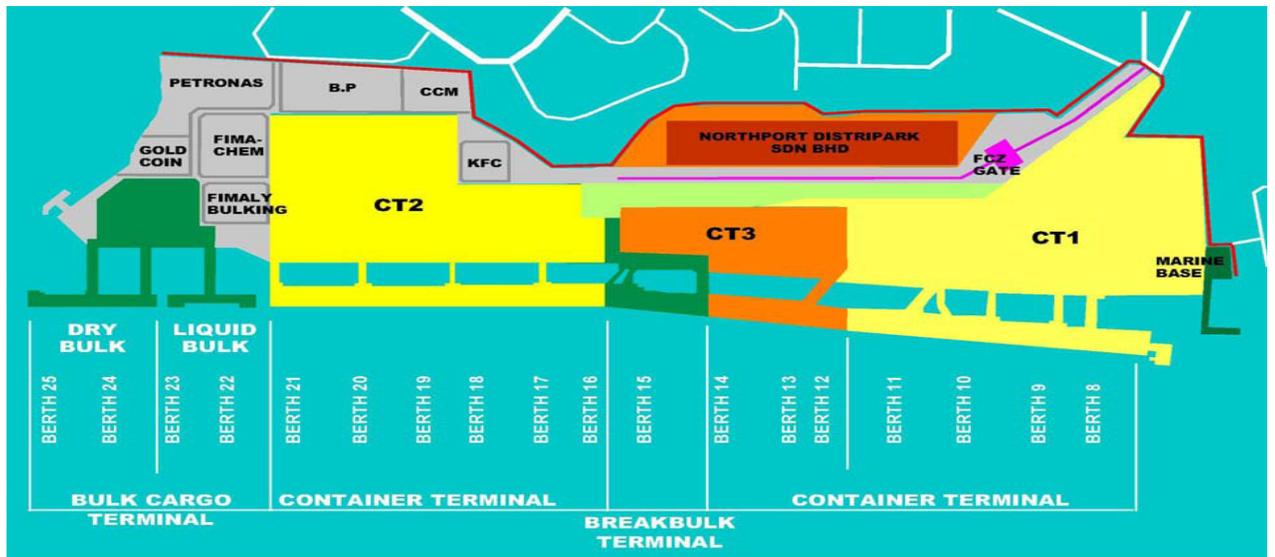


Figure 2, Berth layout plan- North Port

West Port

Petroleum and chemical product are main goods in West Port liquid berth. There are 2 dry bulk terminals at West Ports :

It is estimated that dry bulk cargo will increase from 5.3 million tones in 1995 to over 7.3 million tones by 2010. The major dry bulk imports that pass through Port Klang are fertilizer, wheat, sugar, maize, soya bean and feed meal, while the major export bulk cargo is palm kernel expeller.

DB1

DB1 Terminal is for handling of grains and sugar. There are 2 berths each measuring 200m in length and 15 in depth. It is equipped with a conveyor system and 2 gantry grab unladen capable of discharging 2,000 tones/hour.

DB2

West ports Slag Terminal - With the berth measuring 250m in length and 13.5m in depth, it can accommodate ships of up to 78,000 tones displacement. This terminal is capable of handling silica fertilizer, slag and sand. West ports Cement Terminal - Cement jetty is measuring 285m supported by 8 loading/discharging pipes between jetty and consignee's facilities. It is capable of accommodating vessels up to 35,000 tones displacement with max depth of 11m. Its pumping rate of 800 tones / hour is driven by the latest pneumatic technology available on board specialized cement carriers.

Table 3, Berth Information of the North Port

Terminal		Berth(T)	Max Displacement	Length (m)	Depth (m)	Height Above Chart Datum (m)
Westports	Dry/Break Bulk	B1	80000	200	15.0	7.13
		B2	80000	200	15.0	7.13
		B3	80000	200	15.0	7.13
		B4	80000	200	15.0	7.14
		B5	80000	200	15.0	7.14
		B6	80000	200	15.0	7.14
	Container	B7	80000	300	15.0	7.15
		B8	80000	300	15.0	7.15
		B9	115000	300	15.0	7.15
		B10	115000	300	15.0	7.16
		B11	115000	300	15.0	7.16
		B12	115000	300	15.0	7.16
		B13	160000	300	15.0	7.16
		B14	160000	300	17.5	7.16
		B15	160000	300	16.5	7.16
	Liquid Bulk	LBT1 (Inner)	15000	195	10.0	7.0
		LBT1 (Outer)	15000	195	10.0	7.0
		LBT2	80000	320	14.0	7.0
		LBT3	80000	305	14.0	7.0
LBT4		130000	350	16.0	7.0	
Dry Bulk	Slag	78000	250	13.5	7.0	
	Cement	35000	285	12.0	7.0	

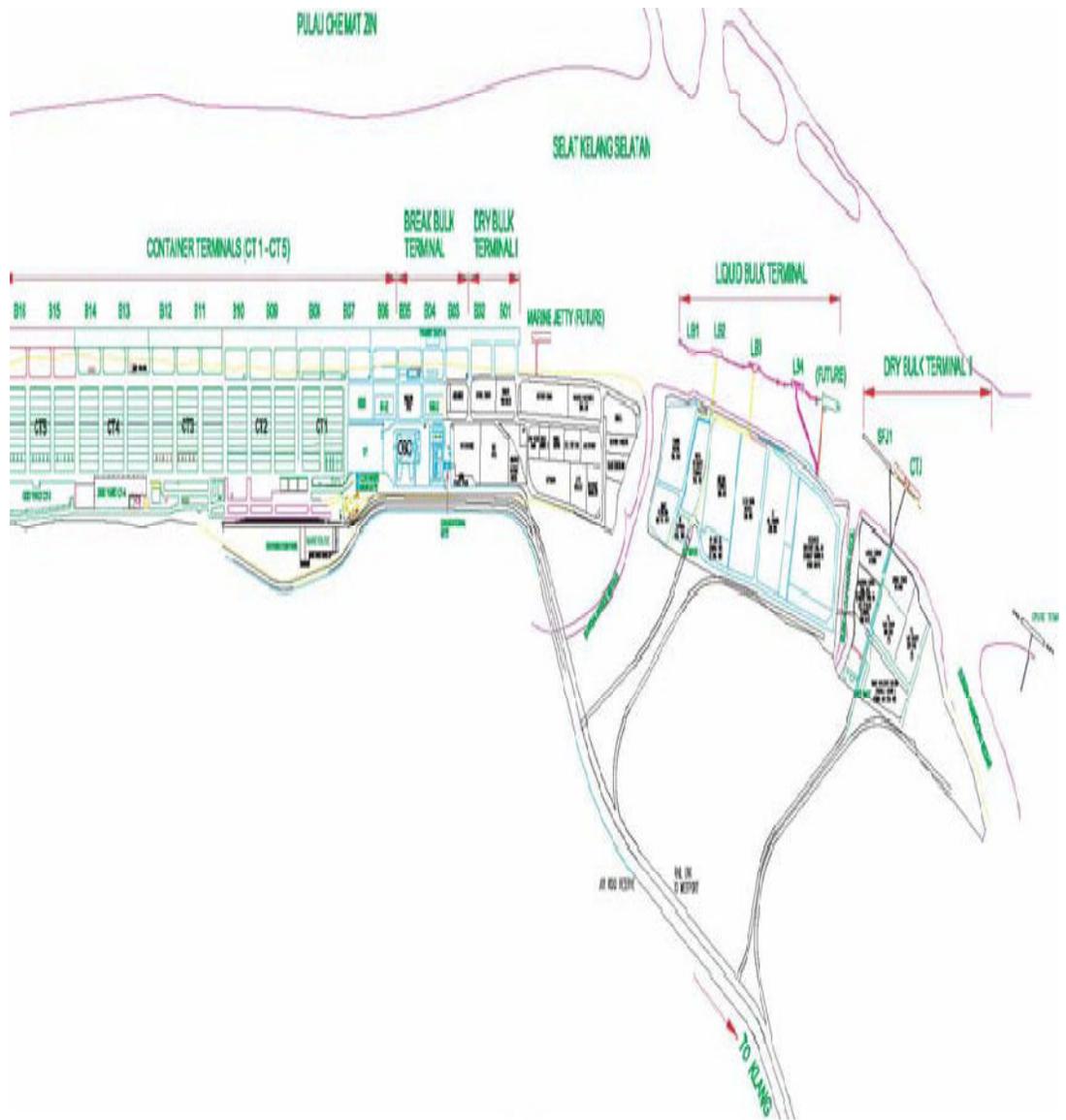
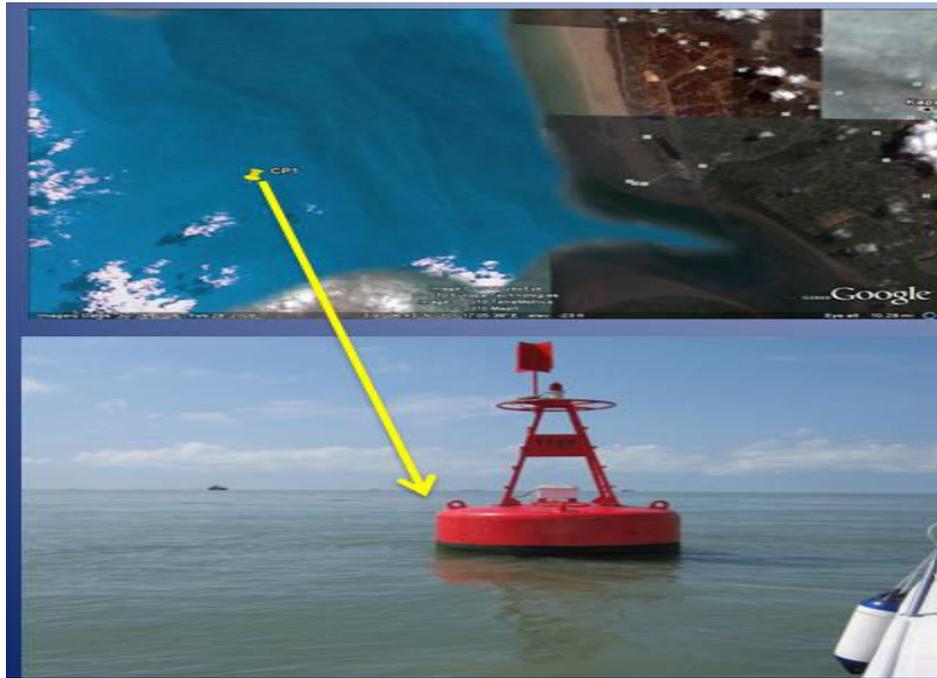


