

POLLUTION STATUS OF THE SUNGAI SKUDAI RIVER SYSTEM
THROUGH HEAVY METALS

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ABSTRACT

This study was conducted to assess the extent of heavy metal pollution in the Sg. Skudai river system. A total of 16 monitoring stations were established along the Sg. Skudai river system. Water, plants (*Phragmites karka*) and sediment samples were collected from the sampling points along the downstream route of the river near the industrial zones. Samplings were conducted six times over a period of 9 months from November 2000 to July 2001. Water quality parameters such as temperature, pH, DO, BOD and COD were monitored to determine their status in relation to the health of the river ecosystem. The results were then compared where possible to the recommended present Interim National Water Quality Standards for Malaysia (INWQS) and DOE Water Quality Criteria for Malaysia with respect to support aquatic life, potable water supply and irrigation. The Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) techniques were employed for the determination of heavy metals in the samples. The method was also controlled by analyzing the reference material for National Institute of Standards and Technology (NIST)-SRM 1572 Citrus Leaves and NIST-SRM 1646 Estuarine Sediment. Data showed a good agreement with the certified values for the elements with more than 83 % recovery. Elemental concentrations of As, Pb, Hg, Cr, Cu, Cd, Ni and Zn were measured. The trend of several pollutants in the river and the statistical analysis of the results were obtained. Then trend of heavy metals in water of the Skudai River system is Zn>Cu>Ni>Cr>As>Pb>Hg>Cd, in plants is Zn>Cr>Cu>Pb>Ni>As>Hg>Cd and in sediments is Zn>Cr>Cu>Pb>Ni>As>Hg. All results were reported between 15-20 % of the standard deviation. Correlations exist for chromium and copper from the correlation analysis between plant and water and plant and sediment. Meanwhile, arsenic and zinc showed that these metals correlate in water and sediment.

ABSTRAK

Kajian ini telah dilakukan untuk menilai takat pencemaran logam berat di Sg. Skudai. Sebanyak 16 stesen pemantauan telah dipilih dan persampelan air, tumbuhan (*Phragmites karka*) dan sedimen telah dilakukan berdekatan kawasan perindustrian, mengikut arah pengaliran sungai ke laut. Pensampelan telah dilakukan sebanyak enam kali dalam tempoh sembilan bulan iaitu dari bulan November 2000 ke bulan Julai 2001. Parameter kualiti air seperti suhu, pH, DO, BOD dan COD telah diukur dan hubungkait statusnya kepada keadaan ekosistem sungai telah ditentukan. Keputusan yang diperolehi telah dibandingkan dengan nilai piawai Interim National Water Quality Standards for Malaysia (INWQS) dengan mengambil kira hidupan akuatik, sumber air minuman dan pengairan. Teknik Analisis Pengaktifan Neutron (APN) dan Spektrometer Jisim - Plasma Gandingan Aruhan (ICP-MS) telah digunakan untuk penentuan kepekatan logam berat daripada sistem Sg. Skudai. Kaedah ini juga telah dikawal dengan menganalisis bahan rujukan piawai Citrus Leaves dan Estuarine Sediment. Peratus perolehan bagi data adalah lebih daripada 83 %. Kepekatan unsur As, Pb, Hg, Cr, Cu, Cd, Ni dan Zn telah ditentukan. Tren bahan pencemar dan keputusan analisis statistik telah diperolehi daripada keputusan analisis logam berat. Penumpukan unsur-unsur lain dalam sampel juga adalah signifikan kerana wujudnya kawasan perindustrian yang banyak. Tren logam berat dalam sampel air adalah $Zn > Cu > Ni > Cr > As > Pb > Hg > Cd$, di dalam sampel tumbuhan ialah $Zn > Cr > Cu > Pb > Ni > As > Hg > Cd$ dan di dalam sampel sedimen ialah $Zn > Cr > Cu > Pb > Ni > As > Hg$. Keputusan yang diperolehi tidak melebihi 15-20 % ralat. Korelasi wujud bagi unsur kromium dan unsur kuprum di dalam hubungan antara tumbuhan dengan air dan tumbuhan dengan sedimen. Ini menunjukkan bahawa tumbuhan ini sesuai dan mempunyai potensi sebagai penunjuk bio bagi kedua-dua unsur ini. Manakala, unsur arsenik dan zink menunjukkan wujudnya korelasi dalam hubungan antara air dan sedimen.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	-	Percent
$^{\circ}\text{C}$	-	degree Celcius
$^{\circ}\text{K}$	-	degree Kelvin
mg	-	milligram
μg	-	microgram
mgL^{-1}	-	miligram per liter
ppt	-	parts per trillion
ppb	-	parts per billion
Conc.	-	concentration
FI-MS	-	flow injection mercury system
HNO_3	-	nitric acid
H_2O_2	-	hydrogen peroxide
ICP-AES	-	inductively coupled plasma atomic emission spectrometry
ICP-MS	-	inductively coupled plasma mass spectrometer
IDL	-	instrument detection limit
INWQS	-	Interim National Water Quality Standards
MDL	-	methods detection limit
NAA	-	neutron activation analysis

QC	-	quality control
QCSS	-	quality control standard sample
RPM	-	round per minute
RSD	-	relative standard deviation

CHAPTER 1

INTRODUCTION

1.0 Background

The beginning of the new millennium seems to be characterized by a steadily increasing attention being paid to the environment. The dramatic increase in public awareness and concern about the state of the global and local environments has been accompanied and partly prompted by an ever-growing body of evidence on the extent to which pollution has caused severe environmental degradation. In addition, the costs of these effects in the depreciation of resources, lost productivity and in cleaning up or improving polluted environments are high and are increasingly occupying the attention of governments and politicians around the world. The first worldwide meeting of heads of state directed to concern for the environment took place at the Earth Summit, formally known as the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro in 1992.

A widely used definition of pollution is the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment (Alloway and Ayres, 1993). Recently, adverse environmental effects like species extinction, loss of forest systems, acid rains, global warming, ozone depletion, hazardous waste disposal problems, frequent and intense eco-accidents are also on the rise. Although these problems are very important for the future of mankind, it is pollution, which arouses the most interest. This is because people realize that pollution impacts on them directly through effects on their health, their food supply, the degradation of buildings, and other items of cultural heritage, as well as overt effects on forests, rivers, coastlines and ecosystems that they are familiar with. A major concern about these pollutants is that they bio-accumulate in the food chain. One of the horrifying

tragedies that brought the world's attention was the outbreak of the *itai-itai* disease that resulted from cadmium ingestion experienced by Japan in the late 1960s (Sax, 1974).

Man and his environment are related to each other and man needs everything from his environment, involving air, water, food, fuel and material resources. On the contrary, environmental pollution is an unfavourable alteration of our surroundings, which may result in loss of recreational facilities, loss of agricultural products, contamination of the air, contaminated drinking water or loss of fresh water fish as a source of food. It comes about as a by-product of man's actions in which he directly changes energy patterns, radiation levels, chemical and physical constituents of our air and water (Hall and Morrison, 1978). Furthermore, studies showed that the endurance of ecosystems to bear stresses put upon them by human activities has exceeded beyond limits, which has imbalanced the environmental equilibrium. Mercury vapours in pesticides caused injuries to vegetation and damage to crops in Los Angeles and the loss have been estimated at \$ 500 000 yearly (Iqbal and Qadir, 1989). In Malaysia, Yusof *et al.* (1995), pointed out that the bay areas of the south of Johore can be categorized as the most polluted with heavy metals and localized species are at risk of taking in these elements, leading to a lethal dose.

Apart from that, most environmental pollution is insidious and its harmful effects only become apparent after long periods of exposure. Many people are exposed to pollutants, which may cause cancer ten or twenty years later, without realizing it. Hamilton and Wetterhahn (1988) reported that humans exposed to chromium compounds are prone to diseases like asthma, lung and nose cancer and also skin allergy. Likewise, rivers can become increasingly polluted and species die out without many obvious signs, at least in the early stages.

During the Industrial Revolution in the 19th century, the River Irwell has been considered one of the most polluted rivers in Europe, suffering from organic and inorganic pollution unable to sustain life (Dixit and Witcomb, 1983). For this reasons, environmental monitoring has become recognized as being vitally important in detecting where insidious pollution is occurring, the pollutants involved and the sources from which they came.

1.1 Water Pollution

Water is an extraordinary chemical compound of absolutely fundamental environmental importance. It is often being described as ‘the universal solvent’ or ‘the liquid of life’. The earth’s water resources, ‘the hydrosphere’, consists of the oceans and seas, the ice and snow of the polar regions and mountain glaciers, the water contained in surface soils and underground strata, lakes, rivers, and streams. It can be said that the waters of the hydrosphere were of natural quality until the Industrial Revolution in Europe and North America initiated the development of technology driven by the energy of the fossil fuels, coal and oil. Now the entire hydrosphere is contaminated by the polluting activities of man (Harrison, 1992).

Water covers some 71% of the earth’s surface and is itself the medium for several different ecosystems. All natural elements are soluble, at least in trace amounts, and all are found in natural water at some place on the earth’s surface. Water is a major reservoir for storing nutrients and other biologically important materials, and it is the main medium in which these materials move from the abiotic to the biotic part of the ecosystem (Clapham, 1983). Philips, (1989) reported that inorganic arsenic is taken up rapidly by phytoplankton and this represents an important route for the introduction of the element into aquatic food web. In addition to that, water plays another, more material role for man. It carries away his wastes. Natural water can purify some of these wastes; it can dilute others until they are harmless; and it can carry the rest out of sight. But with the incessant growth in the world population and industry, one city’s wastes become the next city’s drinking water. Apparently, natural purification breaks down, fish die, odours form, diseases are transmitted, and the central medium of all life becomes a garbage-filled carrier of stinking death (Giddings, 1973).

