POLLUTION STUDY AND BIOREMEDIATION OF HEAVY METAL IN AQUEOUS AND SEDIMENT PHASES OF SUNGAI PINANG RIVER BASIN

by

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LIST OF ABBREVIATIONS

AN	Ammoniacal Nitrogen
ANZECC	Australian and New Zealand Environment and Conservation Council
APHA	American Public Health Association
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
BOD	Biochemical Oxygen Demand
CCC	Criteria Continuous Concentration
CCME	Canadian Council of Ministers of the Environment
CMC	Criteria Maximum Concentration
COD	Chemical Oxygen Demand
DEAT	Department of Environmental Affairs and Tourism
DF	Dilution Factor
DFID	Department of International Development
DID	Department of Drainage and Irrigation
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOE	Department of Environment
DWAF	Department of Water Affairs and Forestry
EB L14	Endophytic Bacteria L14
EC	Electrical Conductivity

EDPHK	Environmental Protection Department, the Government of Hong Kong
EPA	Environmental Protection Agency
ES	Average Shales
FAAS	Flame Atomic Spectrophotometer
FP	Fine Particles
GEC	Glisten Environmental Consultants
INWQS	Interim National Water Quality Standards
IRBM	Integrated River Basin Management
IST	Individual Septic Tank
ISQG	Interim Sediment Quality Guidelines
IWK	Indah Water Consortium
JCSS	Jelutong Central Sewerage System
LCEL	Lower Chemical Exceedance Level
MC	Moisture Content
MCo	Municipal Council
MPPP	Majlis Perbandaran Pulau Pinang
NA	Natural Attenuation
NGOs	Non-Government Organizations
NHDES	New Hampshire Department of Environmental Services
PAHs	Poly-Aromatic Hydrocarbons

PAI	Pesticide Active Ingredients
PCBs	Polychlorinated Biphenyl
PE	Population Equivalents
PEL	Probable Effect Levels
POC	Particulate Carbon
SOD	Sediment Oxygen Demand
SS	Suspended Solids
STP	Sewerage Treatment Plant
SQGs	Sediment Quality Guidelines
TDS	Total Dissolved Solids
THM	Trihalomethane
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solid
USDA	United States Department of Agriculture
USEPA	United State Environmental Protection Agency
UAE	United Arab Emirates
UCEL	Upper Chemical Exceedance Level
WDNR	Wisconsin Department of Natural Resources
WHO	World Health Organization

WQI	Water Quality Index
WRC	Water Research Commission
WWF	World Wildlife Fund

LIST OF SYMBOLS

x	weight before drying (g)
y	weight after drying (g)
C	total metal concentration (mg/kg)
R	concentration read with AAS (mg/L)
v	volume of balance of nitric acid and hydrogen peroxide (mL)
W	weight of sediment sample (g)
$\left(\frac{M}{Fe}\right)_{sample}$	ratio of metal and Fe concentration of the sample
$\left(\frac{M}{Fe}\right)_{background}$	ratio of metal and Fe of the background
C_n	measured concentration in the sediment for the metal *n*(mg/kg)
B_n	background value for the metal *n*(mg/kg)
$C_{m}\ Sample$	measured concentration of the metal *m* in sediment (mg/kg)
$C_m\ Background$	background value of the metal *m*.(mg/kg)
NH_3-N	Nitrogen-Ammonia
NH_4-N	Nitrogen-Ammonium
NO_3-N	Nitrogen-Nitrate

KAJIAN PENCEMARAN DAN BIOREMEDIASI LOGAM BERAT DI DALAM FASA BERAKUA DAN SEDIMEN LEMBANGAN SUNGAI PINANG

ABSTRAK

Sungai Pinang dikenali sebagai salah satu sungai yang paling tercemar di Malaysia. Satu kajian telah dijalankan untuk menentukan status kualiti air di Sungai Pinang dan cawangannya. Lapan lokasi persampelan yang terletak sebelum pertemuan setiap cawangan sungai dipilih. Ciri-ciri fizikal dan kimia air dan sedimen setiap kawasan persampelan telah ditentukan. Beberapa variasi dalam keputusan menunjukkan bahawa kualiti air Sungai Pinang dan cawangannya adalah disebabkan oleh musim, lokasi pensampelan dan parameter yang diuji. Indeks kualiti air yang lebih baik dicapai dalam tempoh hujan berbanding musim kemarau. Menurut indeks kualiti air dan Interim Piawaian Kualiti Air Malaysia (INWQS), kualiti air sungai jatuh dalam Kelas III ke V bagi DO, BOD_5, COD dan AN manakala TDS, TSS, pH dan EC antara Kelas I dan II . Suhu air semasa kedua-dua musim adalah pada julat normal manakala kekeruhan sungai berada dalam Kelas II hingga IV. Penilaian ke atas ciri-ciri dan kualiti sedimen menunjukkan bahawa taburan saiz partikel sungai adalah tinggi dengan pasir dan sedikit kelodak dan tanah liat berhampiran muara sungai. Kajian ini juga mendapati bahawa pH sedimen adalah berasid kecuali Sungai Pinang yang sedikit beralkali. Parameter kimia sedimen yang lain iaitu TOC, kandungan kelembapan dan TKN adalah tinggi di beberapa lokasi persampelan manakala kepekatan PO_4^{3-} rendah telah dikenalpasti. Kaji selidik terperinci serta merujuk kepada data sekunder juga telah dijalankan untuk mengenal pasti masalah utama bagi setiap kawasan berkaitan dengan kegunaan tanah. Empat kumpulan pencemar sungai yang menjejaskan kualiti air sungai dalam Sungai Pinang telah dikenal pasti yang pertama, pembuangan air basuhan yang dijana dari rumah, pasar basah, komersial dan perdagangan dan rumah penyembelihan, kedua, air sisa kumbahan, ketiga, effluen industri dan keempat, diskriminasi pembuangan sisa ke dalam sungai. Kajian yang