Figure 3, Berth layout plan- West Port

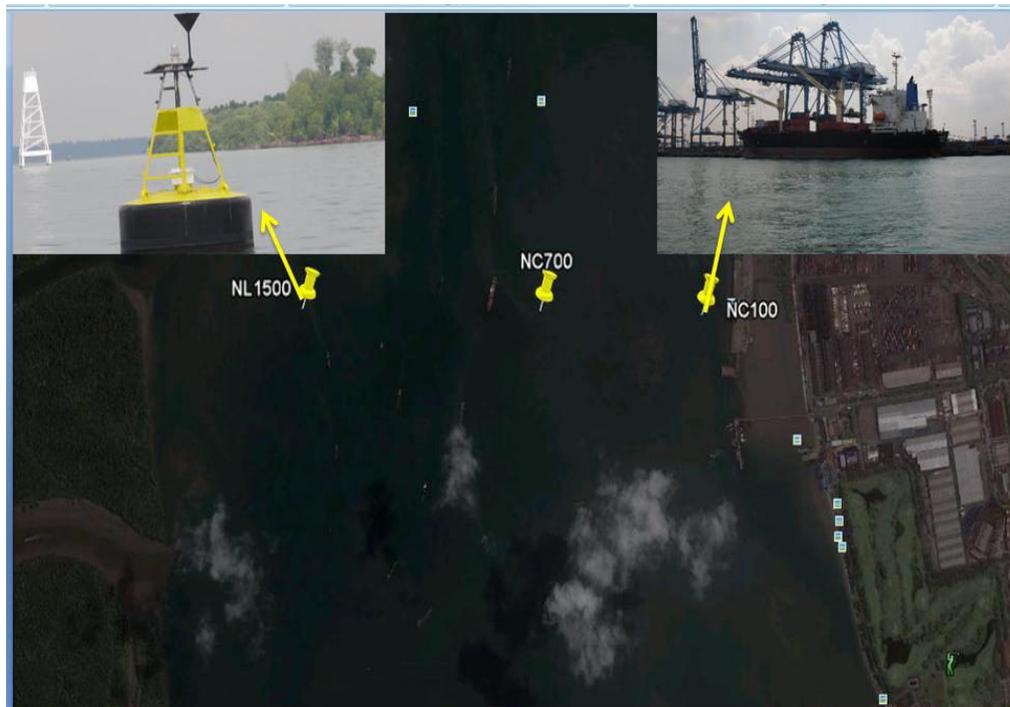
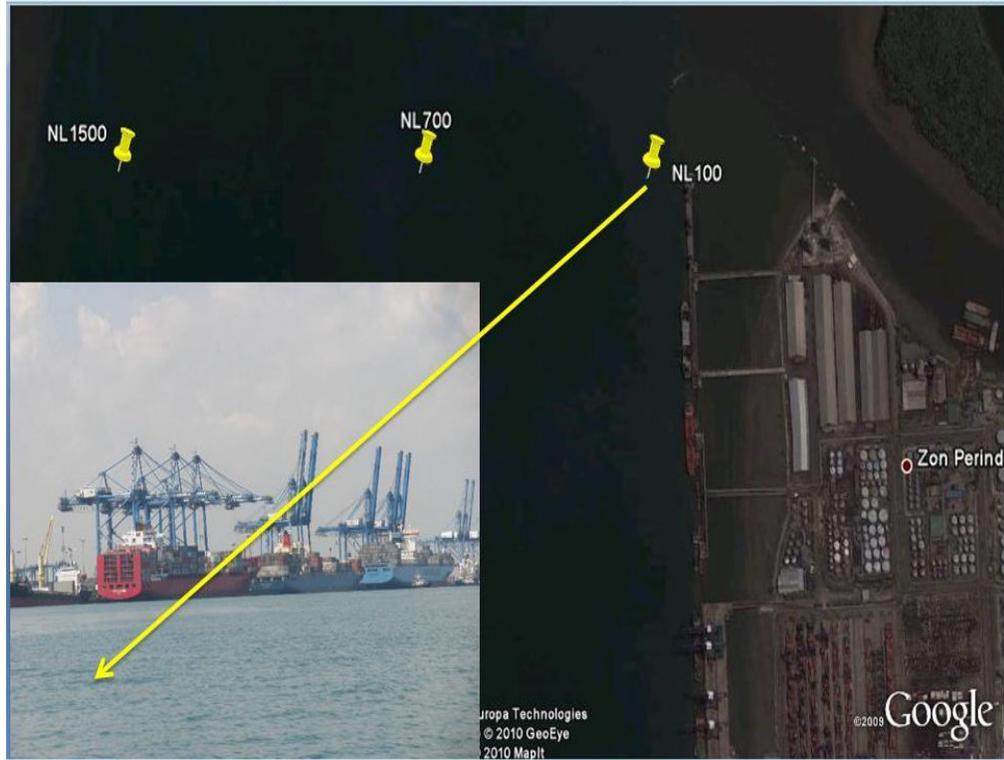
B: Picture of location of stations