Over the past decades, the natural quality of watercourses has been altered by the impact of various human activities and water uses. Most pollution situations have evolved gradually over time until they have become apparent and measurable. Recognition of a pollution problem, usually took considerable time, and application of the necessary control measures took even longer time. However, medieval reports and complaints about inadequate excreta disposal, foul and stinking watercourses within overcrowded cities, and other similar problems were an early manifestation of water pollution (Meybeck *et al.*, 1989). Several studies on the impacts of such activities on water quality in Malaysia have

been reported. Law (1980) has studied the effect of sewage by domestic discharge in the Sg. Kelang where high levels of faecal coliform counts have been recorded. Meanwhile, the Ministry of Environment had reported in November 1995, that two out of three rivers in the country are polluted. Only 28 % of rivers are classified as clean. River water quality in the country had deteriorated by 1.2 % per year in the last decade. Industrial wastes were the major source of pollution (Consumers Association of Penang - Sahabat Alam Malaysia, 1996). As for heavy metal pollution, in the year 1996, 53 rivers were polluted with cadmium, 44 rivers with ferum, 36 rivers with lead, 24 rivers with mercury and copper and 4 rivers polluted with chromium and zinc, according to Kadaruddin (2000).

The chemical and physical forms of water pollutants are even more varied than are pollution sources. One sewer outfall can put thousands of chemical compounds into the water. The array of specific water pollutants is so wide that to study them rationally we must classify them into groups. There are two broad types of water pollution. In one, man simply adds something to the water that was already there in moderate amounts, such as, microorganisms, organic wastes, plant nutrients, sediments or silts, inorganic minerals, acids and bases, heat, radioactivity and heavy metals. In another, man adds chemicals and materials strictly of his own invention that are new entrants into the environment, such as pesticides and industrial chemicals (Giddings, 1973). Pesticides and herbicides industries are two industries that often discharge arsenic in its production wastes (Burrell, 1974).

A few water bodies were polluted rather seriously. Some surface waters, ground waters, and soils in urban areas were polluted by industrial wastewater or inappropriate irrigation with wastewater. Pollution is a killer of plants, animals and human life. Its effects have been witnessed as toxic substances in the water killing plants and animals in our fresh waters. The result is an unpleasant environment for man to live in and since these waters are in some instances the supply of drinking water, the pollution could ultimately be dangerous to human life (Hall and Morison, 1978). The threat to human health and welfare posed by surface water pollution has two principle facets: (1) direct effects, which may result from the consumption of contaminated water supplies and food, and (2) indirect effects, which may result from the impact of pollutants on the quantity and quality of aquatic organisms used for human food, the recreational use of water, the aesthetic quality of the aquatic environment, and the integrity of the biosphere (Weber, 1981).

In early days of national development when resources seemed vast and unlimited, deliberation on the choices of development alternatives did not seem necessary. Today it has become clear that we all live in one biosphere within which space and resources are limited and choices based on sound environmental principles must be made at every turn. Failure to include environmental considerations in resource utilization will inadvertently result in adverse environmental consequences.

One such resource that needs protection and conservation is water, which is very important for development. Its quality has to be maintained for the various uses it is put to. Of all natural environmental resources, water is the most severely threatened by pollution. At the same time it is one of the greatest needs of society, as, life ends wherever there is insufficient clean fresh water. Malaysia has assessed this position with foresight and taken early steps to protect its aquatic environment. This is evidenced by the adoption of the Environmental Quality Act 1974, and also the creation of the Division of Environment to administer the Act (Department of Environment, 1985).

1.2 River Pollution

Rivers in Malaysia have made immense contributions to the overall development of this country. They have provided power generation, water for domestic, agricultural and industrial consumption and have served as means of transportation and communication for the people. The towns and cities of Malaysia began as settlements along rivers while river mouths provided refuge and became homes to fisherman who braved the open seas to seek their living (Department of Irrigation and Drainage, 1992).

Therefore, rivers are an invaluable natural resource, which contribute to the survival of mankind and development of nations. Rivers, as the arteries of natural water resource, supply water for domestic and industrial usage and irrigation. In Malaysia, water is needed for drinking water supply, sanitation, agriculture, industrialization, urbanisation, fisheries, transportation, recreation and to produce hydroelectric power. The demand for water increases about 4% yearly and it is estimated that about 20 billion per meter square (b/m^3) of water is needed by the year 2020. The demand for domestic and industrial use is approximately 0.8 b/m^3 annually during 1980s and this figure is expected to rise up to 4.9

b/m³ annually from year 2000 onwards. Annual demand for industrial and domestic use will increase up to 5.8 b/m³ and the water demand for agricultural purpose will be about 13.2 b/m³ by the year 2020 (Consumers Association of Penang - Sahabat Alam Malaysia, 1996).

Apart from the traditional role of drainage, river transportation and food resource, rivers also have great potential for recreations and tourism. In order to serve the above-mentioned roles and functions, rivers need to be conserved and should remain clean and unpolluted. For example, the Sg. Langat in Selangor plays a significant role in ecology, provide potable water to residents, supply industries and agricultural areas with water for manufacturing and agricultural production, provide other services such as recreational sites and habitats for fish and other aquatic wildlife (M. Nordin and L. A. Azrina, 1998). In India, the Ganga River has many beneficial uses such as bathing, swimming, public water supply, agriculture, industry, fish culture, wildlife boating and non-contact recreation (Devendra Swaroop Bhargava, 1983).

During recent years serious concern has been voiced about the rapidly deteriorating state of freshwater bodies with respect to trace metal pollution. It is also reported that serious metal pollution could result from the discharge of unregulated effluents into the natural freshwater bodies. In Brazil, Veado (1997) pointed out that wastewaters from about 24 legal and several clandestine industries are discharged into the Das Velhas River. In spite of environmental controls carried out by multinational companies, pollution from smaller, sometimes clandestine, industry is still rife and this is the largest environmental problem. Earlier base-line studies have identified elevated levels of certain trace metals in freshwater systems around the world, especially rivers arising mainly from agricultural and industrial processes (Tariq *et al.*, 1996).

In Malaysia, like other countries of the world, the level of metal pollution of freshwater bodies, especially the rivers, is no longer within safe limits for human consumption. In the year 2002, the Department of Environment (DOE) reported that industries such as textile, metal finishing and electroplating, food and beverages, and animal feed could not achieve more than 65% compliance. Some industries were operating either without effluent treatment system (ETP) or with inefficient ETP. These industries had difficulty in complying with parameters such as nickel, copper, lead, zinc and iron (Department of Environment, 2002). In Malaysia there are not less than 1500 rivers. Rapid population growth, urbanization and industrialization have subjected some of these rivers

to increasing stresses giving rise to loss of firm yield of water and power, sedimentation, flooding, water pollution and environmental deterioration. The Department of Environment National River Water Monitoring Programme got started in 1978, but since 1995, it was contracted out to Alam Sekitar Malaysia Sdn Bhd (ASMA) under a privatisation arrangement. In 2003, 926 stations located within 120 river basins in Malaysia were monitored. Out of these 926 monitoring stations, 412 (44.5 %) were found to be clean, 448 (48.4 %) slightly polluted and 66 (7.1 %) polluted. Automatic water quality monitoring stations monitored river quality changes on a continuous basis at Sg. Perai (Pulau Pinang), Sg. Selangor (Selangor), Sg. Kelang (WPKL), Sg. Linggi (Negeri Sembilan), Sg. Melaka (Melaka), Sg. Skudai (Johor), Sg. Perak (Perak), Sg. Keratong (Pahang), Sg. Terengganu (Terengganu) and Sg. Sarawak (Sarawak). Under the pollution prevention and Water Quality Improvement Programme, five (5) additional automatic stations were installed at Sg. Langat (Selangor), Sg. Batang Benar (Negeri Sembilan), Sg. Labu (Negeri Sembilan), Sg. Putat (Melaka) and Sg. Rajang (Sarawak) (Department of Environment, 2003). This is clearly indicated in Table 1.0.

Table 1. 0 : River Quality Monitoring Stations for Automatic Continuous Monitoring (1995 - 2003), (Department of Environment, 2003)

Year	1995	1996	1997	1998	1999	2000	2001	2002	2003
River Basin	2	4	6	8	10	10	10	12	12
Number of the Automatic Continuous Monitoring Stations	2	4	6	8	10	10	10	12	15

Domestic sewage, palm oil mills, rubber factories, industrial wastewater and piggeries are the principal contributors of pollutants in Malaysia (Maketab Mohamed, 1993; Department of Environment, 1998). Severe seasonal depletion of the oxygen levels in major rivers caused a general degradation of their quality and increased difficulties in drinking water treatment. Overloading with biodegradable organic wastes from riparian municipalities and industries was mainly to be blamed. The gradual increase of heavy metal concentrations in sediment and in the water of rivers also reached alarming proportions.

In addition, the trace metals in such waters may undergo rapid changes affecting the rate of uptake or release by sediments thus influencing living organisms via the water-sediment chain.

1.3 Industrial Effluents

Man is responsible for releasing vast quantities of many different chemical substances into the environment each year; the majority of these anthropogenic substances are waste products generated by industry and society consuming the manufactured goods. Man-made fabrics and fibres, pharmaceuticals, fertilizers, pesticides, paints, and building materials, as well as chemicals for industrial processes, are just some of the products of the chemical industry that are integral to almost every aspect of modern living (McCaull and Crossland, 1974).

It is well known that the main polluters of water bodies and rivers are heavily industrialized cities. At present industrial wastes are prevalent in the composition of the wastewaters of giant industrial cities. Furthermore, the industrial era of the nineteenth century resulted in an acceleration of the use of natural substances such as As, Cd, Hg, Pb, Zn, S, etc., that could eventually be released to the aquatic environment. The current production and use of tens of thousands of synthetic chemicals inadvertently resulted in the release of these substances into the general environment. Although industry uses much less water than agriculture, it causes more pollution. Most of the water is used for cooling and cleaning and, although more than 80 per cent of it is returned immediately to the natural water cycle, it is often polluted with by-products of the manufacturing process and other waste material (Hester, 1983). Concentrated effluents from manufacturing and industrial production plants have added hazardous substances to natural water courses and reduced their ability to sustain aquatic life.