lebih lanjut telah dilakukan ke atas jumlah logam berat yang terkandung dalam fasa berakua dan sedimen yang terkumpul dalam Sungai Pinang. Sampel air telah diambil di setiap lokasi pensampelan semasa musim kering dan hujan. Lima unsur-unsur logam berat telah dipilih dalam kajian ini adalah Cd, Pb, Zn, Fe dan Cu. Hasil kajian menunjukkan bahawa semasa musim kering, Cu tidak dikesan manakala Cd, Pb, Zn dan Fe adalah berbeza masing-masing antara 0.01-0.04, 0.14-0.38, 0.04-0.14 and 1.47-2.28 mg/L. Semasa musim hujan, julat kepekatan Cd, Pb, Zn, Fe dan Cu adalah masing-masing 0.001-0.035, 0.02-0.24, 0.02-0.07, 1.04-1.50 dan 0.005-0.06 mg/L. Berdasarkan garis panduan kualiti air terpilih, Cd, Pb dan Fe melebihi had yang dibenarkan manakala Cu dan Zn adalah lebih rendah daripada garis panduan yang dicadangkan. Kepekatan unsur yang serupa juga telah ditentukan dalam sampel sedimen yang dikumpulkan di dalam kawasan kajian. Purata kepekatan logam berat adalah antara Cd 0.01-2.98; Pb 0.01-48.05; Zn 37.18-247.43, Cu 2.00-51.96 dan Fe 1.298.87-1.971.64 mg/kg. Walaupun kepekatan logam berat dikesan tinggi di dalam sedimen berbanding dengan sampel air, berdasarkan pada beberapa garis panduan kualiti sedimen, tahap unsur-unsur dalam sedimen lokasi persampelan adalah lebih rendah daripada had yang dibenarkan kecuali di Sungai Pinang dan Sungai Jelutong. Analisis lanjut mengenai kepekatan logam berat dalam sedimen telah dinilai dengan menggunakan indeks iaiatu faktor pengkayaan (EF), indeks geoakumulatif (I_{geo}), factor pencemaran (CF), indeks beban pencemaran (PLI) dan tahap pencemaran yang diubaisuai (mC_d). Nilai-nilai EF dan CF mendedahkan bahawa sampel sedimen telah teruk diperkaya dengan Cd, Pb dan Zn walaupun nilai I_{geo} mencadangkan bahawa sedimen sungai mempunyai tahap latar belakang bagi kebanyakan unsur-unsur yang diuji. Selain itu, nilai-nilai PLI dan mC_d, yang masing-masing antara 0-1.23 dan 0.40-3.23 menunjukkan bahawa beberapa lokasi persampelan ketara tercemar dengan unsur surih. Satu penyelidikan berkaitan kajian bioremediasi dalam usaha untuk mengurangkan pencemaran logam berat dalam sedimen telah dikaji berdasarkan teknik pengecilan semula jadi dan bioaukmentasi. Sepanjang kajian ini, kedua-dua teknik telah menggunakan sedimen yang telah disterilkan dan tidak-disterilkan dengan dos bakteria yang berbeza (1mL dan 2mL daripada 10^8 sel/mL mikrob). Percampuran bakteria terdiri

daripada *Rhodococcus erythropolis* dan *Bacillus cereus* telah digunakan. Hasil kajian menunjukkan bahawa pengecilan semula jadi serta teknik bioaukmentasi mempunyai keupayaan untuk mengurangkan logam berat dalam sedimen tetapi peratusan pengurangan unsur yang lebih tinggi dikesan pada bioaukmentasi. Cd dikenalpasti sebagai pengurangan unsur tertinggi manakala Fe sebagai pengurangan peratusan terendah dalam sedimen bagi kedua-dua jenis bioremediasi. Disamping itu, peratusan pengurangan logam yang lebih tinggi dicapai dengan peningkatan dos bakteria.

POLLUTION STUDY AND BIOREMEDIATION OF HEAVY METAL IN AQUEOUS AND SEDIMENT PHASES OF SUNGAI PINANG RIVER BASIN

ABSTRACT

Sungai Pinang is known as one of the most polluted river in Malaysia. A study was conducted to verify the status of the water quality in Sungai Pinang and its tributaries. Eight sampling locations which located just before the meeting of each tributary were selected. The physical and chemical characteristics of water and sediment of each sampling sites were determined. Several variations in the results show that the water quality of Sungai Pinang and its tributaries are mainly due to season, sampling location and parameter tested. Better water quality index is achieved during rainy period compared to dry season. According to water quality index and Interim Water Quality Standards of Malaysia (INWQS), the water quality of the river fall within Class III to V for DO, BOD_5, COD and AN while TDS, TSS, pH and EC fall between Class I and II. The temperatures of the waters during both seasons were at the normal range whilst the turbidity of the rivers was in Class II to IV. An evaluation on sediment characteristics and quality showed that the particle size distribution of the rivers were high with sand and a brief of silt and clay near to the river mouth. The results also revealed that the pH of the sediment were acidic except for Sungai Pinang which was slightly alkaline. Other chemical parameters for the sediments which are TOC, moisture content and TKN were high at several sampling locations while low PO_4^{3-} concentrations was determined. Detailed surveys as well as referring to secondary data were also carried out to identify the key problems of each area with respect to land use. Four groups of river polluters affecting the quality of the river water within Sungai Pinang were identified which are firstly, sullage waters generated from domestic, wet markets, commercials and trades and abattoir, secondly, the sewage wastewater, thirdly, industrial effluents and fourthly, discriminant dumping of wastes into the rivers. Further study was performed on the total heavy metal contained in the aqueous and sediments phase accumulated within Sungai Pinang. The water samples were collected at each sampling location during dry and rainy seasons. Five elements of heavy metals were chosen in this study which are Cd, Pb, Zn, Fe and Cu. The results show that during dry season, Cu was not detected while Cd, Pb, Zn and Fe were varied between 0.01-0.04, 0.14-0.38, 0.04-0.14 and 1.47-2.28 mg/L respectively. During rainy season, the ranges concentration of Cd, Pb, Zn, Fe and Cu are 0.001-0.035, 0.02-0.24, 0.02-0.07, 1.04-1.50 and 0.005-0.06 mg/L accordingly. Based on selected water quality guidelines, Cd, Pb and Fe exceed the permissible limits while Cu and Zn were lower than the proposed guidelines. Similar element concentrations were also determined in the sediment samples collected within the study area. The average concentrations of heavy metals are ranged between Cd 0.01-2.98; Pb 0.01-48.05; Zn 37.18-247.43, Cu 2.00-51.96 and Fe 1298.87-1971.64 mg/kg. Although high heavy metal concentrations detected in the sediments compared to water samples, according to several sediment quality guidelines, the levels of elements in sediment of sampling locations were lower than permissible limits except in Sungai Pinang and Sungai Jelutong. Further analysis on the heavy metal concentrations in sediment were evaluated by using multiple indices which are enrichment factor (EF), index of geoaccumulation (I_{geo}), contamination factor (CF), pollution load index (PLI) and modified degree of contaminant (mC_d). The EF and CF values revealed that the sediment samples are severely enriched with Cd, Pb and Zn even though I_{geo} values suggest that the river sediments have a background level for most of the elements tested. Moreover, the values of PLI and mC_d, which are between 0-1.23 and 0.40-3.23 respectively indicating that some of the sampling locations are significantly polluted with trace elements. An investigation of bioremediation study in order to reduce heavy metal contamination in sediment was carried out according to natural attenuation and bioaugmentation techniques. Throughout the study, both techniques have used sterilized and non-sterilized sediments with different dosage of bacteria innocular (1 mL and 2 mL of 10^8 cell/mL microbes). A mixture of bacteria consists of *Rhodococcus erythropolis* and *Bacillus cereus* were used. The results show that the natural attenuation as well as bioaugmentation techniques has the ability to

decrease the heavy metals in sediments but higher percentage of elements reductions were detected in bioaugmentation. Cd was revealed as the highest while Fe as the lowest percentage reduction in the sediments for both types of remediation. Besides, higher percentage of metal reduction is achieved with the increase of bacteria dosage.