Control Station



South Port



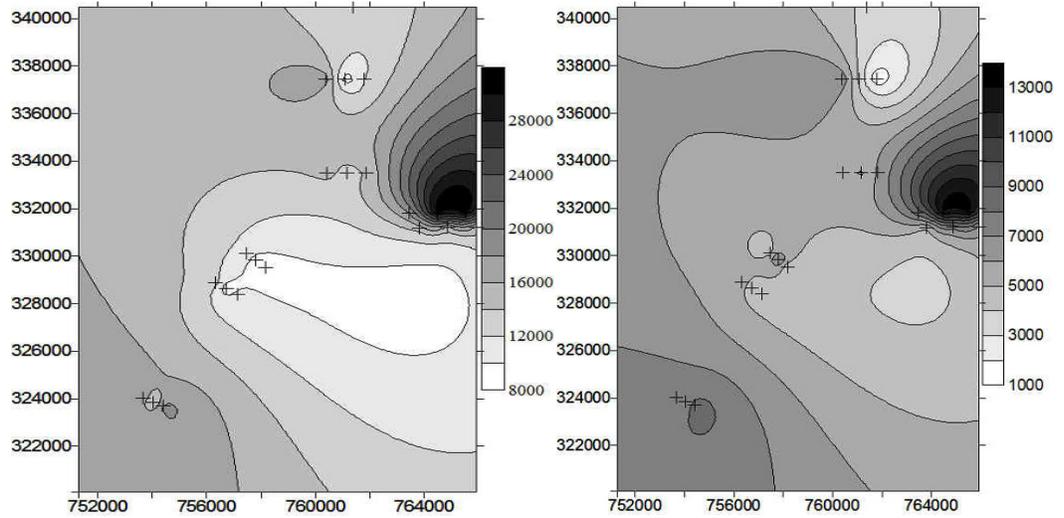
North Port



West Port

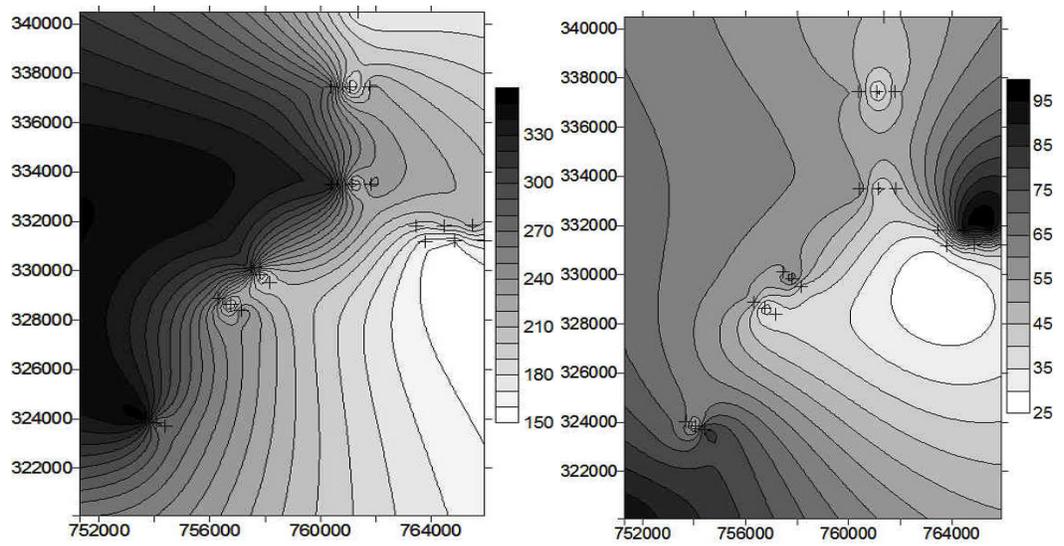
APPENDIX 2

Distribution map



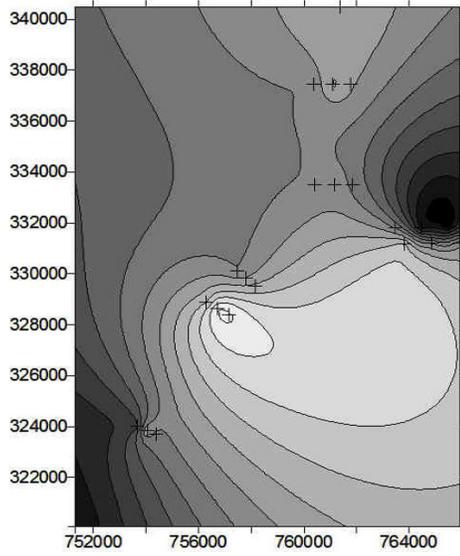
Al

Fe

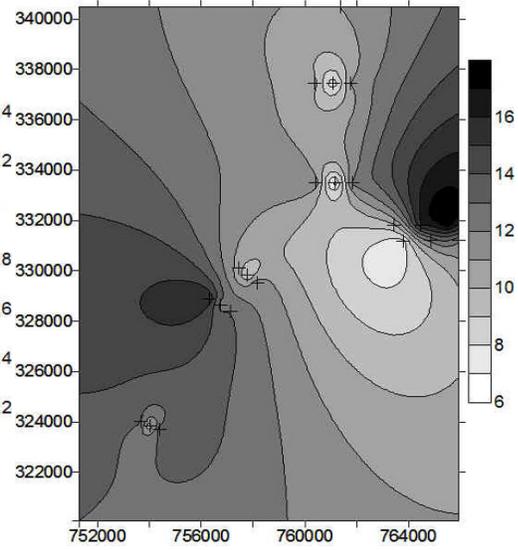


Mn

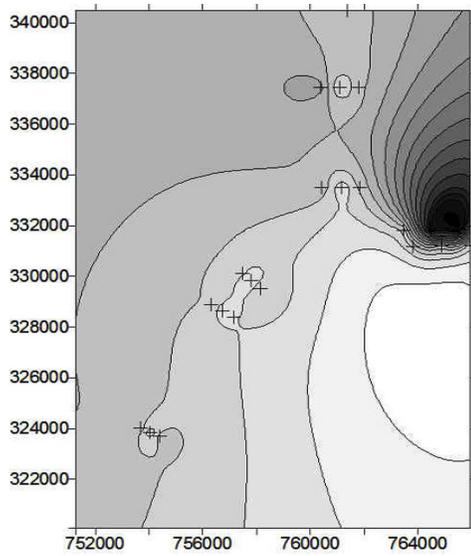
v



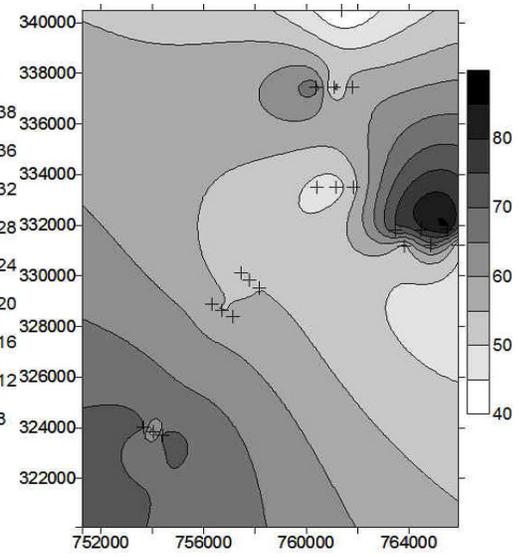
Cd



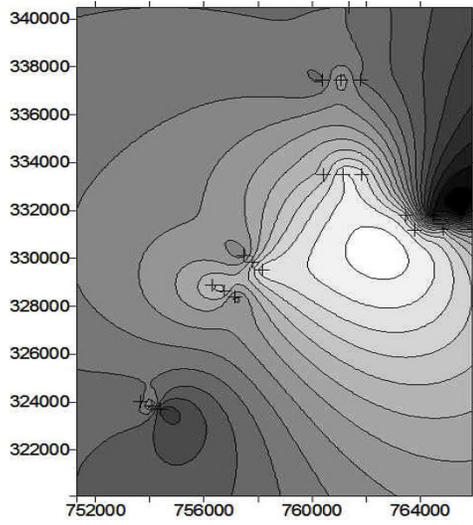
Ni



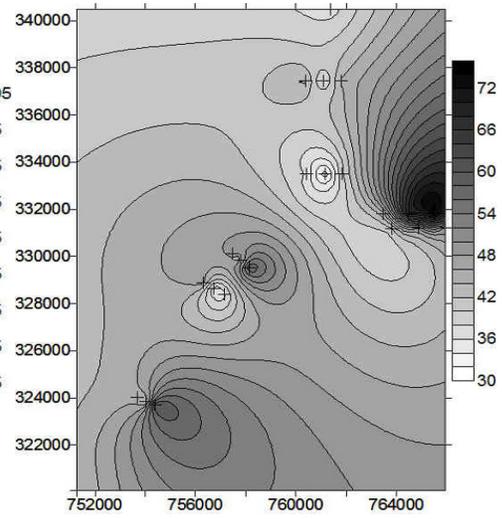
Cu



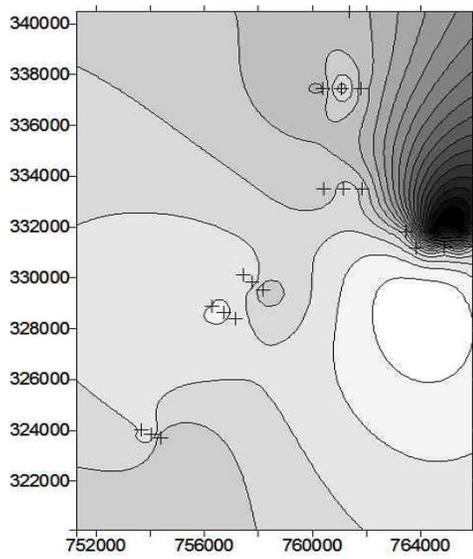
Pb



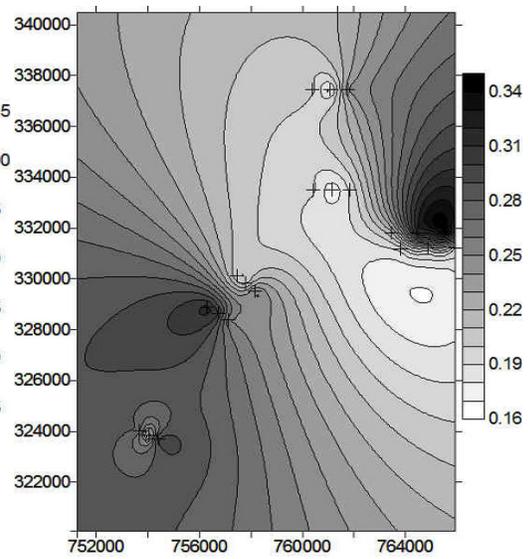
As



Cr



Zn



Hg

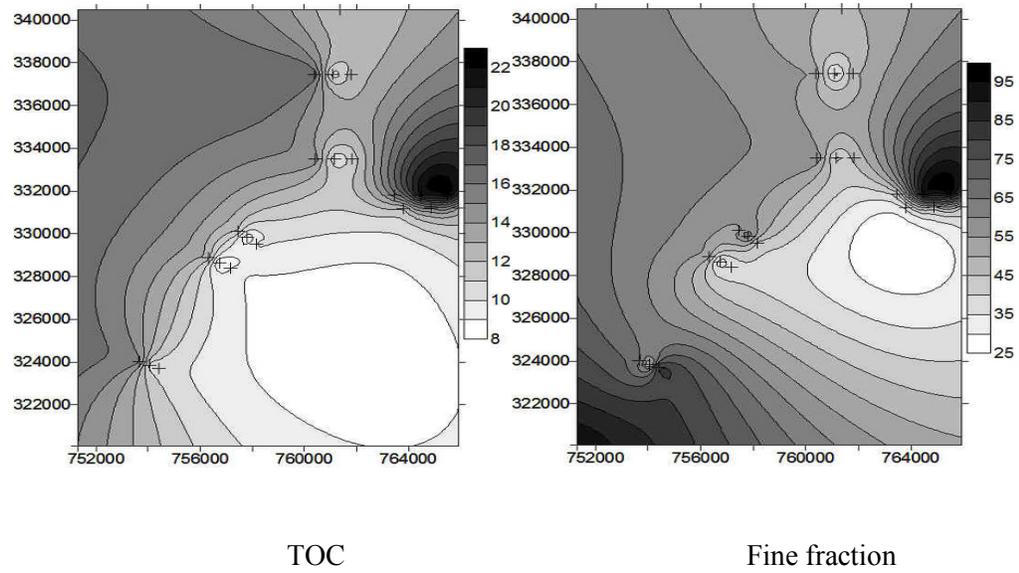
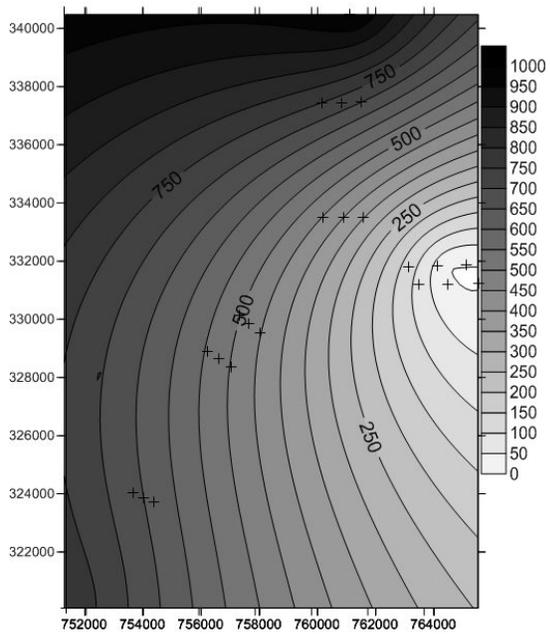