Often, when the environmental issues associated with industry are considered, it is common to focus on the wastes generated during the manufacturing process and the associated environmental problem by the physical state of the waste. Industrial contributions to environmental problems can arise from each of the steps of the life cycle of its products. Subsequently, industry can create additional adverse environmental impact

while processing these materials into products and in the packaging and distribution of its products (Palmer, 1995). Variations in water flows, manufacturing process and production regimes result in effluent discharges which are seldom simple and whose constituents are changing with time. The entry of an effluent will affect the aquatic environment to some degree. A study in India revealed that the physico-chemical characteristics of the water are being altered in the industrial area (Joy *et al.*, 1990). Besides that, Bais *et al.* (1991), reported effects of industrial effluents on the reduced number of zooplankton in the River Dhasan in India.

Water pollution by toxic chemicals present in industrial waste effluents is a worldwide problem now. Both developed and developing countries are seriously affected due to this water pollution. Consequently, major water pollution in Malaysia is also caused by the discharge of industrial effluents. Many industries discharge wastes containing different inorganic compounds including heavy metals into natural freshwater bodies without prior treatment. However, the point sources of pollution in Malaysia come in the form of forest cleaning and earthworks, industrial effluents and wastes typically the agro-based industrial point sources (namely rubber and oil palm mills), domestic or animal farming sewage (Department of Environment, 2002). The Department of Environment (2002) also reported that industries such as tannery, chemical-based, electrical and electronic industries achieved average compliance of 81 %, 85 % and 86 % respectively. However, industries like paper, textile, metal finishing and electroplating, food and beverages, and animal feed could not achieve more than 65 % compliance. In 2003, 129 premises or companies were taken to court and fined a total of RM 1 901 300.00 for offences under the Environmental Quality Act, 1974. Out of the total number of cases, 55 (43%) cases involved offences for polluting inland waters through discharges of effluent above the stipulated standard under section 25(1) of the Environmental Quality Act, 1974 (Department of Environment, 2003).

Furthermore, industries designated with the sources of heavy metals pollution are many and varied. One such listing is presented here in Table 1.1. The ten most common toxic heavy metals are shown to be associated with the twelve groupings of main industries. Most types of industries are important as far as heavy metal pollution is concerned, but a few, such as the fertilizer and basic steel works industries involve much more heavy metals than the textile mill product or leather and finishing (Forstner-Wittman, 1981).

In general, effluents can be classified into groups based on physicochemical similarities and on their effects on aquatic communities. Inert suspension resulting from mining, quarry, and washing processes may impair ventilation and filter feeding rates or decreases photosynthetic rates. Suspensions may also cause habitat modifications that in turn can affect behaviours, or they may carry adsorbed toxic materials. Poisons, such as acids, alkalis, heavy metals, phenols, cyanides, organic toxins, and radioactivity, typically cause generalized depression of physiological rates and increased respiration.

Inorganic reducing agents, such as sulphides, sulphates and ferrous salts from industrial effluents and mine runoff, may be directly toxic or may cause secondary effects, such as lowered oxygen concentrations or pH changes. Organic effluents from sewage treatment facilities, agricultural runoff, paper mills, and other sources may cause enrichment and increase productivity. Severe organic loading may decrease productivity through primary and secondary effects. Finally, some effluents, such as oil refinery wastes, combine many of the above categories and produce wide variations in community response to stress (Matthews *et al.*, 1982).

Table 1.1 : Heavy metals employed in major industries (Forstner-Wittman, 1981)

Effluents	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sn	Zn
Pulp, papermills, paperboard, building paper.		X	X		X		X	X		X
Organic chemicals, petrochemicals.	X	X		X	X		X		X	X
Alkalis, chlorine, inorganic chemicals.	X	X		X	X		X		X	X
Fertilizers.	X	X	X	X	X	X	X	X		X
Petroleum refining.	X	X	X	X			X	X		X
Basic steel works foundries	X	X	X	X	X		X	X	X	X
Basic nonferrous metalworks, foundries.	X	X	X		X		X			X
Motor vehicles, aircraft plating finishing.	X	X	X		X			X		
Flat glass, cement, asbestos product.		X								
		X								
Textile mill product.										
Leather tanning, finishing		X								
Steam generation power plants		X								X

1.3.1 Heavy Metals

Heavy metal pollution is a major environmental problem in the world. The term 'heavy metal' is somewhat imprecise, but includes most metals with an atomic number greater than 20, but excludes alkali metals, alkaline earths, lanthanides and actinides. The heavy metals are those metals that have a density greater than five, include about thirty-eight elements (Salgare, 1991). Apparently, studies on pollution of heavy metals in the urban environment became prominent after the mid sixties, concurrent with enhanced urbanization and industrialization processes worldwide. It was preceded with an earlier shock of mercury poisoning associated with fishes consumed from the Minamata Bay, Japan in the mid fifties (Kudo, 1992).

Meanwhile, in Malaysia, Johor and Penang states recorded the highest incidence of mercury in their coastal waters (Department of Environment, 1994). Inorganic arsenic is taken up rapidly by phytoplankton and this undoubtedly represents an important route for the introduction of the element into aquatic food webs. Philips (1990) reported that total arsenic concentrations of 14 to 42 $\mu\text{g g}^{-1}$ dry weight in three species of zooplankton from offshore waters of the northeast Atlantic Ocean.

Of a large group of heavy metals (more than 40), the most toxic and widespread are Hg, Cd, As, V, Cu, Sn, Zn, Sb, Mo, Co and Ni (Safronova *et al.*, 1997). The metal cadmium became a serious concern following the discovery that it competes with calcium for sites in the human bone formation. Nevertheless, the toxicity of other metals such as coppers, zinc, arsenic, cobalt and a few other minor elements became more prominent with increasing interest for research in the field after the late sixties.

The natural or non-anthropogenic sources of heavy metals in the environment are mainly geological in origin, being part of the earth formation components, through weathering, erosion, leaching and other terrestrial processes, metals become parted from the matrices of the earth to be incorporated with the various components of the soils' masses, to exist in geochemically unstable forms. From here, metals can find themselves in the various environmental sinks. Mining activities are usually one of the major sources of metal contamination in the environment. The main source of mercury, arsenic, zinc, copper and chromium in river waters are from, urban and agricultural run-off, and effluent from industries, sewage treatment plants, domestic discharges, constructions, earthworks and

pig farms (Department of Environment, 2002). Furthermore, the pollution of lead became very much talked about, especially in the drinking water, urban air, food and drinks, cosmetics and newly painted rooms. Concentrations of lead in vegetables from Copenhagen, Denmark were found to be 530 $\mu\text{g/kg}$ due to the polluting activities around the area (Petersen *et al.*, 2002).

Heavy metals move in a rather intricate fashion within the hydrological cycles. An interesting model shows that metals in the atmosphere (highly relevant in the urban environment) will land up in the rainwater, and subsequently into the river water, the estuarine water, seawater and back to the rainwater. Metals in the rain can also land up in the soils and metals in the aquatic ecosystems can be found in the fluvial, estuarine and oceanic sediments (M. Ahmad Badri, 1988). The flow chart in Figure 1.0 shows the interrelated connections quite clearly.

1.3.1.1 Arsenic (As): $Z = 33$

The ancient Greeks, who attributed a sex to metals, gave the name *arsenikon* (male) to the natural sulphides of arsenic. The discovery of this element is sometimes credited to Albertus Magnus in 1250. Arsenic has only one stable isotope, of mass 75. The boiling point for Arsenic (sublime) is 613 $^{\circ}\text{C}$. It is a Group VB element, which behaves as a metalloid. Arsenic forms two series of oxygenated compounds: the arsenates [As (III)] and the arsenates [As (V)] (Haissinsky and Adloff, 1965). Arsenic compound is principally used in the pharmaceutical industry and in the preparation of insecticides and parasiticides.

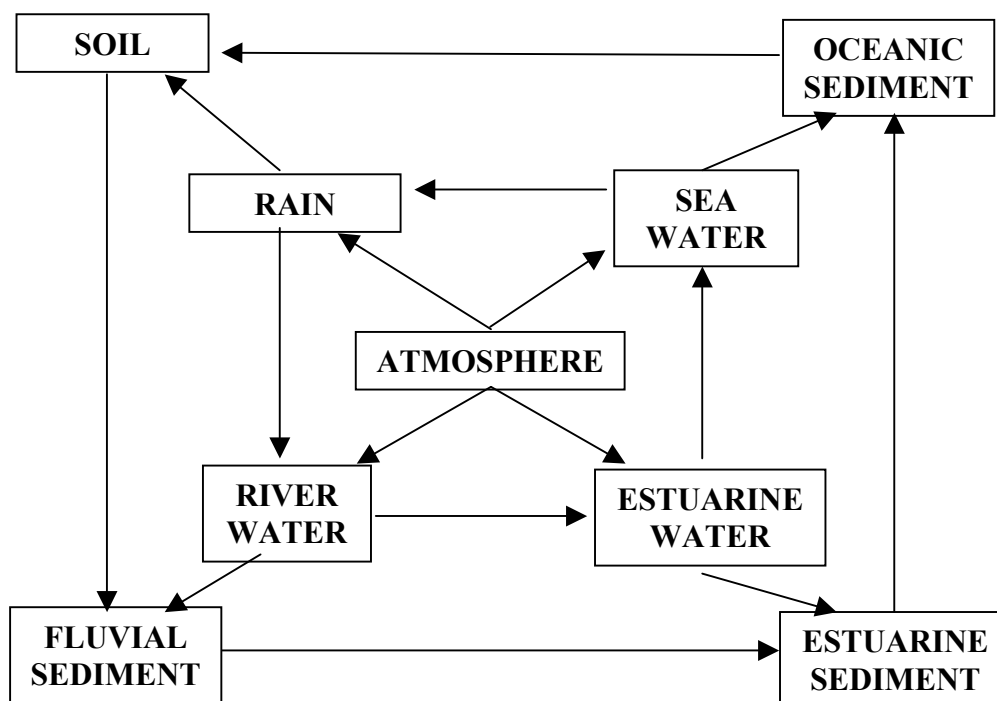


Figure 1.0 Movement of trace metals in hydrological cycle

Arsenic occurs widely in the earth's crust. It is found in soils, many waters and almost all plant and animal tissues. No one would take lightly the presence of this element in food or drink. Yet, arsenic is almost universally distributed in plants and animals, and daily intake, even in the absence of pollution, may be as high as 0.5 mg in all of us. The principal use of arsenic is in the chemical industry and there it is widely employed in pharmaceuticals, agricultural chemicals, preservatives and related compounds. Unfortunately, arsenic is a persistent poison and, even after many years, some streams and locations on farms remain toxic because they were once exposed to these chemicals.