CHAPTER 1

INTRODUCTION

1.1 General.

Rivers have been known to be one of the important water resources in our lives. They have provided water supplies in inland areas for drinking, irrigation and industrial purposes. Rivers also play an important role in assimilating or carrying off industrial and municipal wastewater, manure discharges and runoffs from agricultural fields, roadways and streets. A river also serves as a transportation route for materials and commerce (Neal et al., 2006; Carpenter et al., 1998; Jarvie et al., 1998).

Rivers are dynamic systems and may change in nature several times during their course because of changes in physical conditions such as slope and bedrock geology. They carry horizontal and continuous one-way flow of a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources. This matter moves downstream and is subject to intensive chemical and biological transformations. The surface water chemistry of a river at any point reflects several major influences, including the lithology of the catchment, atmospheric inputs, climatic conditions and anthropogenic inputs. Identification and quantification of these influences should form an important part of managing land and water resources within a particular river catchment (Bellos and Sawidis, 2005).

1.2 Water Quality of Rivers in Malaysia.

Water quality is based on the physical, chemical and biological characteristics of the water itself. Typically, rivers are diverse and biologically productive environments in their natural form. The presence, abundance, diversity and distribution of aquatic species in surface waters are dependent upon a myriad of physical and chemical factors such as temperature, pH, suspended solids, nutrients, chemicals and in-stream and riparian habitats. The water quality reflects the composition of water as affected by natural causes and human's cultural activities. It is expressed in measurable quantities and is related to intended water use (Vladimir and Harvey, 1994).

Water quality is determined and measured by comparing physical, chemical, biological, microbiological and radiological quantities and parameters to a set of standards and criteria. In Malaysia, the Water Quality Index (WQI) was used as a basis to assess water bodies. The outcome which is in turn based on a number of water quality parameters were then classified into a number of classes with their beneficial uses (DID, 2000). The Interim National Water Quality Standard for Malaysia (INWQS) adopted by the Department of Environment (DOE) is also used to measure the water quality of the river.

Rapid development in recent years has affected the water quality of many rivers in Malaysia. These waterways have become polluted due to the wastes that have been discharged into the rivers. Consequently, DOE has set up 1063 monitoring stations located at 577 rivers in order to monitor the water quality status of these waterways (DOE, 2009). Out of these monitoring stations, 578 (54%) were found to be clean, 378 (36%) were slightly polluted while 107 (10%) were found to be polluted (Figure 1.1).

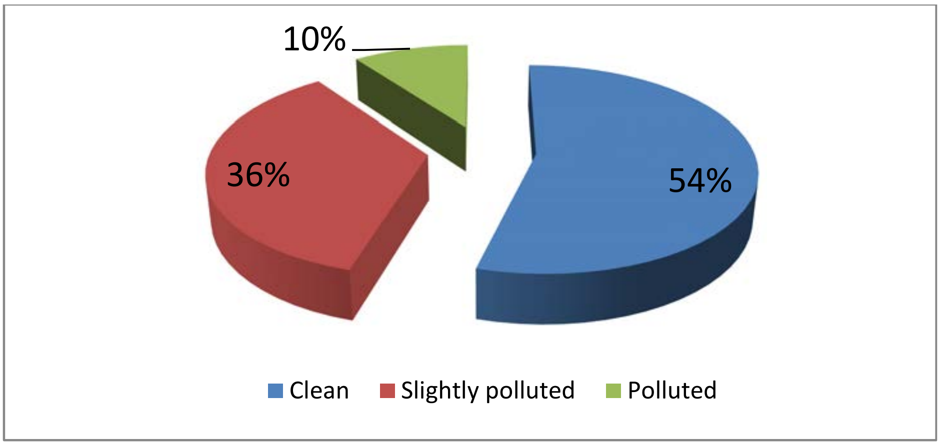

Figure 1.1 Status of water quality monitored at selected river monitoring stations in Malaysia (Source: DOE 2009).

DOE (2009) also has recorded that for over five years (2005-2009), there has been a significant reduction in the number of clean rivers in Malaysia. In 2009, there were 306 clean rivers as compared to 334 in 2008 while the slightly polluted and polluted rivers have increased from 197 to 217 and 48 to 54 respectively (Figure 1.2).

There are two factors identified by the DOE (2008) which contribute to the decrease in the number of clean rivers in Malaysia. The first factor was the increasing number of pollution sources such as sewage treatment plants, agro-based factories and pig farms which contributed to an increase in pollutant load. The second factor is the natural occurrence where the decrease in the amount of rainfall has caused the reducing in its volume, thus, the reduction in the assimilative capacity leading to the deterioration in the river condition.

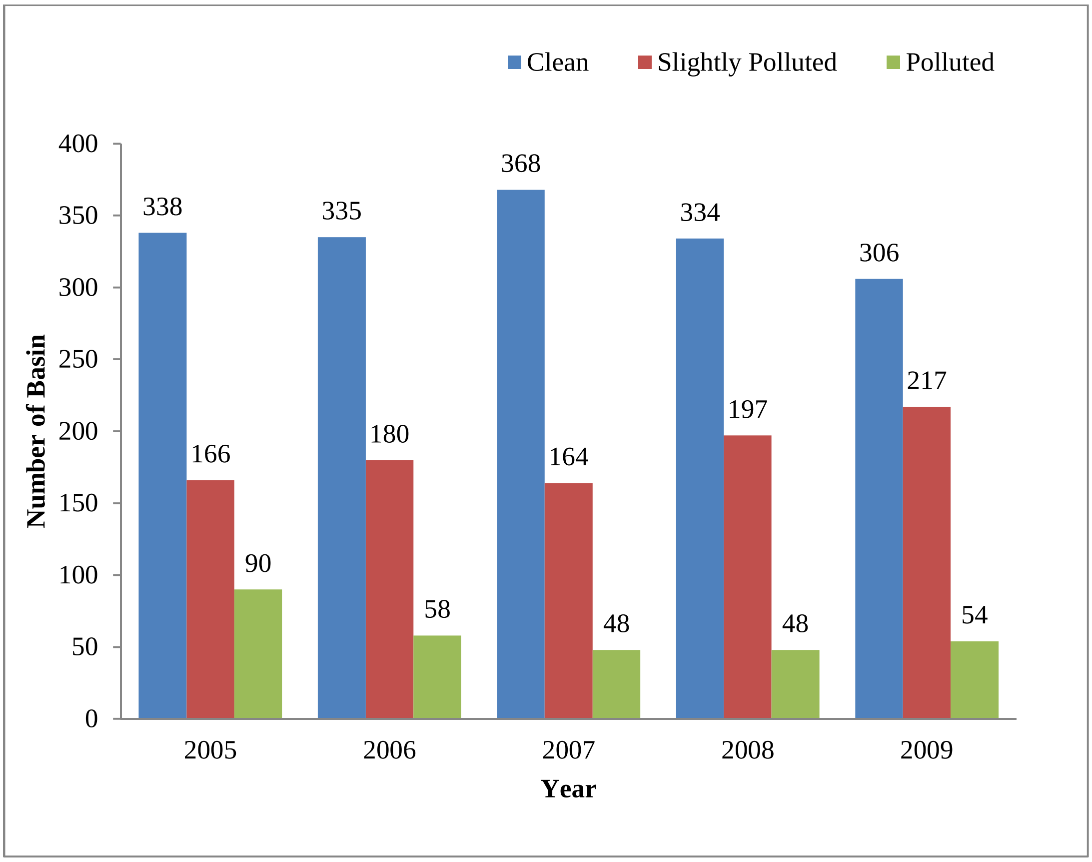

Figure 1.2 River water quality trend (2005-2009) (Source: DOE, 2009).