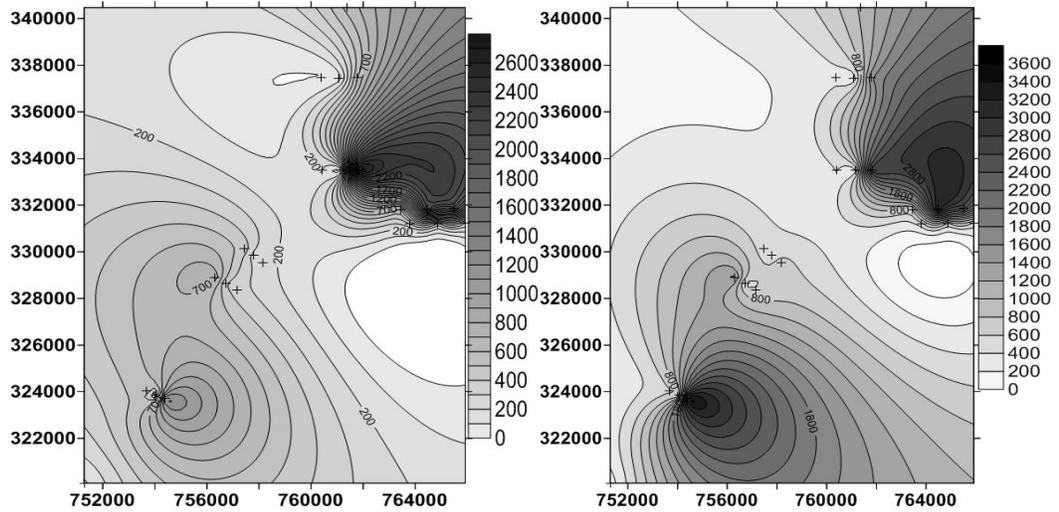


Figure 1, Spatial distribution of heavy metals, TOC and fine grain sized sediment in the Klang Strait

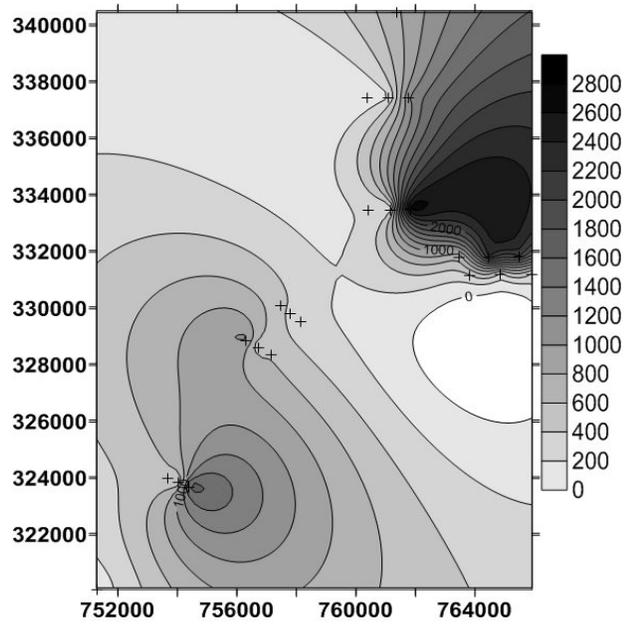


Figurer 2, Spatial distribution of benthic organisms in surface sediment of Klang Strait



Combustion PAH

Total PAHs



Toxic PAHs

Figure 3, Spatial distribution of PAHs compounds in Klang Strait

APPENDIX 3

Part A: chromatography graphs of PAHs analysis

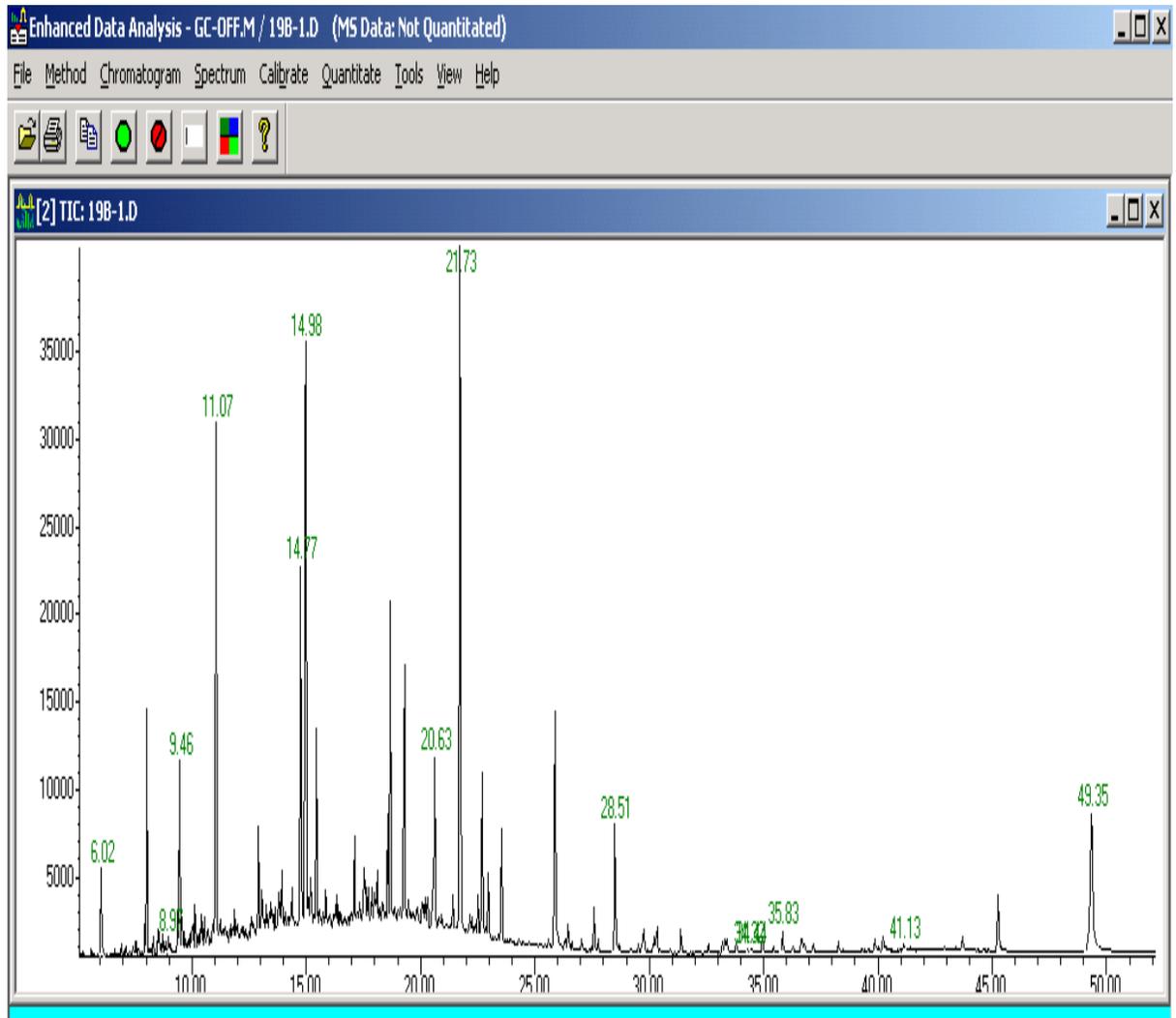


Figure 1, Aromatic hydrocarbon profile of a typical sediment sample along berth line in the West Port (station 13, close to terminal container)