Furthermore, the major uses of arsenic compounds currently are in agriculture and forestry, much smaller amounts are used in the glass and ceramic industries, cloth and semiconductor manufacturing, feed additives and drugs (Sittig, 1979). Compounds used as pesticides are lead arsenate, copper acetoarsenite, sodium arsenate and organoarsenic compounds. In addition to that, wood preservatives containing a mixture copper sulphate, potassium dichromate and arsenic pentoxide are being used increasingly in treating piling timbers and roof-trusses (Seiler *et al.*, 1994). The preserved timber is resistant to both fungal and insect attack.

In Malaysia, the presence of arsenopyrite and other arsenical ores in association with tin, iron, gold, lead, copper and zinc ores have been reported in various mines both in the Peninsula as well as in Sabah and Sarawak (Department of Environment, 1986a). Major anthropogenic sources which release arsenic into the air, water and soil are ore smelters, cement manufacturing, combustion of fossil fuels and extensive use of arsenical pesticides. Some monitoring data obtained through Global Environmental Monitoring System (GEMS) under the coordination of WHO shows the total arsenic concentration for Sg. Skudai is 0.005 mg/L (Department of Environment, 1986a). Besides that, from the studies in the Sg. Langat basin, levels of arsenic have been reported to range between 0.003 to 0.049 mg/L (Department of Environment, 1998). Accumulation of arsenic in herbs in Poland was found to be 1.05 mg/kg (Lozak *et al.*, 2001). In Nigeria, arsenic in crude oils was determined and recorded levels ranged from <0.06 ppm to 0.166 ppm (Oluwole, 1992). Five species of macro algae in South Australia were analysed and concentration of arsenic were determined to be in levels ranged from 18-31 $\mu\text{g g}^{-1}$ (Maher and Clarke, 1984).

For the general population, ingestion through food and water forms the major route of intake. Transplacental transfers of arsenic to foetal tissues, particularly the central nervous system, have also been demonstrated and may pose a potential health threat in early foetal development. Nevertheless, the *in vivo* toxic effects are essentially due to enzyme inhibition by the formulation of arsenic-sulphur bonds between trivalent arsenic and thiol groups (Lederer and Fensterheim, 1983).

The Food Act 1983 and Food Regulations 1985 in Malaysia allows less than 1 $\mu\text{g g}^{-1}$ of arsenic in food. Normally, acute poisoning by ingestion usually manifests first as a feeling of throat constriction followed by difficulty in swallowing, epigastric discomfort, violent abdominal pain with vomiting and diarrhoea, intense thirst, muscle cramps, severe hypertension and collapse. Death may result from cardiac failure and is preceded by restlessness, convulsion and coma. Furthermore, residual effects of acute poisoning include peripheral neuropathy, cardiac and congestive heart failure, anaemia, leucopenia and skin lesions (Ndiokwere, 1985).

1.3.1.2 Cadmium (Cd): $Z = 48$

Unlike mercury and lead, Cd is not an 'ancient' metal, at least in terms of its use by man. It is only in recent years that it has found widespread industrial application, mainly in the metal plating and chemical industries. However, it is quite likely that it was unsuspected used, and that humans experienced its highly toxic effects, for many centuries. Its presence in zinc, for instance, is well known and in many instances in which 'zinc poisoning' was believed to have occurred, it was probably cadmium that was the toxic agent. Even minute amounts of cadmium are sufficient to cause poisoning. Moreover, since the metal is soluble in organic acids, it easily enters acid foods with which it comes in contact. Cadmium is a highly toxic element. It has been described as 'one of the most dangerous trace elements in the food and environment of man.

Cadmium is a divalent metal, homologous with zinc and mercury in the periodic table. Cadmium is generated in waste streams from pigment works, textiles, electroplating and chemical plants. Natural cadmium is a mixture of 8 isotopes with mass numbers between 106 and 116, the most abundant being ^{112}Cd (24.07 %) and ^{114}Cd (28.86%). The *itai-itai* disease in Japan was probably due to the transport of cadmium containing particulates in water to the irrigation fields. Shellfish can accumulate cadmium from the sediment and concentration of around 0.01 mg/L can retard the growth of aquatic plants (Rao, 1991). Although, cadmium plating is the most important application of the element, it is also used in fusible alloys, solders, stereotype plates, and bearings for automobiles, photoelectric cells and alkaline accumulators (Forstner-Wittman, 1981).

Strohmeyer, who isolated the element and gave it this name to denote the association of the two metals, recognized the presence of cadmium in zinc oxide in 1817. The boiling point of cadmium is 765°C . Only one, very rare, ore of cadmium is known, namely genocide (sulphide), the metal is normally extracted from zinc ores. Concentration of cadmium in coal is 0.01 to 65 mg kg^{-1} and more than 1 mg kg^{-1} in crude oil. In marine sediments it was around 0.1 to 1 mg kg^{-1} . Soil normally contains less than 0.5 mg kg^{-1} (Herber, 1994).

On the contrary, absorption through food is the most important route of cadmium uptake for the general population. Acute ingestion of contaminated food and drink causes nausea, vomiting, abdominal cramps, diarrhoea and shock. Chronic inhalation of cadmium fumes produces effects on the kidneys causing renal tubular damage, lung emphysema as well as anaemia, liver damage and later disturbances in calcium/phosphate metabolism. An incident due to chronic ingestion that shows rise to renal tubular damage is the itai-itai disease in Japan (Lepp, 1981a). In Malaysia, the death dose for cadmium poisoning is 10 mg (Food Act, 1983).

Under the WHO monitoring program, cadmium concentrations studied in Sg. Skudai were found to be below detection limit (<0.001 mg/L) (Department of Environment, 1986a). Cadmium also induced changes in the histology of kidneys had been reported in common carp, *Cyprinus carpio* (Cyprinidae) from the National Fish Seed Farm (NFSF) Jyotisar, India (Singhal and Jain, 1997). Cadmium concentrations in Malaysian rivers recorded levels ranged from 0.06 to 0.48 $\mu\text{g g}^{-1}$ (Universiti Kebangsaan Malaysia-Department of Environment, 2000). In Central Italy, cadmium was found to be in range of 0.24 $\mu\text{g g}^{-1}$ to 0.95 $\mu\text{g g}^{-1}$ in lichens collected from the environs of the town of Pistoia (Loppi, *et al.*, 1994).

1.3.1.3 Chromium (Cr): $Z = 24$

Chromium was discovered by Vauquelin in 1787 in a Siberian ore, and was isolated in 1854 by Bunsen. Its name comes from colour, and refers to the varied tints of its compound and ores. Chromium is a transition element of sub-group VIA, and it can assume the oxidation states 0 (chromium hexacarbonyl) and I to VI. Apparently, chromium is commonly used as a coating for the protection of alloys and metals, owing to its high resistance to corrosive agents (electrolytic chromium plating). It is a constituent of oxidation-resistant, refractory, very hard alloy. It is also a constituent of alloys for electrodes and thermocouples (Hamilton and Wetterhahn, 1988).

Chromium is widely distributed in the earth's crust, though concentrations are generally relatively low, at about 0.04 per cent of the total solid matter: Its toxicity to industrial workers has been recognized for many years. The most common industrial sources are the alloy industry, wood treatment, and chromium mining operations. Besides that, Cr is used extensively for manufacture as stainless steels, decorative and wear-resistant surface treatments and manufacture of chemicals.

Furthermore, chromium salts are used in chemical analysis, tanning, dyeing, ceramics, and in the dyestuffs industry. The major uses of chromium are in the metallurgical industry for the production of stainless steel and other alloy steels, and in the refractory. Other uses are in the electroplating, metal finishing and leather tanning industries and in the production of fungicides, pigments, oxidants, and catalysts and in the glass and photographic industries (Stoeppler, 1992). The usage of chromium and its compounds is estimated almost 10-100 million tones per year (Mason and Moore, 1982). Chromium is a mixture of 4 isotopes of masses 50, 52 (83.76%), 53 and 54. The boiling point for chromium is 2672 °C (Herold and Fitzgerald, 1994).

Sediments from the Indus River Pakistan showed chromium concentrations from 3.2 to 23.5 $\mu\text{g g}^{-1}$ (Tariq *et. al.*, 1996). Monitoring data from WHO shows that chromium concentration in Sg. Skudai was found to be 0.001mg/L (Department of Environment, 1986a). Previous studies of chromium of Malaysian rivers recorded concentrations ranging from 0.01 to 4 $\mu\text{g/L}$ (Universiti Kebangsaan Malaysia-Department of Environment, 2000). Besides that, many plant species are adversely affected by chromium (VI) concentrations of 5 mg/L (Rao, 1991). Plants from urban areas of Punjab, Pakistan showed concentration of Cr in range of 1.866ppm to 4.743 ppm (Iqbal and Qadin, 1989). Plants grown on serpentine soils rarely contain chromium concentration larger than 100 mg/kg and Cr concentration in excess of this value is due to soil contamination (Brookes, 1987).