The deterioration of water resources is also faced by other countries. In Iran, an evaluation of water quality of the Beshar River has been carried out by Boustani et al.

(2011). The outcome of the study shows that the water quality of the river has declined while the pollution sources have increased. It is found that the Beshar River has been contaminated by various sources such as effluent of industrial factories, agricultural, urban surface runoff as well as effluent from wastewater treatment plants.

In another study conducted in China by Zhao et al. (2011) on the pollution source of surface water quality of Min River showed that surface water quality was worse in the middle reaches of the river than that in the lower reaches and its tributaries. Point sources from wastewater treatment plants and industrial effluents were identified as dominant inputs to the middle reaches of the Min River while diffuse sources from agricultural fertilizer and soil erosion were point out as the contributor to the lower reaches.

This is in agreement with the work done by Mvungi et al. (2003) in Zimbabwe, where the impact of runoffs from different land uses has reduced the water quality in a tributary of the Marimba River, in Harare. They found that the major water quality pollutants were phosphate, TKN, ammonia, feacal coliforms, iron and lead. These parameters have been associated with the high-density urban environment, contributing a substantial pollution load to the downstream tributaries and exceed the regulated values. Improper solid waste management practice, sewer overflows and polluted runoff have been identified as the sources of pollution in this area.

1.3 Sungai Pinang River Basin.

Sungai Pinang River Basin is embraced within the Districts of Timur Laut and part of Barat Daya of Penang (Figure 1.3). The major rivers in this basin are Sungai Pinang, Sungai Jelutong, Sungai Air Hitam, Sungai Dondang, Sungai Air Putih and Sungai Air Terjun. Sungai Pinang is one of the main rivers on Penang Island and together with its tributaries, the basin covers a catchment area of approximately 12 000 acres (GEC-DID, 1999).

The topography of the catchment can mainly be divided into two geomorphic units namely the lowland coastal plains and the interior hills. The hill terrains, which are mainly located in the central and northern part of the island, are generally rugged and steep with an average slope of more than 30%. In general, the elevation ranges from 300 to 800 m, while the highest peak is Bukit Western (830m) located at Penang Hill (DID, 2008).

The Sungai Pinang Basin runs through the highly developed and densely populated area of Georgetown, the capital city of Penang. However, the condition of the river has degraded over the years in terms of pollution, river environment and ecosystem. This situation has reduced the main river use for water supply and jeopardized the river potential for recreation, navigation and tourist attraction (DID, 2008).

Figure 1.3 Sungai Pinang River Basin.

1.4 Sources of River Pollution.

River pollution can be from development and activities in the river basin as well as from natural causes. The sources of river pollution can be categorized as point and non-point sources. Point sources pollution denoted the pollutants originated from the specific points of discharge. Contaminants enter into the water body from unclassified points such as surface runoffs can be classified as non-point sources (Huang and Xia, 2001). Therefore, Loague and Corwin (2005) had come up with the statutory point and nonpoint sources of pollution shown in Table 1.1.

Table 1.1 Statutory point and nonpoint sources of pollution (after Novotny and Olem, 1994), (Source: Loague and Corwin, 2005).

Statutory Point Sources
• Municipal and industrial wastewater effluents • Runoff and leachate from solid waste disposal sites • Runoff and infiltrated water from concentrated animal feeding operations • Runoff from industrial sites not connected to storm sewers • Storm sewer outfalls in urban centres with populations of more than 100 000 • Combined sewer overflows • Leachate from solid waste disposal sites • Runoff and drainage water from active mines, both surface and underground, and from oil fields • Other sources, such as discharges from vessels, damaged storage tanks, and storage piles of chemicals • Runoff from construction sites that are larger than 2 ha.

Statutory Nonpoint Sources

• Return flow from irrigated agriculture
• Other agricultural and silvicultural runoff and infiltration from sources other than confined concentrated animal operations
• Unconfined pastures of animals and runoff from range land
• Urban runoff from sewered communities with a population of less than 100 000 not causing a significant water quality problem
• Urban runoff from unsewered areas
• Runoff from small and/or scattered (less than 2 ha) construction sites Septic tank surfacing in areas of failing septic tank systems and leaching of septic tanks effluents
• Wet and dry atmospheric deposition over a water surface (including acid rainfall)
• Flow from abandoned mines (surface and underground), including inactive roads, tailing, and spoil piles
• Activities on land than generate wastes and contaminants, such as:
  ◦ Deforestation and logging
  ◦ Wetland drainage and conversion
  ◦ Channelling of streams, building of levees, dams causeways, and flow-diversion facilities on navigable waters
  ◦ Construction and development of land
  ◦ Inter-urban transportation
  ◦ Military training, manoeuvres, and exercises
• Mass outdoor recreation

Many studies had been done to identify the sources of river pollution. In Poland, Dojlido (1997) has stated that the water quality in Vistula River Basin had changed drastically since 1945 due to industrialization and urbanization. Both organic pollution and increasing saline concentrations in the water become problematic.

The classification to indicate the origin of the contaminants has been used by House (1997) to the Salmon's Brook, the Irwell catchment and the rivers in the Southwest National Rivers Authority Region. Point and non-point sources which were from the discharge of sewage effluent as well as intermittent highway runoff were identified to cause the deterioration of water quality in selected rivers studied.

Another similar study in China was done by Li et al. (2011) on the water quality of Hongze Lake and Gaoyou Lake along the Grand Canal pointed the dominant contribution of pollutants were from point sources which account for 85.6% of the total pollutant amount. It was identified that the pollutants had flowed into the lakes via three ways: firstly; wastewater from restaurants located in the surrounding study areas were released directly into the lakes. Secondly, both point and non-point pollutants from the urban area flowed into the lakes and thirdly; wastewater from neighbouring provinces entered the lake via other tributaries.

Marsden and Mackay's (2001) finding on the water quality of Scotland waters are congruent to that of Li et al. (2011) and House (1997) where the pollution were identified as a result of human activities. They concurred that the point and non- point sources were the causes affecting the water quality of the rivers in Scotland. These sources which have been ranked in order of scale of impact to the environment were sewage effluent, diffuse agricultural pollution, acidification, urban drainage, mining, agricultural point sources and industrial effluent.