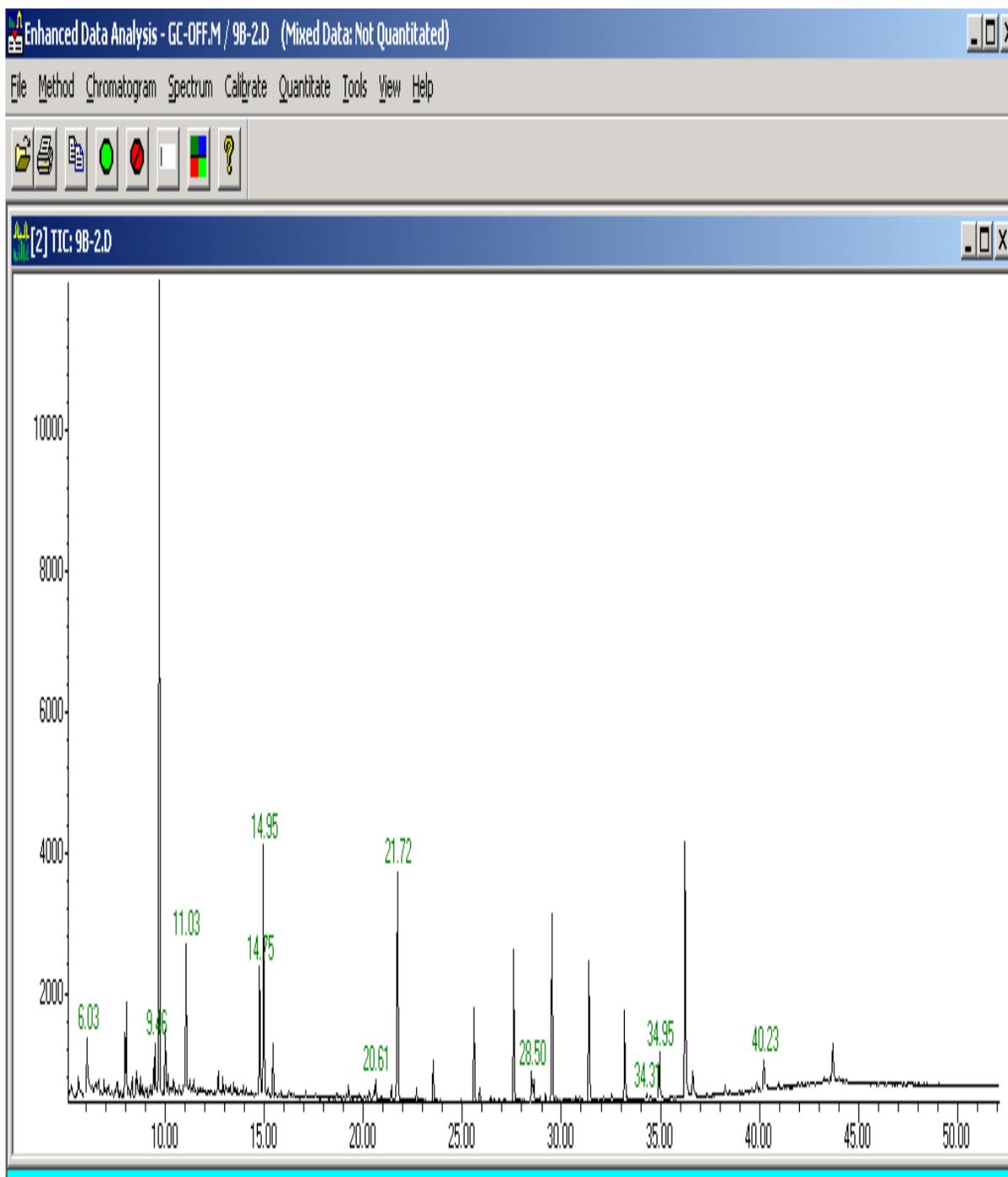


Figure 2, Aromatic hydrocarbon profile of a typical sediment sample along middle part of the West Port (station 14, 500 meter far from berth line).

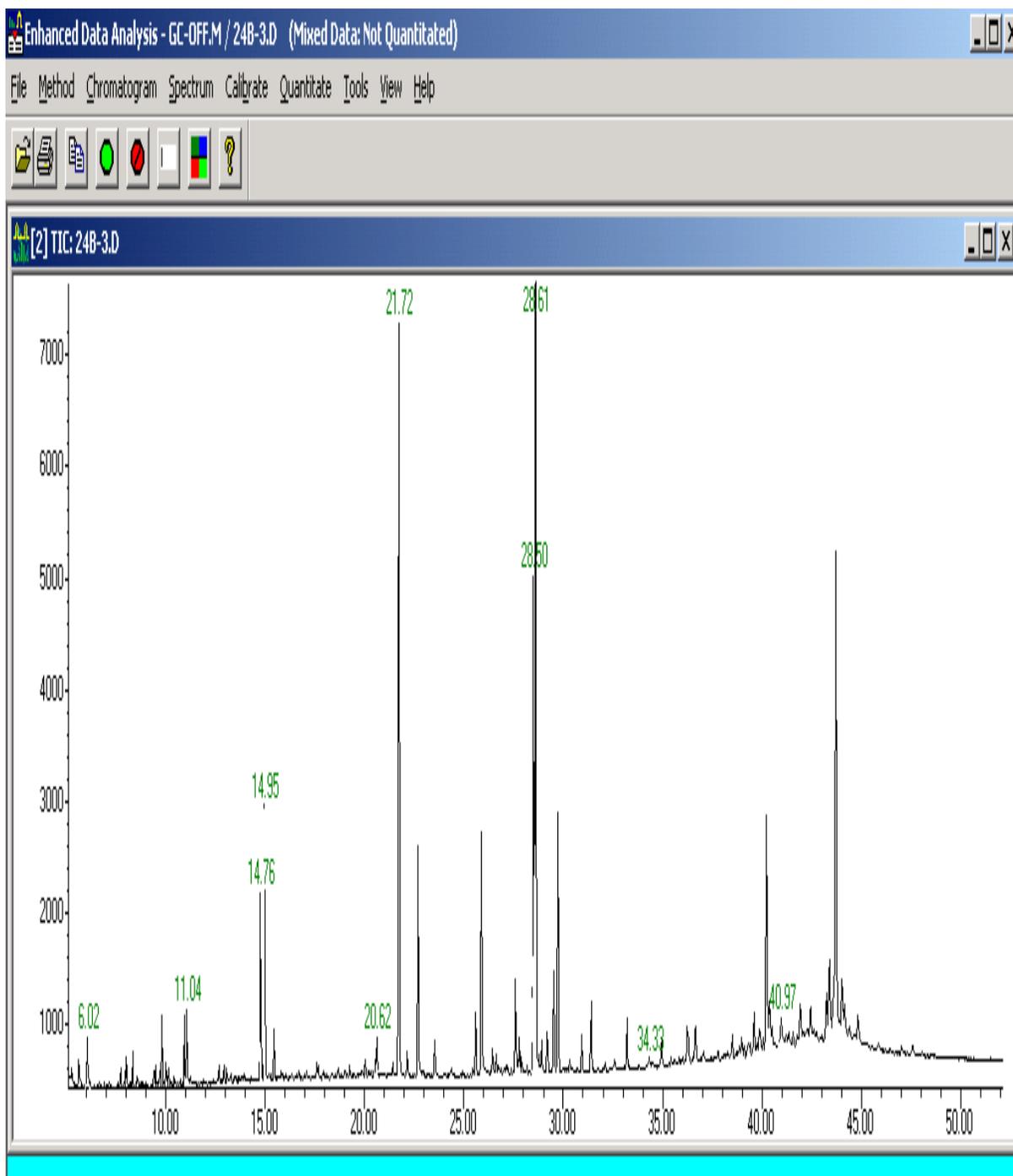


Figure 3, Aromatic hydrocarbon profile of a typical sediment sample along mangrove line in the West Port (stations 9, 1000 meter far from berth line).

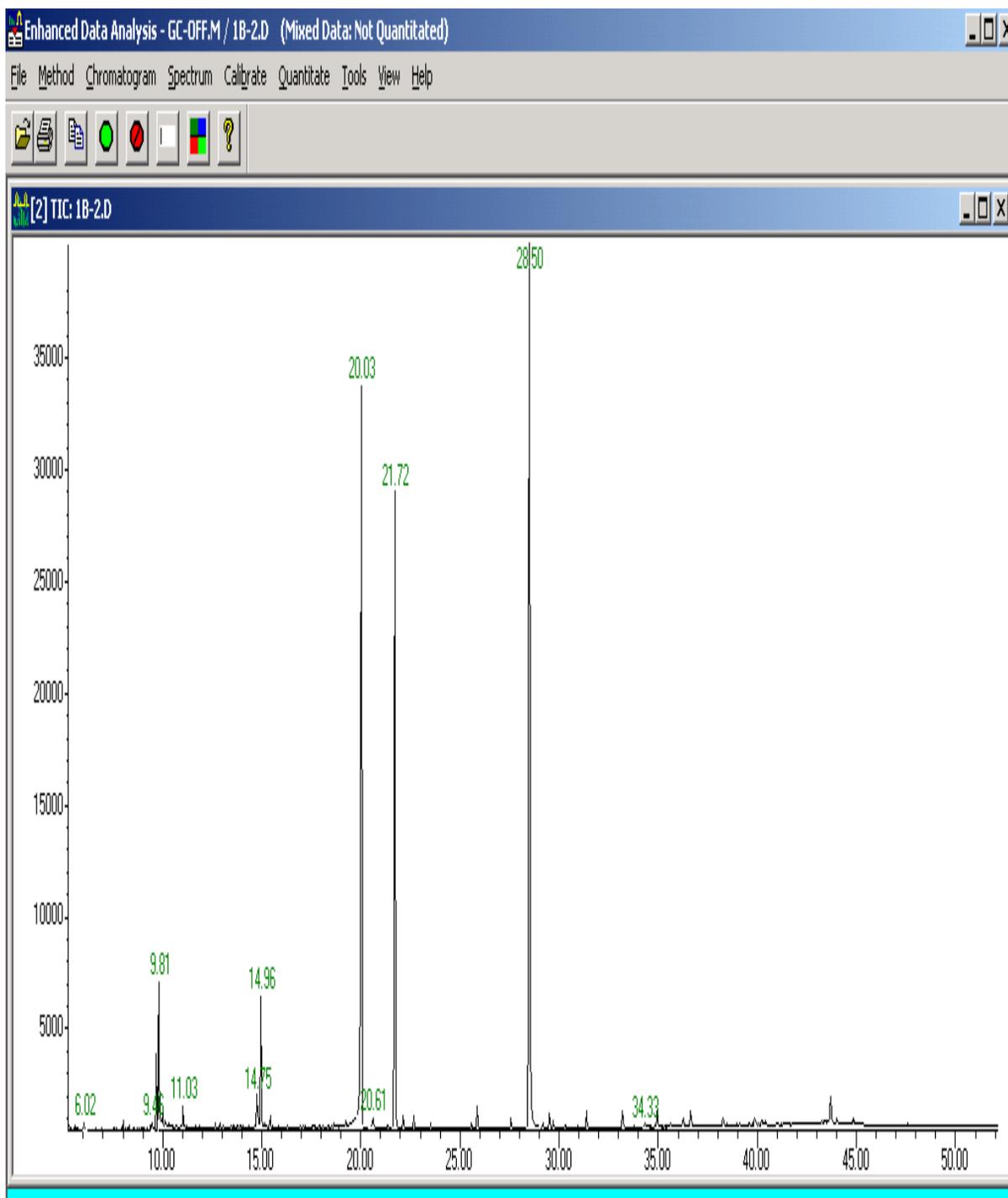


Figure 4, Aromatic hydrocarbon profile of a typical sediment sample along Berth line in the North Port (station 4, close to container terminal).