Chromium can be carcinogenic and causes asthma and skin allergy. Apparently, skin ulcers result from local exposure to hexavalent chromium compounds, and present as deeply penetrating ulcers over the fingers, hands and forearm. Dermatitis may either be due to acute primary irritation, or allergic reactions. Other reported health effects include cardiovascular damage, nephrotoxicity and liver necrosis (Herold and Fitzgerald, 1994). The permissible level of chromium in food in Malaysia is 1.0 $\mu\text{g g}^{-1}$ (Food Act, 1983).

1.3.1.4 Copper (Cu): Z = 29

The use of copper dates back to the beginnings of civilization itself. The metal was already used in the Badarian period, the earliest Egyptian civilization, 5000 years before our era. It was known in Cyprus by the name of *oes cyprum*, which was changed to *aes curium* and then to *cuprum*, whence the name of the element is derived. Copper is malleable, ductile metal, and is an excellent conductor of heat and electricity.

Today, the primary use of copper, accounting for about half of the world production is in the manufacture of electrical cables and equipment. It is still extensively used for plumbing, though plastic piping has been taking over in recent years. Copper is still occasionally used in sheets for roofing buildings, as well as for covering the hulls of boats. A major use continues to be as a component of alloys, with zinc, tin, cadmium and other metals. Copper salts have important pharmaceutical and agricultural uses.

However, anthropogenic sources of release of copper into the environment include corrosion of brass and copper pipes by acidic waters, industrial effluents and fallout, sewage treatment plant effluent and the use of copper compounds such as copper sulphate as aquatic algacides. Major industrial sources of copper include smelting and refining industries, copper wire mills, coal burning industries and iron and steel producing industries. Large quantities of copper can enter surface waters, particularly acidic mine drainage waters, as a result of metallurgical processes and mining operations. Copper has two stable isotopes of masses 63 (69.09 %) and 65 (30.81 %) respectively. The boiling point of copper is 2567 °C.

Copper in herbs in Poland was found to be 1.00 mg/kg (Lozak *et al.*, 2001). The range of copper concentration found in sediments from the Chao Phraya River is 3.34 to 37.50 $\mu\text{g g}^{-1}$ and in water is (ND) non-detectable - 68.7 $\mu\text{g g}^{-1}$ (Polprasert, 1982). On the contrary, monitoring study conducted by WHO reported 0.008 mg/L of copper concentration for Sg. Skudai river water (Department of Environment, 1986a). Meanwhile, levels of copper in Malaysian rivers have been reported to range from 5.96 to 21.20 $\mu\text{g/L}$, (Department of Environment, 1998). Miryakova (1993) pointed out that the maximum concentration of copper in gramineous pondweed is 23.5 $\mu\text{g g}^{-1}$. Acute gastrointestinal symptoms may also result from ingestion of copper in contaminated food and beverages, or copper salts in suicide attempts. Severe cases may produce fatal hepatic and renal damage.

Metal-fume fever, an influenza-like illness lasting about 24 hours, occurs after exposure to 0.1 mg/g of copper fumes or dust. Febrile reactions and haemolytic anaemia have also occurred in patients due to absorption of copper from dialysis equipment (Stoeppler, 1992).

Copper poisoning had also been associated with brain damage. Furthermore, copper ions form stable complexes, such as chelates with organic substances. Copper is an element of Sub-group IB of the periodic table, and the most important valency states are II and I. Apparently, most Cu^{2+} salts are soluble and coloured. The salts of Cu (I) and Cu (II) form many complexes with mineral acids, ammonia, amines, pyridine, etc. The compounds of Cu (II) are poisonous (Nriagu, 1979). Copper toxicity is also found in the livestock, notable sheep and cattle. Livestock grazing in areas accommodating power lines had been shown to result in increased Cu concentration in their milk, in comparison with the ones not subjected to this exposure. These were attributes to Cu leaching from the power lines and the subsequent grass uptake of the metal from the soils, and consequently the Cu found in the milk (M. Ahmad Badri, 1988). The 1983 Food Act in Malaysia allows 30 mg kg^{-1} of copper in food.

1.3.1.5 Lead (Pb): $Z = 82$

Lead has been known since ancient times. Lead belongs to the fourth column of the periodic table (Group IVB); its maximum valency is therefore IV, but II is far more stable. The divalent *plumbous* salts exhibit certain similarities to the alkaline earth salts. Tetravalent lead forms few compounds, though mention should be made of PbO_2 , the alkali plumbates, PbCl_4 , and $\text{Pb}(\text{SO}_4)_2$, which are very powerful oxidizing agents. Often, it is one of the most widely used metals in industry: in piping, conducting materials, accumulators, lead chambers, printing characters, soldering, anti-knock substances and coloured pigments (Tscuchiya and Kenzaburo, 1979). In storage battery industry, lead - antimony alloys is used as grids and lugs; litharge (PbO), red lead (Pb_3O_4) and grey lead (PbO_2) as active material pasted on the plates. Red lead and yellow lead chromate are used as pigments in paints (Haissinsky and Adolff, 1965).

However, there is no doubt that lead is seriously toxic to human beings and evidence is accumulating that considerable differing effects result in different human beings who have absorbed similar amounts. Bowen (1966) explained that lead is not essential as a trace metal to nutrition in animals, but is a cumulative poison. In natural form, lead comprises 4 isotopes with mass numbers of 204 (1.48 %), 206 (23.6 %), 207 (22.6 %) and 208 (53.3 %). Boiling point for lead is 1749 °C. It would seem that absorption through food and drink is the main pathway for adults, though estimates of the percentage intake (and absorption) through this route compared with inhalation differ quite widely (Hester, 1983).

Previous studies of the Sg. Semenyih showed levels of lead ranging from 0.1 to 1.76 $\mu\text{g L}^{-1}$ (Department of Environment, 2002). Lead poisoning in children was also traced to the consumption of lettuces containing high levels of the element. The sources of Pb were found to be old lead batteries that had been dumped on the ground within the neighbourhood of vegetable plots (Lepp, 1981b). NAS (1976) reported that grass was contaminated by lead within 152 m downwind of roads in Colorado, USA. It was also reported that lead in soils ranged from 128-700 $\mu\text{g g}^{-1}$. Whereas, the monitoring study conducted by WHO found that the concentration of lead in the Sg. Skudai river water was 0.8 mg/L (Department of Environment, 1986a). In Poland, herbs were found containing 0.94 mg kg^{-1} of lead (Lozak *et al.*, 2001).

Nevertheless, lead has detrimental effects on the human body and its functions, affecting the metabolism, blood and kidneys. Furthermore, lead is also known to accumulate in the body more rapidly than it is excreted. Lead is known to retard haemoglobin production, the cause of anaemia. Other effects are damages to the nervous systems, the kidneys and the brain. Lead is also known to cause precipitation of protein, through the interaction of lead ions with the sulphydryl (-SH) groups of proteins. Studies on human skeletons prove that lead tends to be accumulated in bones, and its excretion out of the human body is rather slow (Seiler *et al.*, 1994). Maximum lead levels allowed in fish for consumption in Malaysia is 2 $\mu\text{g g}^{-1}$ (Food Act, 1983).

1.3.1.6 Mercury (Hg): Z = 80

Mercury was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs dating from 1500 B.C. The element owes its name to the planet Mercury; the symbol is derived from the latin *hydrargyrum*, liquid silver. In the middle ages the element was called *argentum vivum*. Mercury is a mixture of 7 isotopes with atomic number between 196 and 204, the most abundant being ^{202}Hg (29.80 %). The tendency to form covalent bonds is found in a considerable number of compounds of Hg with S, N, and C. The organometallic derivatives of mercury are remarkably stable. Mercurial compounds are insoluble, with the exception of the nitrate, chlorate, and perchlorate. However, mercury is very slightly soluble in water ($0.3\ \mu\text{mol/L}$) and organic solvents; it dissolves many metals at normal temperatures, particularly Pb, Zn, Ga, Cd, Tl, In, and the alkali and alkaline earth metals, forming amalgams, which may be simple solid solutions or intermetallic compounds; these alloys are used in analysis and in industry (Watson, 1979).

Today, Hg is valued and widely used in industry, mainly because of its chemical properties. It is used as a catalyst in a variety of industrial and laboratory reactions, some of great economic value. Its physical property of high conductivity makes the liquid metal valuable in the electrical industry. Of particular significance in recent years have been the serious instances of poisoning, especially by organic mercury, through industrial pollution. Mercury can still be considered among the most dangerous of all the metals we are likely to meet in our food. Man's industrial activities, including the combustion of fossil fuels, also contribute to the environmental mercury burden.

Mercury and its compounds play an important part in electrochemistry. The metal itself is used as a coolant in certain types of reactors, in the metallurgy of gold and silver, as a catalyst in organic chemistry, and in the manufacture of lamps, relays, and switches. Both mercury and its compounds are highly toxic. Out of the 10 000 tones of mercury produced worldwide yearly, it has been estimated that 25 % is consumed by the chlor-alkali industry, 20 % in electric equipment, 15 % in paints, 10 % in control and measurement system, 5 % in agriculture, 3 % in dental practice, 2 % in laboratory and 20 % in others which include detonators, catalysts, preservatives and cosmetics (Palmer, 1995). Nevertheless, major uses in Malaysia also cover the above-mentioned areas including chlor-alkali industry, electrical equipment, paints and dental practice. In a recent survey of a wide range of paint products

available in local market, 12 out of 16 brands of emulsion paints were found to contain mercury ranging from 0.005 % to 0.066 %, while 5 out of 7 brands of gloss paints (solvent based) range from 0.003 to 0.037 % (Department of Environment, 1985).

