HEAVY METAL DISTRIBUTION IN SUSPENDED LOAD AND BED LOAD AT THE PERAI RIVER

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by

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ABSTRAK

Pulau Pinang kini menghadapi masalah dengan berkaitan persempadanan Sungai Muda di antara dua negeri Kedah dan Pulau Pinang. Oleh itu, Sungai Perai merupakan sumber air alternatif kepada Pulau Pinang untuk pengambilan air baharu. Objektif kajian ini adalah untuk mengenal pasti logam berat dalam pepejal terampai dan bahan dasar dan mewujudkan korelasi antara logam berat dalam pepejal terampai, sampel pukal, dan bahan dasar. Empat logam penting, iaitu besi, merkuri, aluminium, dan zink diperoleh daripada pepejal terampai, sampel pukal, dan bahan dasar di sebelas tempat pengambilan sampel . Pengambilan sampel telah dijalankan pada bulan Februari dan April dan, sampel air sungai dan bahan dasar telah diproses dan dianalisis untuk logam berat; Al, Hg, Zn, dan Fe, menggunakan ICP-OES. Logam berat yang ditemui di sungai berada dalam julat: untuk jumlah Hg iaitu sebanyak (0.1175-0.4202 mg/L); Al (6.4358-103.0910 mg/L); Fe (1.5837-41.2027 mg/L); Zn (0.0618-0.3315 mg/L), untuk pepejal terampai Hg (0.0131-0.2149 mg/L); Al (2.0788-44.6050 mg/L); Fe (1.0110-27.6687 mg/L); Zn (0.5514-7.5588 mg/L), dan untuk bahan dasar Hg (0.0115-0.1577 mg/L); Al (531.7650-6710.72 mg/L); Fe (165.1470-2056.1300 mg/L); Zn (1.3631-13.6802) untuk setiap kepekatan logam berat masing-masing. Korelasi antara kepekatan logam berat dalam jumlah pepejal terampai, dan bahan dasar telah meluputi kesemua titik pengambilan sample dan ianya mempunyai korelasi linear yang sangat baik. Keputusan yang dicapai oleh regresi linear ini adalah dalam persetujuan yang sangat baik dengan nilai yang diukur secara bebas untuk kepekatan logam berat pepejal terampai dan bahan dasar. Berdasarkan garis panduan Standard Kualiti Air Kebangsaan (NWQS) dan Kementerian Kesihatan (KKM), empat logam berat ini telah melebihi had maksimum yang dibenarkan dan boleh dikategorikan sangat tercemar untuk Sungai Perai.

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ABSTRACTS

Penang is currently having a problem with the water authority due to the transboundary of the Muda River between two inter-states Kedah and Penang. Therefore, the Perai River is an alternative water resource to Penang and a backup plan for a new water intake. The objective of this study to identify the heavy metals in suspended load and bed load and establish the correlation between heavy metals in the suspended load, bulk sample, and bed loads. Four significant metals, namely iron, mercury, aluminum, and zinc were obtained from the suspended load, bulk sample, and bed loads at eleven sampling points within the catchment. Sampling campaigns were conducted in February and April within the basin. The river water and bed load sample were processed and analyzed for heavy metals; Al, Hg, Zn, and Fe, using ICP-OES. The heavy metals found in the river were in range: for total recoverable Hg (0.1175-0.4202 mg/L); Al (6.4358-103.0910 mg/L); Fe (1.5837-41.2027 mg/L); Zn (0.0618-0.3315 mg/L), for suspended loads Hg (0.0131-0.2149 mg/L); Al (2.0788-44.6050 mg/L); Fe (1.0110-27.6687 mg/L); Zn (0.5514-7.5588 mg/L), and for bed loads Hg (0.0115-0.1577 mg/L); Al (531.7650-6710.72 mg/L); Fe (165.1470-2056.1300 mg/L); Zn (1.3631-13.6802) of concentration heavy metal respectively. The correlation between the concentration of heavy metals in total recoverable suspended loads, and bed load hold for all sampling points has very good linear correlations. The results achieved by these linear regressions were in very good agreement with independently measured values for the concentration of heavy metals in total recoverable, suspended loads, and bed load taken at the same sampling points. Based on the National Water Quality Standard (NWQS) and Ministry of Health (MOH) guidelines, these four heavy metals exceeded the maximum permissible limit and as far and is very highly polluted in the Perai River.

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LIST OF ABBREVIATIONS

Ag	Silver
As	Arsenic
Cd	Cadmium
Cu	Copper
Pb	Lead
Hg	Mercury
Al	Aluminium
Fe	Iron
Ni	Nickel
Cr	Chromium
TSS	Total suspended loads
NPS	Non-point sources
DOE	Department of Environment
SPM	Suspended particular matter
MR	Main River
GPS	Global Positioning System
HNO_3	Nitric acid
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
IWK	Indah Water Konsurtium
MOH	Ministry of Health
NWQS	National Water Quality Standard

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CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metals are metallic elements with a high density, specific gravity, or atomic weight that have toxic characteristics (Khan and Saleem, 2018). With population growth, urbanisation, and the latest technological developments, the daily accumulation of heavy metals in our environment (particularly in the river) has increased in recent years because of their toxicity, accumulative tendencies, and persistence in the environment, heavy metals create long-term severe health risks to humans, with the potential for environmental change into even more toxic compounds (Ayenimo, Adeeyinwo and Amoo, 2005). Therefore, in most developing countries metropolitans, river water pollution has become more of a concern due to heavy metals.