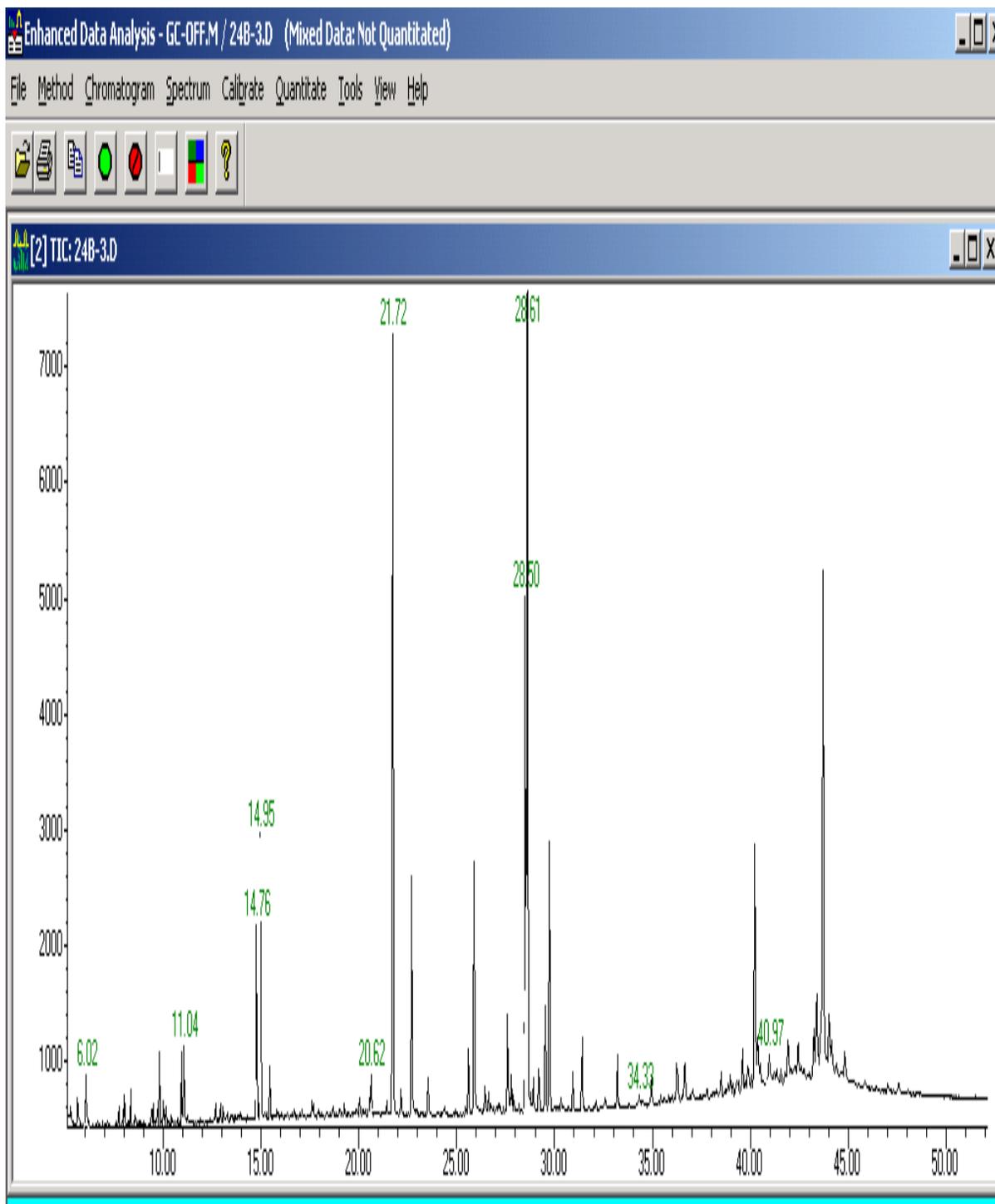


Figure 5, Aromatic hydrocarbon profile of a typical sediment sample along mangrove line in the North Port (station 6, 1500 meter after berth line).

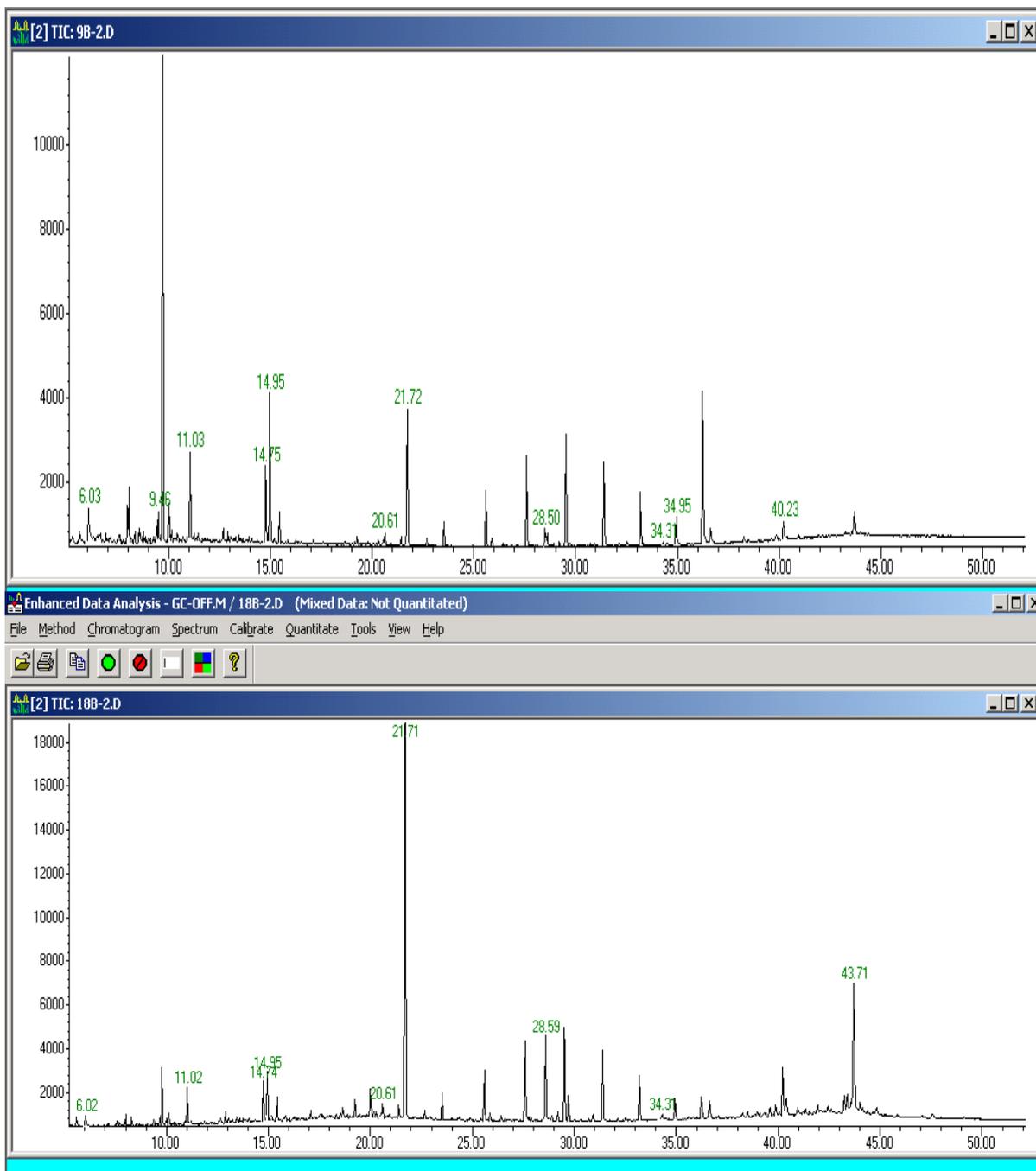


Figure 6, Aromatic hydrocarbon profiles of a typical sediment sample in the South Port (Close to Klang River).