Apparently, a monitoring study found 0.1 mg/L concentration of Hg in the Sg. Skudai (Department of Environment, 1986b). Meanwhile in the Sg. Langat, mercury level is reported to be 0 to 0.004 mg/L (Law and Singh, 1986). Because of the toxic nature of mercury, the Malaysian government established a limit for public water supplies of 0.002 mg/L of mercury. The average concentrations for aquatic plants, benthic invertebrates and fish in the Ottawa River were 14.2 ppb, 233 ppb and 162 ppb, respectively, for total mercury (Kudo, 1992). In Canada, Stokes and Dreier (1983) reported that concentration of mercury in water were (10 - 30 ng/L) and sediment concentrations were quite variable from 36 to 150 ng/g. Polprasert (1982) reported that mercury levels in aquatic plant from the Chao Phraya river estuary ranged from 0.75 to 1.26 ppm in leaves and 0.28 to 0.68 ppm in floating stems.

On the contrary, the earliest cases of methyl mercury poisoning were described, as neurological features were predominant, presenting as paraesthesia, constriction of visual field, dysarthria, ataxia and astereognosis after an asymptomatic period of 3 to 4 months from exposure. The syndrome as in Minamata, resulting from consumption of fish contaminated by methyl mercury, and later in Niigata (Sakai *et al.*, 1986). Other reports clinical effects due to methyl mercury include dermatitis, exfoliative dermatitis and cardiovascular damage. Moreover, intrauterine exposure to mercury has been reported to cause psychomotor retardation, severe brain damage resulting blindness and hypotonia, and learning difficulties with poor intelligence test performances (Hans *et al.*, 1994). Several cases of wildlife poisoning from seeds treated with methyl mercury were documented in Sweden during the period 1948 - 1965 (Lindquist *et al.*, 1984).

1.3.1.7 Nickel (Ni): $Z = 28$

Cronstedt discovered nickel in 1751; its name is derived from the Swedish *kopparnickel* (goblin copper). Nickel possesses 5 isotopes with mass numbers 58 (67.88 %), 60 to 62, and 64. Its principal valency is II, but compounds corresponding to the oxidation states of 0, III, IV, and I are also known. The boiling point of nickel is 2732 °C. Nickel is a hard, malleable, ductile metal, crystallizing in the face-centred cubic system. The metal is produced by roasting the sulphide ores and reducing the oxide with carbon; it is purified by electrolysis (Adriano, 1986).

The main uses of nickel are in the manufacturing of stainless steels and high nickel alloys (about 40 % of total Ni produced). Nickel also enters into the composition of numerous alloys: 36 % Ni-steel or Invar has a coefficient of expansion which is almost zero; alloys with high resistivity (constantan, manganin, nichrome) are used as resistances and for the manufacture of thermocouples; the 68 % Ni-alloy (3 % Cu, 2 % Fe) Monel has high chemical resistance. Nickel is used as a protective coating by electrolytic deposition (nickel plating). Nickel has been shown to be essential for the growth of some microorganisms. The growth of blue-green algae *Oscillataria spp* and of the bacterium *Alcalegenes eutrophus* has been shown to depend on the presence of nickel in specially purified media (Eisler, 1981).

However, other major contributors of Ni are the miners, smelters, and refiners, casting of alloys, and electroplating industries, and in nickel-plating (about 20 % of Ni produced). Nickel is found in coins, household materials and food-processing equipment. Other uses of nickel include nickel-cadmium batteries (nickel hydroxide), electronic components (nickel carbonate), and catalyst in industrial and oil refining and in certain fungicides. Nickel is also present in many domestic cleaning products.

In man, the health effects of nickel compounds are predominantly on the skin and respiratory system. Some of these effects are hypersensitive in nature, including bronchial asthma and contact dermatitis. Allergic skin reactions from nickel are very common among the general population as well as exposed workers, and may result in chronic changes such as lichenification. Nickel also has acute inflammatory effects on the nasal membrane (Reilly, 1991). Ure and Berrow (1982) in a recent survey from the world literature quoted 93 mg/kg for nickel in soils. The concentration of nickel in the Sg. Skudai was found to be

0 - 10mg/L (Department of Environment, 1986b). Nickel concentration found in the Sg. Langat basin ranged from 16.42 to 31.83 ppb (Universiti Kebangsaan Malaysia – Department of Environment, 2000). A study conducted in Vietnam found that the concentration of nickel in the *Imperata cylindrica* grasses is 0.79 ppm (Tran Van and Teherani, 1989a). They also reported that the concentration of nickel in the Dalat lake sediment in Vietnam is 3.68 ppm (Tran Van and Teherani, 1989b). Lozak *et al.* (2001) reported that nickels in herbs in Poland were found to be 1.00 mg/kg.

1.3.1.8 Zinc (Zn): Z = 30

Zinc has been known for a very long time; it was used in alloys since the 7th century in India, and in the 11th century in China. Marggraf isolated the metal, in 1776. The element is essentially divalent. Despite that, several zinc compounds are covalent: the sulphide, selenide, telluride, and oxide, as well as the organozincs, which were the first organometallic derivatives known. Apparently, zinc is prepared by the reduction of ZnO with carbon monoxide, or by electrolysis of a salt, and purified by fractional distillation. It is used in galvanizing iron or steel, and enters into the composition of important alloys: brasses, nickel silver and mouldable alloys. Zinc is a mixture of 5 isotopes with mass numbers of 64 (48.89 %), 66 - 68, and 70. Boiling point for Zinc is 907 °C (Seiler *et al.*, 1994).

Zinc is also an important element in batteries and accumulators. Moreover, zinc chloride is used as a desiccant, in the conservation of wood, and in the manufacture of batteries. Meanwhile, ZnS finds an important application as pigment and zinc peroxide, is used as an antiseptic. The principle minerals of zinc are the sulphides (blende or sphalerite), carbonates (smithsonite), and silicates (calamine). Zinc also plays an important part in the human organism, and is also indispensable to the nutrition and growth of plants. The maximum level of zinc allowed in fish and fish product is 100 µg g⁻¹ (Food Act, 1983).

Zinc is used mainly in the production of non-corrosive alloys, brass and in galvanizing steel and iron products. Galvanized products that appear widely include automobile parts and household appliances. Zinc undergoes oxidation on the surface of the galvanized product and this protects the enclosed metal from degradation. About 33 % of the world production of zinc is used in galvanizing (hot-dip and electro galvanising), spraying, painting and sheradising; 25 % in the production of alloys for die-casting; 20 % in the production of brass and the remainder in the production of zinc oxides, zinc sheets for batteries etc. Zinc oxide, which accounts for the largest quantities of zinc compounds, is used in rubber and as a white pigment. While, zinc sulphate is therapeutic and is used in the treatment of zinc deficiency in humans (Jackson and Jackson, 1996).

The carbonates (organic zinc compounds) are used as pesticides. Inhalation of zinc chloride fumes may produce acute pneumonitis and fatal pulmonary edema, occasionally resulting in pulmonary fibrosis. Consequently, ingestion of zinc may also produce symptoms of food poisoning such as nausea, vomiting, diarrhoea and abdominal pain. Metal fume fever, an influenza-like illness with headache, fever, sweating, chest pain and leucocytosis is caused by inhalation of zinc oxide fumes. The illness lasts for 6- 48 hours, coming on within a few hours after exposure, and is never fatal (Solomons and Cousins, 1984).

Besides that, a study on plants, lichens (*Parmelia caperata*) in Central Italy recorded $74.12 \mu\text{g g}^{-1}$ of zinc (Loppi *et al.*, 1994). Bowen (1966) reported $100 \mu\text{g g}^{-1}$ of zinc in plants. A study of grass (*Imperata cylindrical*) plant (*Mimosa pudica*) and rice in Vietnam showed 7.58 ppm, 19.46 ppm and 17.01 ppm concentrations of zinc respectively (Tran Van and Teherani, 1989a). Previous studies of zinc in Malaysian rivers such as Sg. Gombak , Sg. Kelang , Sg. Semenyih and Sg. Selangor recorded zinc concentrations ranging from 0.27 to $38.33 \mu\text{g L}^{-1}$ (Universiti Kebangsaan Malaysia, 1996). Meanwhile, concentrations of zinc along the Sado River, Portugal recorded levels ranging from 110 to $1800 \mu\text{g L}^{-1}$ (Monteiro *et al.*, 1995). Sakai *et al.* (1986) reported that sediments from the Toyohira River, Japan recorded $152 \mu\text{g g}^{-1}$ of zinc.

1.4 Aquatic Ecosystem

Water covers about three quarters of the earth's surface, almost all as oceans. Virtually all surface waters contain life in one form or another; hence, aquatic ecosystems would be important for their sheer volume, if for nothing else. In addition, aquatic ecosystems are simpler in many ways than terrestrial systems, since the omnipresent factor that sets the tone for all aquatic ecosystems, regardless of their biotic complexity, is water. It is the medium within which all aspects of the ecosystem coexist, both living and nonliving. It is the source of all nutrients for aquatic life, including the gaseous nutrients such as oxygen and carbon dioxide. It is the medium by which organic and inorganic wastes and sediments are distributed throughout the ecosystem (Karr, 1995).

There are a number of reasons why biological studies are important. Drinking water, eating fish, and using aquatic ecosystems as recreational resources of course, also link man to the freshwater community. We can consider the effects of pollutants we record on the biological community as an early warning system for potential effects on ourselves. Biological communities may also respond to unsuspected or new pollutants in the environment. Finally, some chemicals are accumulated in the bodies of certain organisms, concentrations within them reflecting environmental pollution levels over time. In any particular sample of water, the concentration of a pollutant may be too low to be detectable using routine methods, but nevertheless will be gradually accumulated within the ecosystem to concentrations of considerable concern in some species (Harrison, 1996).