Like in the countries mentioned above, the deterioration of rivers in Malaysia has pushed the DOE as well as the Department of Irrigation and Drainage (DID) to look into the origins of the pollutants. There were 20702 water pollution point sources identified in 2009. The results had shown that the water quality had been mostly affected by pollutants from manufacturing industries (9762: 47.15%), sewage treatment plants (9676: 46.74%), animal farms (769: 3.71%) and agro-based industries (495: 2.39%).

1.5 Water Quality Management System.

All over the world, overuse and misuse of land and water resources in river basins (both in advanced industrial countries and developing countries) is the main reason for the degradation of rivers, contributing to about millions of environmental refugees in 2001 (Chan, 2005).

Therefore, water quality management in river plays an important role in order to protect the quality of watersheds. The purpose of water quality management is to maintain and improve ambient water quality, which requires designation of water usage, establishment of criteria to protect designated uses, and development of water quality management plans accordingly (Wang, 2001). However, Huang and Xia (2001) has stated that the present situation of water quality management in the world is far from satisfactory due to the pressures of increasing population and developing economy all over the world.

According to Wang (2001), one of the causes of water quality problem derives from urban land use as a result of the increasing intensity of human activities. Thus, the hydrological relationship between water systems and the land requires coordination between the water management and land management fields. Once the relationship is identified, it leads to the need of protecting water quality through proper land use planning by identifying cost-effective pollution prevention and pollution correction approaches that can address all the sources of pollution in a comprehensive way.

Besides that, Thomas and Furuseth (1997) have stated that the management of point and non-point sources should be coordinated. Such effort involves all level of government, other agencies and stakeholders in a structured and focused process since a sustainable community is interconnected with surrounding communities and the sustainability of the larger region is supported by the collaboration of these communities.

Pollution prevention is an especially important strategy for controlling the pollutant in the water quality management (Ruslan, 1998). It is economically sustainable and to produce long-term benefits. Pollution prevention can be implemented if society reduces its consumption of resources and recycles these materials. Business activities which contribute pollutants to the river should work with those businesses to control the release of those pollutants.

Ruslan (1998) also stated that the success of protecting water resources can be achieved if the citizens adopt a higher sense of responsibility. Each member of the society should contribute to the cleanup costs and pollution prevention relative to their contribution to the pollution. Education, incentives and regulation will encourage responsible behaviour. Environmental education plays an important role in educating the public and industries. From the environmental education, population will learn to understand the concept of conservation and be able to apply simple conservation measures in their lives. It is from environmental education that helps build demand from the public on what industries they prefer. Thus, it will press on the industries to fulfill the demand.

1.6 Heavy Metals in River Water and Sediments.

Heavy metals are released to the rivers from numerous sources. Metals in rivers come from natural as well as artificial sources and can become a major issue on the water quality. Naturally introduced metals into the river are typically from such sources like weathering of the rocks, soil erosion, or the dissolution of water-soluble salts. These metals occur in nature, move through aquatic environments unconstrained by human activities, carrying little or no adverse effects. However, as the river catchment with its main river and tributaries undergo development and become industrialized, the metals stemming from human activities have affected the water quality of rivers and ultimately the receiving seas. Typical sources of metals from human activities are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural cultivation and fertilizers. Some of these metals are needed for proper metabolism in all living organisms yet toxic at high concentrations; other metals currently thought of as non-essential are toxic even at relatively low concentrations (Garbarino et al., 1995).

The heavy metals are those having densities five times greater than that of water, and the light metals, those having lower densities. Well-known heavy metallic elements are iron, lead, and copper. Six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg et al., 1979). These metals can become toxic or aesthetically undesirable when their concentrations are too high. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods, and are nonessential for human health. Heavy metals are transported as either dissolved species in water or as an integral part of suspended sediments. Heavy metals may be volatilized to the atmosphere or stored in riverbed sediments and when the metals dissolved in water, they have the greatest potential of causing the most deleterious effects (Garbarino et al., 1995).

No specific health guidelines for heavy metals associated with suspended or bed sediments have been established by the U.S. Environmental Protection Agency (USEPA). This lack of national guidelines based on concise scientific criteria causes difficulty when evaluating the environmental effects of heavy metals in sediments.

There have been numerous studies on the heavy-metal water quality of the Mississippi River that have been conducted in the early ‘70s and mid ‘80s that stressed mostly on the water quality in specific regions of either the lower reaches of the river (Everett 1971; Hartung, 1974; Presley and Trefry, 1980; Shiller and Boyle, 1983; Newchurch and Kahwa, 1984; Trefry et al., 1986).

Domestic and industrial wastewaters and their associated solid wastes are the major sources of toxic metals as mentioned above. USEPA estimated that circa 81 percent of the metals going into the sewage treatment systems come from industries that dispose of their wastes into municipal sewer systems and that about 19 percent come from households in the form of common cleaning products used at home (USEPA, 1986). The two main by-products of sewage treatment systems are solid wastes and treated wastewater. In the most common form of treatment, 70 to 90 percent of cadmium, chromium, copper, lead, and zinc are removed as solid wastes (Lester, 1983). The other 10 to 30 percent of these heavy metals remain dissolved in the water that is released back into the river. The solid waste or sewage sludge is commonly disposed in landfills or sold as fertilizer where these heavy metals are released through leaching in landfills. Sewage sludge also contains plant nutrients and in the United States have been used to replace other fertilizers in crop production. However, it also contains some toxic heavy metals, such as cadmium, which have been found at quite high concentrations in corn kernels harvested from soils fertilized with sewage sludge (Kiemnec et al., 1990).

1.7 Bioremediation study

With the prevalence of water pollution throughout the world in general and Malaysia, specifically, prevention or treatment is part of the many solutions available. In opting for treatment, there is also a multitude of methods being tested and proven to perform to a certain level of satisfaction. One of these is bioremediation or biological treatment.

Biological treatment has rapidly become the technology of choice for remediation of contaminated water and soil. Bioremediation may be defined as the use of living organisms to remove environmental pollutants from soil, water and gases. Organic compounds are metabolized under aerobic or anaerobic conditions by the biochemical processes of microorganisms (Collin, 2001).

Bioremediation of contaminants can occur by natural attenuation; or treated by either bioaugmentation or biostimulation with microbes. Sanchez et al. (2000) described natural attenuation as a collection of biological, chemical and physical processes that occur naturally resulting in the containment, transformation, or destruction of undesirable chemicals in the environment. Processes include some combination of sorption, volatilization, dilution and dispersion coupled with biodegradation.

Nevertheless, biostimulation is the process by which a stimulus to the microorganisms that already exist in the contaminated system by adding nutrients and other growth substrates, together with electron donors and acceptors, while bioaugmentation is a process of introducing exogenous microorganisms into the site (Wang and Mulligan, 2006).

According Sarkar et al. (2005), bioremediation has several benefits over landfill disposal and incineration, such as the conversion of toxic wastes to non-toxic end products, a lower cost of disposal, reduced health and ecological effects and long-term liabilities associated with non-destructive treatment methods, and liability to perform the treatment in situ without unduly disturbing native ecosystems. Frankenberger Jr. (1992) agreed that bioremediation is an attractive approach because it is simple to maintain, applicable over large areas, cost-effective and leads to the complete destruction of the contaminant.