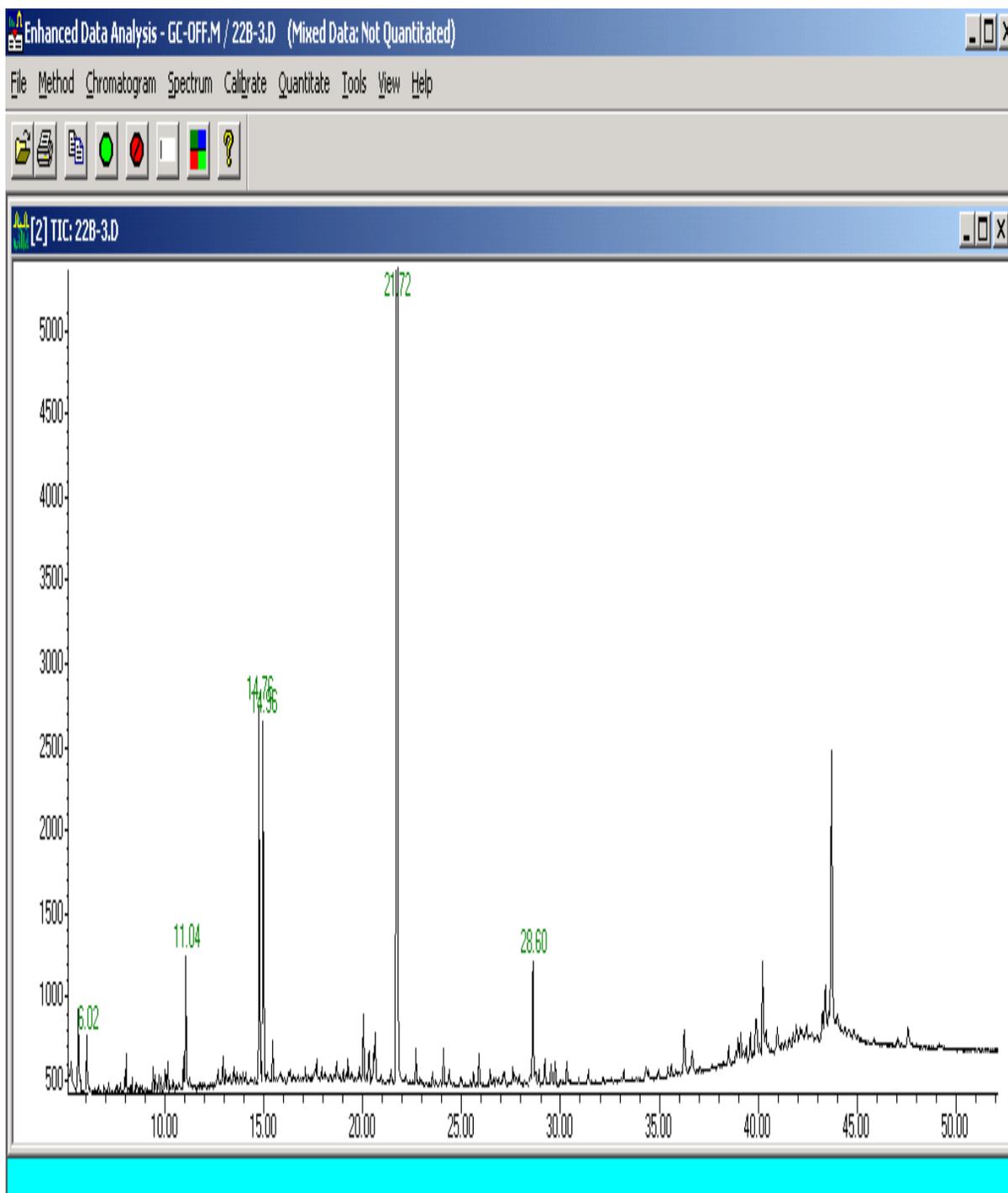


Figure 7, Aromatic hydrocarbon profiles of a typical sediment sample in the Control station.

B: Example for benthic community assessment based on the biotic indices

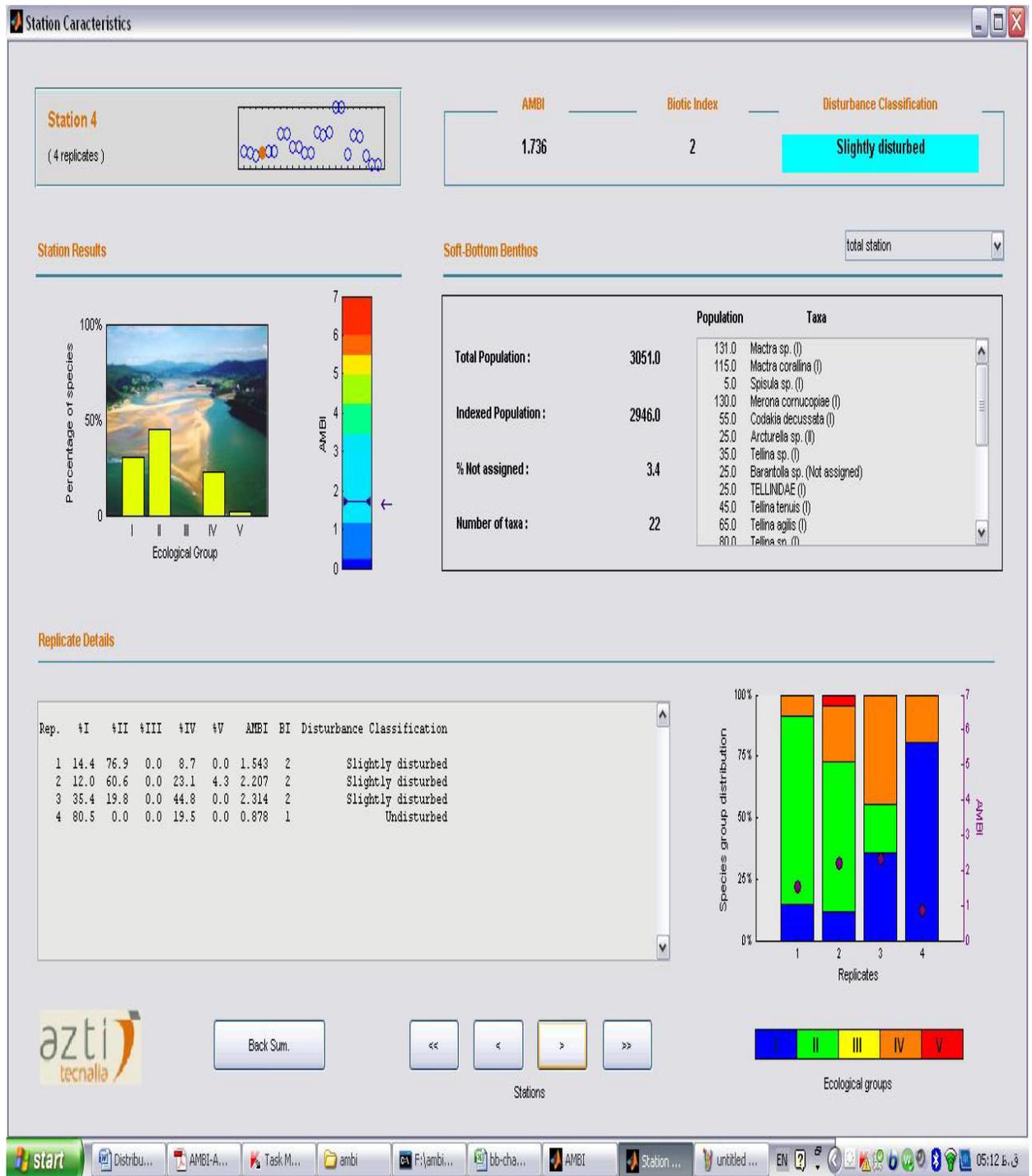


Figure 8, Results of ecological indices to assess pollution level based on the benthic responds to disturbance in station 4 in North Port.