The natural world is organized into interrelated units called ecosystems. An ecosystem is a region in which the organisms and the physical environment form an interacting unit. Weather affects plants, plants use minerals in the soil, and affect animals, animals spread plant seeds, plants secure the soil, and plants evaporate water, which affects weather. There are many kinds of aquatic ecosystems, but the most meaningful breakdown is based on the salinity, or amount of material dissolved in the water. Most of the earth's surface water (99.99 %) is in the oceans, which contain about 35 parts per thousand (‰) dissolved salts. Of the remainder, most is fresh water with a salt content under 1/5 (‰) found in both lakes and ponds (still water) or in rivers and streams (running water). The most common transition zone between a river and the sea is the estuary, which has a dissolved solid content intermediate between those of fresh and marine waters. Water bodies such as ponds, lakes, estuaries, and rivers may be viewed as ecosystems. Each of

these ecosystems contains different individuals, species, populations, and communities, which occupy their own niche in the system. They interact with each other in many ways, including through the control of the food chain, birth and death rates, and the provision of suitable living spaces (Greenberg *et al.*, 1979).

However, to determine that an environmental change is going to result in pollution requires a careful study of ecosystems. An ecosystem is simply how living things relate to their environment. A study of fresh water ecology is an ideal way to introduce the ecosystem concept. The biotic components consist of plants, animals and protists. The abiotic components consist of soil, water, and such physical factors as light, wind, and temperature (Hall and Morrison, 1978). Anyway, when monitoring background levels and more specific pollution on land or in the sediments of a water body, measurements will often be made of levels in the plants or organisms that the soil or sediments support. In many cases flora or fauna provide excellent indicators of the degree of pollution as they may act as bio concentrators (for example of heavy metals from suspended material in shellfish). The simultaneous measurements of pollutant levels in soils and plants as well as in water, sediments, and aquatic biota are therefore often carried out (Seaborg, 1980).

Metal contamination of aquatic organisms may be employed in monitoring for three main purposes. First, is for the protection of human health and for organisms harvested as food. The identification of potentially unknown areas of elevated contamination and local to individual discharges, there is the need to assess the extent of the zone of contamination. Temporal change is to be monitored to identify the trend of contamination, especially near effluents, in order to identify stability, improvement or more importantly deterioration.

Biological monitoring must also take into account the vast diversity of effluents and receiving waters as well as the possibility that a number of different types of effluents may enter the system. Five ways pollution may harm aquatic life in a river:

1. Reduction in oxygen levels may occur through biotic or abiotic oxidations of reduced compounds.
2. The chemical or its breakdown product may be toxic.
3. Temperature shocks and fluctuations may be harmful in that they affect critical physiological processes.
4. Physical properties of the effluents may result in abrasion and smothering by sedimentation.

5. Habitat alteration may result from increased turbidity, sedimentation, or other such effects (Matthews *et al.*, 1982).

Meanwhile, the materials discharged to the rivers and streams flow via larger rivers and lakes to the oceans. On the way they may become incorporated into the sediment. Alternatively they may be metabolised by the plant and animal life in the water and thus enter into their food chain. Hence, wherever in the environment the samples are collected, they represent the same process of pollution although occurring in different time spans. Furthermore, soil, vegetation, sediment, lake water samples, etc., can give a measure of the pollutants released over a longer time period, often representing in fact an integration of the pollution that has occurred over previous months or years. For example, mercury contamination of fish and mussels in the Derwent Estuary of Tasmania observed similar tissue concentrations of 2.0 ppm wet weight (Goulden, 1978).

Apparently, ecosystem pollutant pathways provide the route between pollutants stored in environmental sinks and pollutants found in biological organisms. At the ecosystem level, exposure is assessed in terms of species of organism or entire trophic levels. In general, exposure is related to the trophic status of organisms, with the greatest exposure experienced by biota occupying the highest trophic positions. The transfer of pollutants through ecosystems is usually described within a series of compartments, each representing one stage in a known food chain. It is at the single organism level that the effects of a given exposure are most easily detected, and most widely studied (Yusof Samiullah, 1988).

1.4.1 Aquatic Plant

The increasing pollution of rivers connected with disposal of wastes originating in industrial emissions and in industrial, agricultural and household uses of water is well known. Experts estimate that wastewater fed directly into water bodies may introduce as many as a million different pollutants into our aquatic ecosystems. Moreover, major factors for sensitivity of aquatic ecosystems to pollution, besides role of these systems as receiving bodies for effluents, may be related with structure of food chain. Subject of heavy metals pollution of different aquatic environments has received the much-needed attention recently. Also, recent studies have shifted emphasis towards impacts on metabolism of aquatic organisms and their ability to accumulate both essential and non-essential metals. Impacts caused in an aquatic system may depend on the toxicant distribution within the three compartments: water, suspended matter and sediment (Wollast, 1982).

Nevertheless, the fates of pollutants in the biosphere have received much attention during past decades. The cycling of heavy metals, radioactive wastes, and atmospheric pollutants has been studied in terrestrial and marine systems (Hester, 1983). Moreover, living organisms have influenced the steady state levels of elements in the atmosphere, in freshwater systems, in the soil, and in the oceans through geological time. Inorganic and organometallic compounds have been synthesized, changed, and decomposed through biological activities for five billion years. An important link in the transfer of trace elements from soil to man is plants. Element content of essential elements in plants is conditional, the content being affected by the geochemical characteristics of a soil and by the ability of plants to selectively accumulate some of these elements. Bioavailability of the elements depends on the form of their bond with the constituents of a soil. Plants readily assimilate through the roots such compounds, which dissolve in waters and occur in ionic forms. Additional sources of these elements for plants are: rainfall; atmospheric dusts; plant protection agents; and fertilizers, which could be adsorbed through the leaf blades (Lozak *et al.*, 2001).

The advantages of using plants, as indicators are summarized below:

- (1) Vegetation samples are more practicable to collect than soil because they weigh less.
- (2) In thick (dense) vegetation, plant sampling is quicker.
- (3) Large plants exploit the equivalent of many kilograms of soil and hence can be more representative.
- (4) Deep-rooted plants can reveal mineralised areas not accessible by surface sampling of soil.
- (5) Chemical analysis of plant tissues is less complicated and quicker than soil analysis.
- (6) Where the plant accumulates an element, this can produce a more sensitive method of detection than soil sampling.

In this study, an aquatic plant was selected according to its availability along the Sg. Skudai river system. The local name of this plant is rumpud gedabong (malay), it is a common reed and its scientific name is *Phragmites karka*. This plant belongs to the Gramineae (Poaceae) family and other synonyms for it are *P. communis*, *P. filiformis* and *P. roxburghii* (Lim *et al.*, 1998). A brief description of this plant is it is perennial, gregarious plant up to 4 m tall, erect, with creeping stolons up to 20 m long. Stems hollow, many noded, up to 1.5 cm wide. Its leaves are about 20 – 60 cm long by 8 - 30 mm wide, alternate. The plants has inflorescence of about 20 - 70 cm long on drooping panicles, dense, with many fine branches, brownish when young but turning silver on maturity. It can be propagated by seed and stem cuttings. The inflorescence is normally a feathery panicle up to 75 cm long, often purplish. Lower florets usually sterile or male and upper florets are bisexual (Cook, 1990). An illustration of this plant had been described by Ahmad Azly (1988) as in Figure. 1.1. The common habitat for this plant is in moist and water logged areas, both fresh water and brackish, along rivers, ditches, lake shores, ponds, lakes and abandoned tin mining areas. Its distribution is widespread throughout Malaysia and also can be found in other countries such as India, Sri Lanka, Myanmar, Thailand, Indonesia and Australia (Kress *et al.*, 2003). Figure 1.2 and 1.3 show the pictures of the plant sample that was collected all through the nine months of sampling for the Sg. Skudai river system.

Only during the past 200 years have industrial activities dramatically changed the distribution of the elements at the surface of the earth. Organisms have been and are adapting to these changes. Furthermore, monitoring studies of heavy metals had also included most types of aquatic organisms, including phytoplankton. The use of plants had been quite extensive and they are generally accepted as good and effective indicators of heavy metal pollution. Various parts of the plants had been studied including the leaves, bark, roots, and rhizomes of grasses, fruits and flowers (Iqbal and Qadin, 1989). Among numerous representatives of the biological world, the higher aquatic plants have their advantages, as they represent a convenient object for observations, are nonmigratory and are capable of uptaking and accumulating substances of different chemical nature (Gulati, 1987). These properties were used to investigate the pollution of different parts of the river.



Figure 1.2 *Phragmites karka* growing naturally by the river bank



Figure 1.3 Close-up of inflorescence of *Phragmites karka*

However, plant life is abundant in a slow-water ecosystem. It includes rooted vascular plants such as pondweeds and grasses, firmly attached aquatic mosses, and large multicellular filamentous algae. Very small floating plants such as duckweed may cover much of the surface of the slowly moving stream, especially in its slowest backwaters. Apparently, from these multiple representatives of higher aquatic vegetation, basically submersed types of plants, was chosen in this study. For higher aquatic vegetation, water and bed material are the sources of mineral nutrition. Many heavy metals in natural waters are microelement, and in small quantities (10^{-3} to 10^{-5} %), they enter into the composition of cells and play an important role in the process of metabolism of aquatic organisms. Depending on the conditions of their habitats, plants may accumulate heavy metals in quantities considerably exceeding their content in the habitat (Miryakova, 1996). Furthermore, the environmental effects resulting from the bioaccumulation and evidence that a persistent material may be present in an effluent necessitates assessment of its rate and degree of uptake by aquatic organisms exposed to low levels of the chemical, with analysis of organs and tissues (Wollast, 1982).

1.4.2 Sediment

Among the abiotic sinks, the more easily sampled, analysed and determined are water, soils and sediments. Sediment samples became increasingly popular as the media for heavy metal analyses. Sediment samples are not only used to monitor heavy metals pollution in natural waters but also within the framework of international cooperation in ocean and coastal waters. It may represent the largest reservoir for heavy metals within an aquatic system, and it is also particularly useful in detecting pollution sources and in the selection of critical sites for routine water sampling (Forstner and Wittmann, 1981). This is important in monitoring works in both water and the sediments.

Bottom sediments represent an important indicator of contamination because they tend to accumulate pollutants in aquatic systems. They therefore help identify areas, which have become contaminated and reveal spread patterns from sources and contaminant input history. They show much less temporal and spatial variation than the water column and thus provide more reliable time integrated information than water column data. In addition, metal levels in sediments are generally one to two orders of magnitude higher than the amount of dissolved forms in water (Beckett *et al.*, 1991).