Numerous studies have been reported in relation to bioremediation processes on heavy metal contaminants in the environment. For instance, Wang and Mulligan (2006) have verified that the natural attenuation practices can remediate the arsenic-contaminated soil and groundwater. Likewise, Jézéquel et al. (2005) also explained the potential of soil augmentation by using *Bacillus* sp. in reducing the phytoavailable Cd of an agricultural soil. Similar to authors mention above, Lovley and Coates (1997) also gave a good review on the use of microorganisms for the remediation of metal-contaminated environment.

1.8 Problem statement.

Many studies have been carried out relevant to the water quality of Sungai Pinang and its tributaries. This is due to the fact that Sungai Pinang River Basin is one of the polluted rivers in Malaysia (DID, 1999). Most of the river water quality studies are mainly based on the water quality parameters while the sediment quality of the river is lacking in information. It is known that sediment phase of the river plays a role in determining the status of the waterway since it is a natural sink for pollutants. Therefore, this study is conducted in order to evaluate the status of the rivers according to water and sediment parameters tested. Besides that, this study also gives information on heavy metals in water and sediment phase of the river. Information on common values of heavy metals in river sediment is also limited.

An immediate action should be taken in order to improve the water quality status of the catchment. This is because, Sungai Pinang acts as recipient of domestic discharges, industrial effluent and other pollutants, and has been classified as a very polluted river in Malaysia. Therefore, the severe pollution has destroyed the natural eco-system of the rivers. Hence, the Water Quality Management Plan has been trusted to improve the water quality status of the catchment.

The industrial effluents either produced by legitimate and illegal industries discharged into the rivers can be reduced if close cooperation and coordination with the industries and local authorities is implemented. Similarly, the water quality of the rivers can be improved if the domestic discharges coming from residential, commercial, industrial as well as from squatters colony are directly channeled to centralized system of the wastewater so that the contaminants are treated before being released into the water bodies. Likewise, the application of equipment such as aerators, oil-water separator and nutrient traps at selected premises may catch pollutants originated from sullage waters and industries from entering the rivers thus reducing the contaminants in the catchment.

1.9 Objectives of study.

The objectives of this study are as follows:

(i) To determine the status of water quality of Sungai Pinang through water quality characteristics, effect of seasons and land use.

(ii) To identify pollution sources that influence Sungai Pinang water quality.

(iii) To assess the characteristics of sediment phase and the sediment quality of Sungai Pinang

(iv) To determine the effect of exogenous microorganism on the bioremediation of contaminated sediment.

(v) To perform a comparative evaluation of natural attenuation and bioaugmentation for bioremediation of sample.

1.10 Outline of Thesis Structure.

Chapter 1 gives a brief information on the river water quality and source of river pollution, the heavy metals and bioremediation study. The problem statement is presented and the objectives of the study are outlined.

Chapter 2 covers literature survey on water quality and environmental management and the detailed sources of pollution. Review on the heavy metal in the environment as well as bioremediation studies are also reported in this chapter.

Chapter 3 explains the detailed description of experimental procedure used in the research study.

Chapter 4 shows the results and discussion. The characteristics and quality of water and sediment phases of rivers within Sungai Pinang are reported. Besides that, the sources of pollutions in the study area are also determined. The level of heavy metal in water and sediment of the rivers within Sungai Pinang are also being assessed and compared with selected quality guidelines. Further evaluations on heavy metals in the sediment are carried out by using multiple indices. The bioremediation study on reducing heavy metal in sediment was examined according to natural attenuation and bioaugmentation techniques. The studies compared the treatment capabilities and the percentages of reduction of selected heavy metals in the sediment are determined.

Chapter 5 reports the conclusion on the research works and recommendation for further study.

CHAPTER 2

LITERATURE REVIEW

2.1 River Water Quality and Catchment Management

Water is an essential element for life. Fresh water comprises 3% of the total water on earth. Only a small percentage (0.01%) of this fresh water is available for human use (Hinrichsen and Tacio, 2002). Unfortunately, even this small proportion of fresh water is under immersing stress due to rapid population growth, urbanization and unsustainable consumption of water in industry and agriculture (Azizullah et al., 2011).

According to Kimura et al. (2011), water is considered polluted when it contains anthropogenic contaminants, comprising their use for the purpose it is intended. The main ways of contamination of a watercourse are chemical, physical and biological. The chemical changes the composition of the water by reacting with the environment while the physical adjustment may adversely affect the life of the ecosystem. On the other hand, the biological form is the introduction of foreign microorganisms or organisms to that ecosystem, or the increase of certain harmful organism or an existing microorganism.

Historically, the rivers provided water supplies for the population and industry, a means of waste disposal and, in some cases, a transport route for materials and commerce. Many of the urban and industrial rivers declined in water quality due to these activities (Neal et al., 2006). Same agreement also stated by Ward and Elliot (1995) who said that rivers play a major role in assimilating or carrying industrial and municipal wastewater and manure discharges and runoff from agricultural fields, roadways, and street, i.e., major sources of river pollution.

As said by Ngoye and Machiwa (2004), the water quality in rivers is generally linked with land-use in the catchment that can affect the amount and quality of runoff during the following rainfall. Similar concurrence also affirmed by Lee and Bastemeijer (1991), who declared that many problems of water pollution are caused by changes in land-use patterns on catchment areas due to population pressure and increasing economic activity. This is because, lots of anthropogenic influences are part of the larger process of catchment land use or land cover change that can affect water quality in rivers and lakes, as well as downstream estuarine and coastal waters (Mouri et al., 2011).

Similarly, Madsen et al., (2003) also stated that there is a connection between land use and water quality. This is because; steady development has transformed farms, wetlands, and forests into residential and commercial areas. New development brings increasing water use, growing discharge from sewage treatment plants, and higher level of runoff from roads, rooftops, and other man-made surfaces. These changes deliver more sediment, organic nutrients, pesticides, and other chemicals to rivers and lake, which cause water pollution to the water bodies.

Hence, the concern over the future of water resources has increasingly engaged governments, non-governmental organizations (NGOs), and communities throughout the world. More and more countries seek to implement water management policies that at the same time address economic development and environmental sustainability (Lemos and Oliveira, 2004).

According to Ramadasan et al. (2000), indiscriminate development and environmental mismanagement through various human activities have resulted in disruption of water resources as well as ecological processes. Therefore, Integrated River Basin Management (IRBM), which is an integrated and holistic system, must be applied. This is because; IRBM can coordinate the use and management of land, water and other natural resources and activities within a catchment as well as to optimize the use of resources and ensure its stability and productivity. Similar notion was also proposed by DID (2008) which stated that this ideal concept can be achieved with the involvement of community, cooperation between agencies, commitment from political leadership and the use of appropriate technology (Figure 2.1).