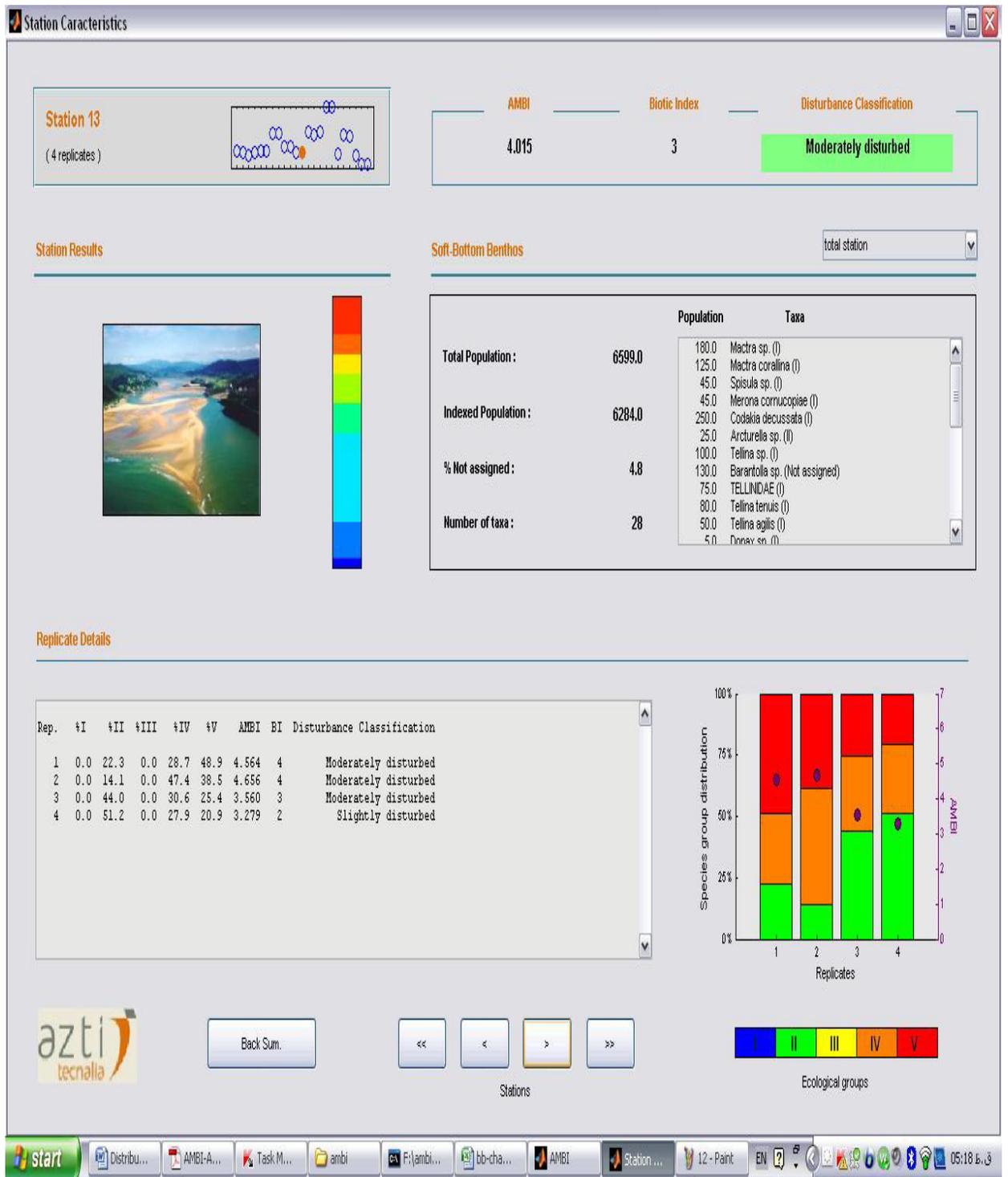


Figure 9, Results of ecological indices to assess pollution level based on the benthic responds to disturbance at station 13 in the West Port.

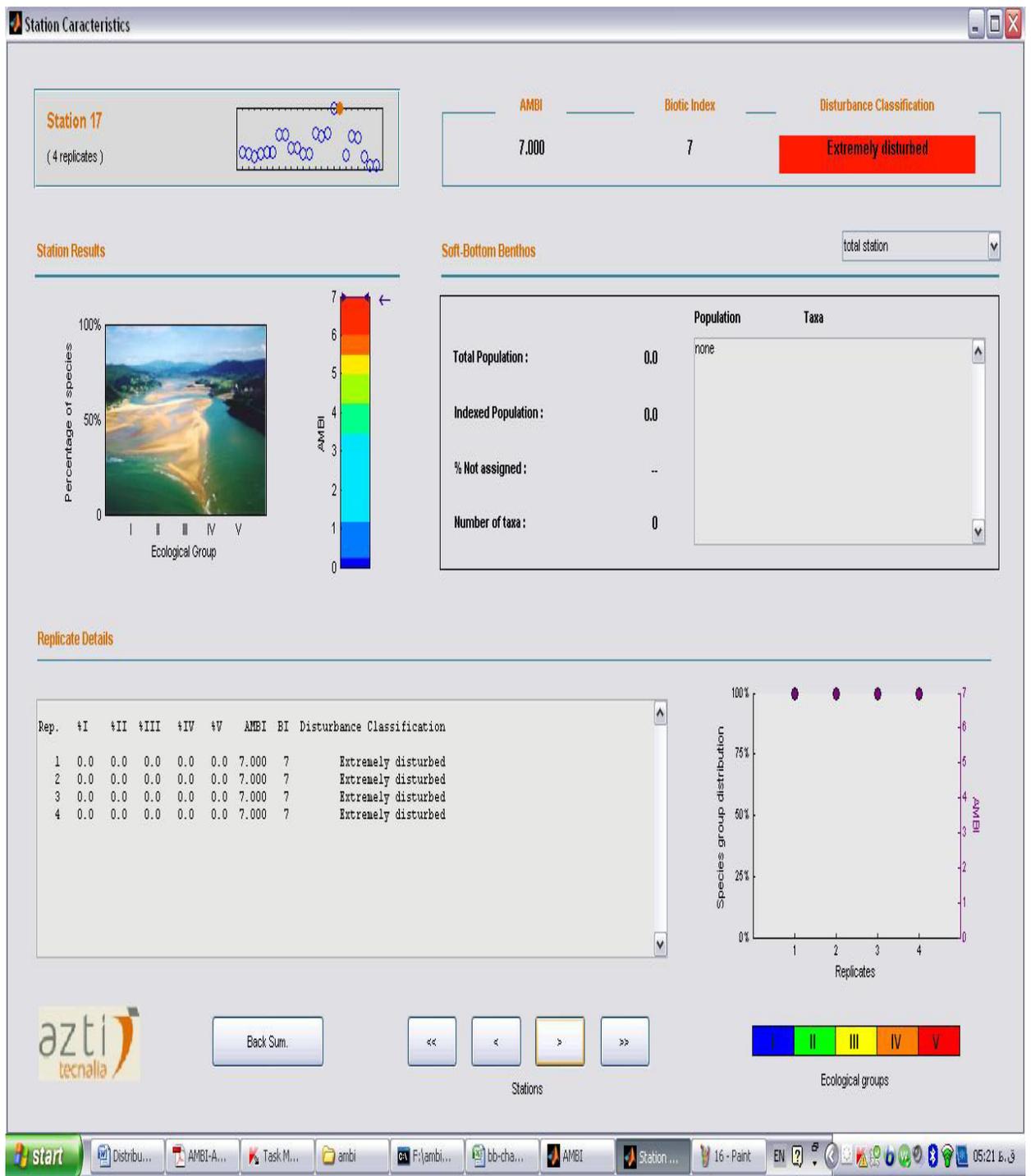


Figure 10, Results of ecological indices to assess pollution level based on the benthic responds to disturbance at station 17 (close to Klang River) in the South Port.

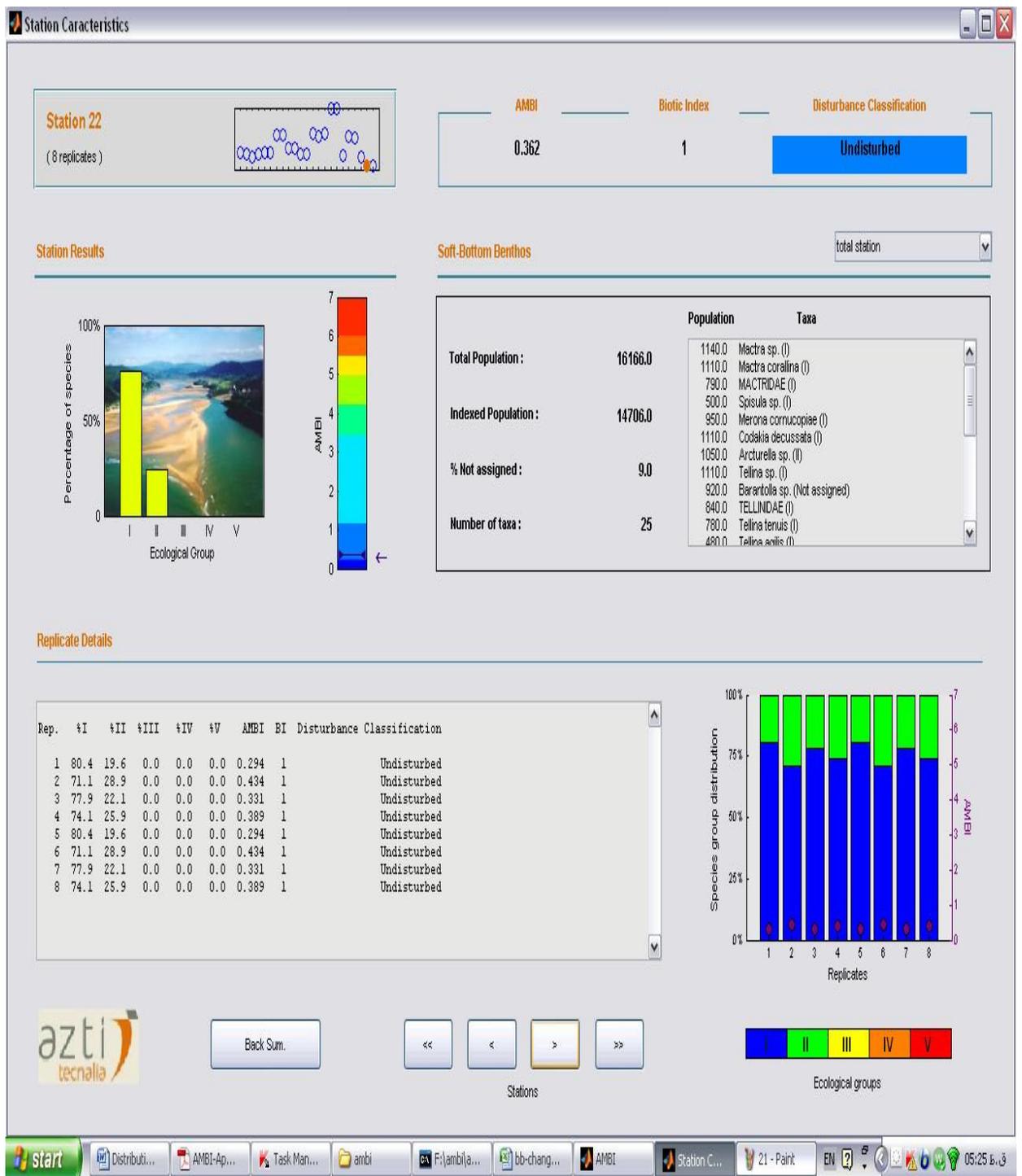


Figure 11, Results of ecological indices to assess pollution level based on the benthic responds to disturbance at station 22 (control Station)