Furthermore, sediment analyses may also provide a quantitative approximation of the metal concentrations of associated waters. It is also important for assessing the relative importance of the sediments as a source of metals to the aquatic organisms as well as to determine what fraction of the sediment - sorbed metals is “bioavailable”. Generally, the solid matrices are popular for heavy metals pollution and monitoring studies due to the easier operational procedures in terms of sampling, laboratory analyses and storage. They are also often accepted as the final recipient of metals of pollution origin from the air, water, soil and the degradation of biota (Sakino *et al.*, 1980).

Apparently, sediments are broken up rock fragments that may or may not be chemically altered by weathering. In many ways, sediments are intermediate between rocks and soils, overlapping in certain characteristics with each. Just as rock particles are worn away by wind and water, sediments are deposited when the erosive- transportive force is no longer sufficiently powerful to erode or transport materials. Depositional areas can be any place where the velocity of the transportive medium decreases, such as flood plains along rivers, in lakes, or in the sea. The oceans are the ultimate depositional sites for all sediments. In spite of that, sediments interact most strongly with living organisms in aquatic ecosystems. They are the bottom of lakes and oceans, as well as of streams that do not flow directly over bedrock. Nutrients collect in the sediments, and many aquatic ecosystems depend to a large extent on the cycling of nutrients back and forth between the sediment and the water. Sediments are also the rooting medium for aquatic plants and home for burrowing animals (Dixit and Witcomb, 1983).

1.4.3 Heavy Metal Cycle in Aquatic Ecosystem

Most of the pollutants enter the environment as emissions to the atmosphere or as discharges to water bodies. These may be either in concentrated point sources, such as from factory smoke stacks and sewage discharges, or in a diffuse form such as from automobiles exhaust and run-off from agricultural land (Goulden, 1978). Due to the multiplicity and the cumulative effects the actual toxicity of a particular metal is not often easily observed in normal situations, with the exceptions of incidences such as the Minamata or *itai-itai* cases. Moreover, heavy metals of pollution origin may exist in various forms of the environmental solid and non-solid media, which can be referred to as the abiotic sinks (such as sediments, soils, dusts, water) and the biotic sinks (such as plants, livestock, fish and other aquatic life, earthworms, and including human).

Nevertheless, several metals are present in rivers and lakes as a result of domestic and industrial human activities. Heavy metals are not biodegradable and enter into the food chain by a number of pathways. The accumulations of Cr, Cu, Zn and other elements in the aquatic environment raise the risk of toxic concentrations of these elements that interfere with a number of life processes (Veadó *et al.*, 1997). Furthermore, the urban environment, the location of which is usually in association with an aquatic ecosystem (lake, river, estuary and seaside) can be shown to have a rather interesting heavy metal cycle. One such schematic presentation can be seen in Figure 1.4. It can be observed that man can be exposed to pollution of heavy metals directly from the biota e.g. fish, surface water, ground water or vegetation.

The metals in the aquatic biota are in constant interaction with the metals in the surface water, suspended matter, sediment and the interstitial water (water within sediment columns). The ground water used by municipalities in various parts of the world may actually be in constant equilibrium with soils, surface water and the interstitial water. These interactions show that metals can move quite freely once they are deposited in any one of the environmental ecosystems or media (Harrison, 1996).

Consequently, tidal waters and the sea do not have unlimited capacity to assimilate all constituents of liquid effluents without some risk to their ecological systems. However, these environments can continue to be a useful facility for disposal of industrial liquid wastes, provided that a decision to proceed with discharge has been based on an ordered and controlled approach. This must involve investigative and engineering techniques appropriate to the particular circumstances on the site where the effluent is produced and to the nature of the receiving water. A small number of well-publicized adverse ecological effects, caused by persistent chemicals and major oil spill, have given rise to public concern about pollution of the aquatic environment. In turn, this has resulted in proliferation of legislation aimed at limiting the levels of chemicals in the environment. Establishing controls and monitoring to ensure compliance presents problems to the administrator, the controlling authority and the discharger (Hester, 1983).

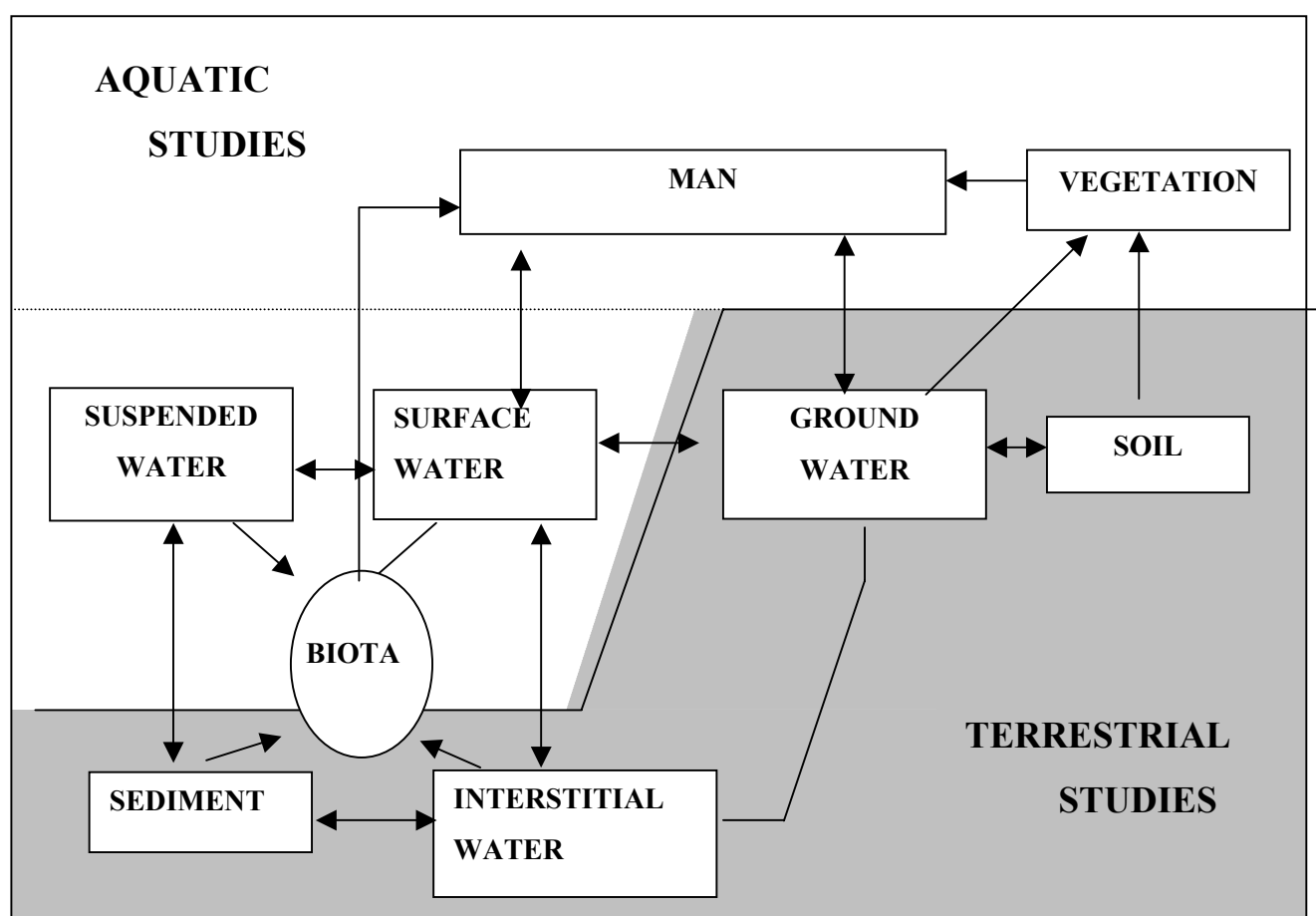


Figure 1.4 Schematic presentation of metal reservoirs and their interactions in aquatic and terrestrial systems, (M. Ahmad Badri, 1988).

1.5 Research Objectives

River pollution is not a recent problem. The pollution of rivers really began at the time of the industrial revolution, in the early nineteenth century. Hence, contamination by hundreds of pollutants through industrial discharges into the river is one of the major causes of environmental problems in our river system. This is due to the industrial activities occurring along or close to the rivers. Releases of chemicals to the water and soils may degrade environmental quality and result in the destruction of ecosystems and their flora or fauna, bioaccumulation of chemicals in food chains, and or short- or long- term human health effects in the exposed population. It is therefore, imperative to determine the impacts of river system pollution on the aquatic ecosystem due to industrial pollutants in rivers of Malaysia.

The research objectives can be outlined as follows:

- To determine the river water quality using a number of parameters and to compare it with the Malaysian Water Quality Guidelines.
- To produce data of heavy metal concentration levels in water, plant and sediment samples from Sg. Skudai using nuclear and spectrometric analytical techniques.
- To carry out correlation studies on the uptake of heavy metals in the water, plant and sediment samples from the river.
- To determine the uptake and accumulation of heavy metals by a plant species from the river.

1.6 Scope of Research

- To analyze the river water quality for pH, DO, T, BOD and COD and to compare it with the Interim National Water Quality Standard (INWQS) for Malaysia.
- To analyze the concentration level of heavy metals such as Hg, As, Pb, Cu, Cd, Cr, Zn and Ni in water, plants and sediment samples using NAA and ICP-MS techniques.
- To compare the result of elemental concentration in this study with the recommended level by the Interim National Water Quality Standard (INWQS) for Malaysia and the DOE Water Quality Criteria for protection of aquatic life
- To conduct correlation studies on the uptake of heavy metals such as Hg, As, Pb, Cu, Cd, Cr, Zn and Ni in river water, plants and sediment samples.
- To observe the trend of heavy metal pollution based on uptake and accumulation of a plant species.