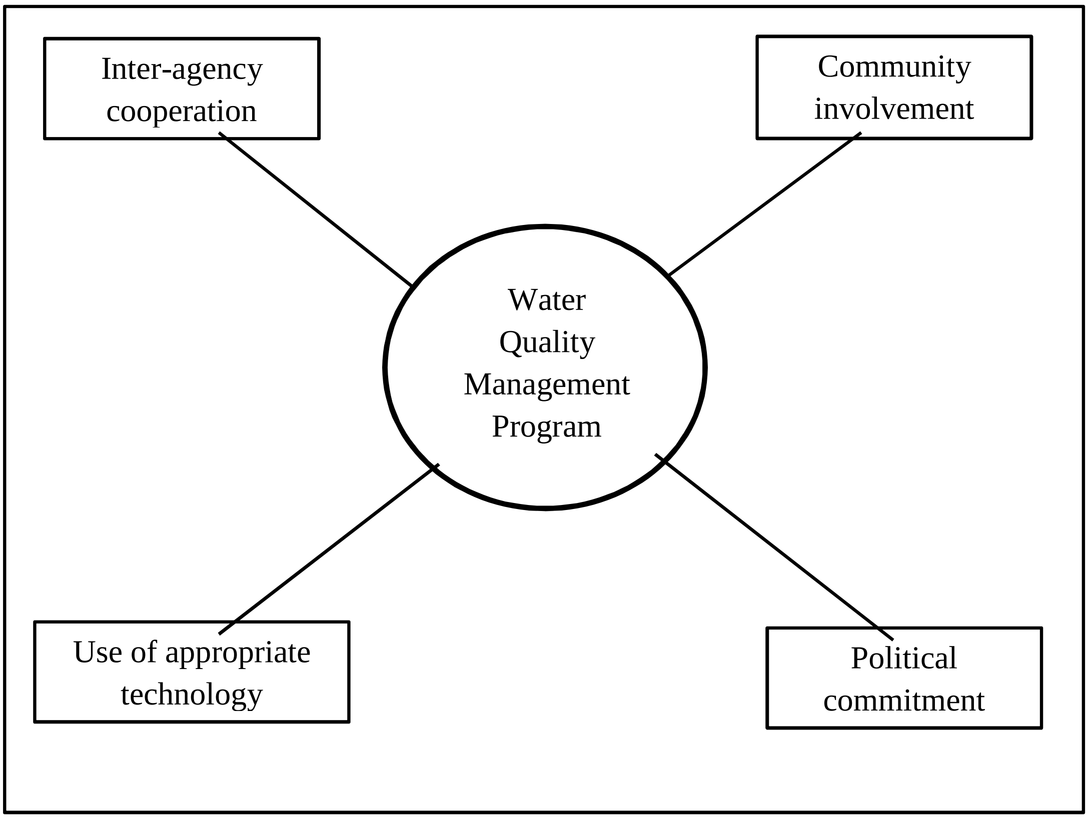

Figure 2.1 Components of IRBM (Source: DID, 2008).

The responsibility for water resource administration is fragmented and is shared among a number of federal and state agencies each of them have their own specific involvement in water related issues (Welch and Keat, 1987). Therefore, the cooperation of inter-agency by exchanging information between the agencies in their respective interests may help in improving the river water quality. For example, where new land-use developments are involved, the Municipal Council (MC) may seek an advice from the DOE and DID, since the potential pollution loads from a proposed development are clearly a relevant issue for planning authorities. Hence, the MC does not have to put so much effort on the enforcement of detailed operational controls but in ensuring that poor location choices are not made which would otherwise exacerbate subsequent pollution problems. Similar opinion is also shared with Macrory (2001) who said that an effective action aims to prevent problems occurring before they cause significant harm or damage must be implemented.

The use of appropriate equipment and technology can also help in the conserving and improving of water quality. The application of technology or tool especially on polluted rivers may help in reducing contaminants from being discharged into the receiving water bodies thus improving the water quality in a long term. Similar agreement is also shared with Malakahmad et al. (2009) who explained that the equipment, which is designed, constructed and maintained plays a critical role in protecting water quality in the receiving streams and lakes by removing or filtering out pollutants in runoff.

Moreover, a successful water quality improvement can be achieved if the political leadership gives full commitment in protecting the environment. The implementation of policy and strategy to conserve as well as to achieve the target in water quality improvement should been carried out. For instance, a policy introduced by the USEPA (2003) on Water Quality Trading that uses the market-based approaches in order to provide greater flexibility and potential to achieve water quality and environmental benefits. These market-based programs can achieve water quality goals at a substantial economic savings as well as can create economic incentives for innovation, emerging technology, voluntary pollution reductions and greater efficiency in improving the quality of the waters. Likewise, Fohrer (2003) also reported that the implementation of long-term monitoring programs covering catchments all over Europe have provided valuable data to assist the decision-makers evaluate the impact of management alternatives on water balance and water quality.

Participation and involvement of community either individuals or groups is also a component that should be considered in order to restore and improve the water resources. As said by Mokhtar and Tan (2011), the participation of local populations in the design, planning implementation and evaluation of water related projects is encouraged although the implementation of development plans and projects are still handled by the related ministries and agencies. Thus, strong and smart partnerships are essential to create win-win solutions, with the community and other stakeholders accepting their share of responsibility to ensure success and sustainability in the long term. (Keizrul, 2011). Similar opinions were also shared among many scholars and practitioners who believed that an ideal management system must involve meaningful public participation throughout the process of policymaking and implementation (Li et al., 2011; Maaren and Dent, 1995; Tang et al., 2005; Abdulbaqi et al., 2007).

2.2 Water Quality and Pollution of Rivers in Malaysia.

Like other places in the world, Malaysia also faced an environmental problem especially in the quality of her watercourse. Many of her rivers are in bad condition, which is of high concern regarding their status. Therefore, the Department of Environment (DOE) Malaysia has come out with an initiative to monitor the quality of the river water through her river water-monitoring program to detect the changes in the water quality as well as to determine the sources of pollution.

According to DOE (2009), a total of 577 rivers consisting of 1063 water quality monitoring stations are monitored with 10% out of the rivers found to be polluted. Moreover, the causes of water deterioration are also identified with the source of the water pollution originating from point and non-point sources. The point sources include sewage treatment plants, manufacturing and agro-based industries, as well as animal farms. On the other hand, non-point sources are mostly from agricultural activities and surface runoffs. However, in Malaysia, the DOE has mainly maintained records of point sources with 20702 water pollution point sources documented in 2009 comprising of manufacturing industries (9762), sewage treatment plant (676 inclusive of 736 Network Pump Stations), animal farms (769) and agro-based industries (495). The distribution of the point source of water pollution is illustrated in Figure 2.2.

BOD, NH_3-N and SS have been detected as the major pollutants in water quality of Malaysia. The largest contributor of BOD is attributed by treated domestic and partially treated sewage, followed by pig farming and agro-based manufacturing industries. The main sources of NH_3-N were livestock farming and domestic sewage whilst the sources for SS were earthworks and land clearing activities.

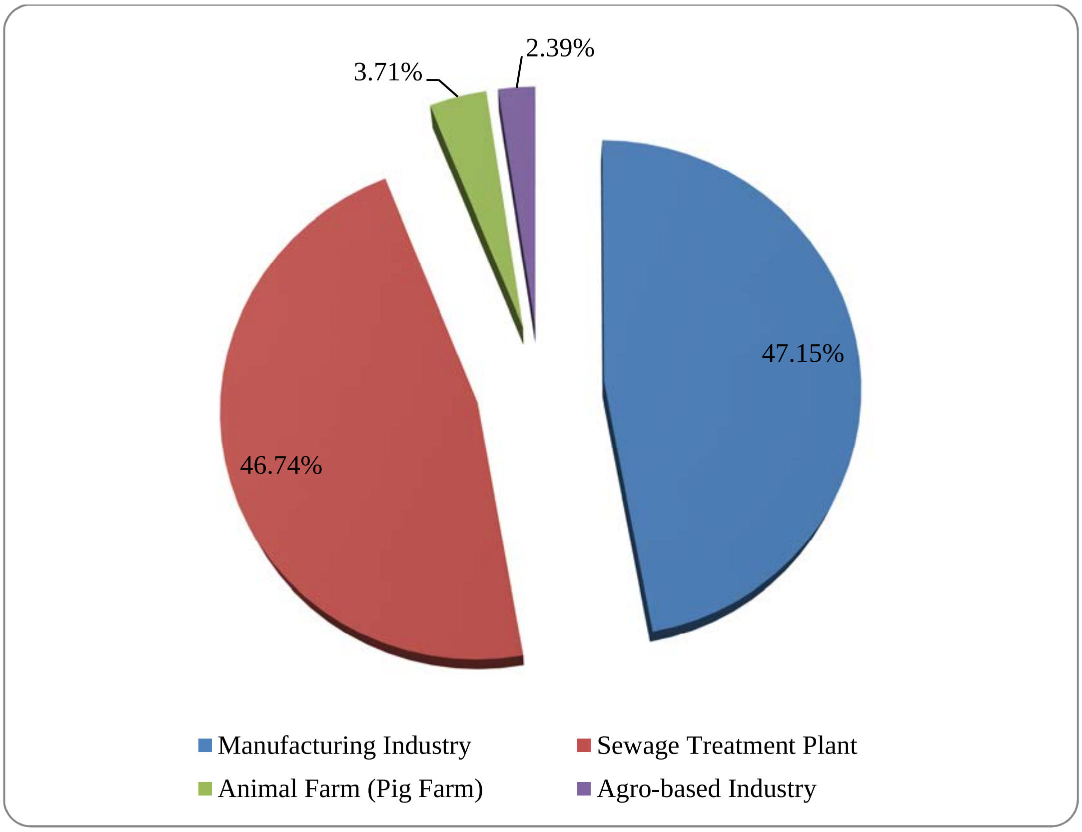

Figure 2.2 The distribution of the point source of water pollution recorded by DOE in 2009.

In Malaysia, Sungai Juru, Sungai Kinta and Sungai Langat are among the polluted river in the country. The main sources of pollution of these rivers are from anthropogenic activities. For example, the anthropogenic activities such as industrial, agricultural and unplanned settlements surrounding Sungai Juru have deteriorated the river with their wastewater discharges (Alkarkhi et al., 2008). Similarly, Nayan et al. (2009) revealed that Sungai Kinta is influenced by the changes of the land use due to urbanization, agricultural, industrial and human settlement which cause an extreme density of BOD, COD, SS and AN, thus affecting the population's water supply. Likewise, Lee et al. (2006) as well as Suki et al.

(1988) also proved that the anthropogenic activities affected the water quality of Sungai Langat. Industrial discharge, domestic sewage from treatments, construction projects and pig farming are the main sources of the pollution of the river.

2.2.1 Major Water Pollution of Rivers.

As exposed by other researches, the deterioration of water quality is becoming an issue throughout the world. Many studies have been done to identify the sources of water pollution, thus indicating that anthropogenic activities as the major source of pollution. For example, a study has been done by Ntengwe (2006) who investigated the quality of Kitwe Stream's water located in the city of Kitwe, Zambia that runs through industrialized towns, which are heavily populated. They discovered that the deterioration of the stream is from point and non-point sources. Sewage plant and domestic wastewaters particularly those with detergents from car washing activities; industrial effluents as well as urban and fertilizer run-offs have contributed to the elevated pollutant levels in the water bodies of Kitwe Stream.

According to Ma et al. (2009), industrial and domestic effluent as well as from agricultural activities are the major sources that affect the quality of water in the Wuwei Basin of Shiyang River, China. The main sources of industrial pollution in Wuwei city are wastewater from the paper mills, the Gansu RH Co., the sugar refinery, the distillery, the brewery and the railway station which discharged their effluent into the middle and upper reaches of Shiyang River. Besides that, the water resources in urban areas are also threaten by the lack of proper sewage discharge as well as by of solid waste disposal systems. Furthermore, the use of fertilizers and pesticides also revealed an adverse contribution to water quality as these chemicals can be transported into water bodies through rainwater or irrigation.

In Pakistan, research done by Ullah et al. (2009) revealed that the industrial pollution has become the major source of water quality degradation where their effluents are released directly into the nearby drains, rivers, streams, ponds, ditches and open or agricultural land. The major industries contributing to water pollution are textile, pharmaceuticals, ceramics, petrochemicals, food industries, steel, oil mills, sugar industries, fertilizer factories, and leather tanning have been determined by Sial et al. (1996) and reported likewise by WWF (2007). Their findings concur with those found by Azizullah et al. (2011), who identified domestic and municipal wastes as a serious threat to Pakistan's water.

Ngoye and Machiwa (2004) also carried out research on similar issues when they assessed the impacts of land-use patterns in the Ruvu River Basin, Tanzania on the water quality in the river system. Their study on the the Ruvu River Basin is crucial because the basin is shared by two regions, Morogoro and Coast; and passes through areas of different land-uses including forests, cultivated areas and urban areas. They showed that impairment of the water quality of the river was caused by anthropogenic activities in the catchment, which agreed with the findings of many research done in other countries as mentioned above. They verified the cause from anthropogenic activities when samples from stations within forested catchments had high levels of DO and low level of NH_4-N and NO_3-N compared to those from farmland, industrial, residential and market places.

Another research confirms the role played by anthropogenic activities on water quality by Milovanovic (2007) who conducted an assessment of the water quality as well as determination of pollution sources along the Axios/ Vardar River, Southeastern Europe. Release of heavy metal pollution from industrial activities within the area is the major cause of water pollution in the basin. The research also reveals that the area also succumbs to the untreated domestic wastewater from municipalities that pollute the surface water with nutrients and heavy metals. The disposed solid waste in the illegal dumping site located in the protected area of the Axios River delta also contributes to the river water pollution. Agricultural runoff is another source that contaminates the river, which agricultural activities, the use of fertilizers and pesticides, in the cultivated land fields have increased nutrient concentrations in the river water.