According to the previous study (Paul, 2017), bioaccumulation and biomagnification may occur due to heavy metals entering the environment. These heavy metals are not easily degradable and can build up to dangerous levels in animal and human bodies, causing unpleasant effects beyond a certain threshold. Heavy metal exposure has been related to mental retardation, kidney damage, cancer, and even fatalities in high-exposure cases.

However, heavy metals impact aquatic habitats and are a major role in pollution migration and river transformation (Li *et al.*, 2019). Heavy metals are a component of the ecosystem and aquatic zone building in stationary water (Vercruysse, Grabowski and Rickson, 2017; Hu *et al.*, 2019). Hence, heavy metals are crucial in managing the water

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and bed load response rate, the food chain cycle, and the metabolic rate of biota (Turner and Millward, 2002; Al-Saadi *et al.*, 2010).

Heavy metals are released into the environment as a result of anthropogenic activity from a variety of sources, including as excrement, runoffs, automobiles, roadwork, landfills, and garbage dumps. Metal mining, smelting, foundries, and other metal-based businesses are the main sources of heavy metal pollution. The use of herbicides, insecticides, fertilisers, and other heavy metals in agriculture has been another secondary cause of heavy metal contamination (Briffa, Sinagra and Blundell, 2020).

Then, to be more specific the contributors of heavy metals in parts of the Perai rivers are considered to be a nearby urban runoff, riverside industry, fishing and shipping operations, and land transportation pollutants (Foo *et al.*, 2021). Consequently, the Perai River's aquatic biota and water quality will be impacted by industrial effluent that penetrates directly into water bodies, which is considered the main cause of environmental toxicity (Singh and Singh, 2006). Accordingly, the most significant anthropogenic sources of heavy metals in the Perai River are a variety of industry and home waste. The continued discharge of home sewage or industrial waste into aquatic environments will raise the levels of heavy metals in river water (Ali et al., 2016; Rodríguez Martín et al., 2015; Y. Wang et al., 2010)

Therefore, from that anthropogenic activity either industrial or urbanization will harm the environment, especially on water bodies (Perai river) (Shikazono *et al.*, 2012). Previous studies have found silver (Ag), arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) contamination in several Malaysian rivers, as well as Cd, Pb, and Zn contamination in some coastal bed loads (Zulkifli *et al.*, 2009; Yap *et al.*, 2011).

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One of the major components of the river is bed load. Weathering processes and biological activity combine to generate the bed load, which is consists of sand, organic and inorganic particles. As a result, the form became loose and unconsolidated. In general, these particles were formed naturally as a result of rock weathering and erosion. Because silt is a good geo marker, pollutants can always be discovered through it. Bed load is the ultimate sink for heavy metals, yet it is not indestructible (Hsu *et al.*, 2016). No wonder bed load is an important part of the aquatic environment since it helps shape the landscape and create ecological niches. (Vercruysse, Grabowski and Rickson, 2017; Wang *et al.*, 2018). Additionally, bed load serves as a pollutant trap, and it's been recognised as a useful method for analysing environmental concerns (Simpson *et al.*, 1995). Hence, the links between the environment and anthropogenic variables can thus be identified by researching bed load and its associated pollutants.

The bed load carried by a river or stream is typically a mixture of bed load originating from various sites and source types within the contributing watershed. As a result, a relatively small section of the catchment, for example, could contribute the majority of the bed load at the watershed outflow if it is underlain by a specific rock type or supports a specific land use. Therefore, information on bed loads in rivers serves as a particle signal, providing information on particle-related pollution within a river's reach (Walling, 2005). Pollutant concentrations on bed loads in small to medium-sized catchments remained consistent over time at a given location, indicating that they are likely a reflection of urban/industrial pressure and/or geological history in the upstream area. Schwientek et al. (2013) found that bed load concentrations are favourably connected with catchment population density and negatively correlated with specific bed load yields.

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Heavy metal is also easily transferred to water bodies by suspended loads carriers (Nasrabadi *et al.*, 2018). As a result, suspended particles have been extensively studied as vectors of potentially accessible metal species in recent years (Beck *et al.*, 2013; Beltaos and Burrell, 2016; Helali *et al.*, 2016; Pourabadehei and Mulligan, 2016). As mentioned previously, heavy metal is usually transported by SS, simultaneously, and the fate of suspended particle matter (SPM) emitted into the water will be considered (Helali *et al.*, 2016). SPM has an average particle size of 0.45–63 μm and can combine with contaminants and deposits at the river's bottom (Zheng *et al.*, 2008; Lamba, Karthikeyan and Thompson, 2015). The physical and chemical properties of SPM in river systems are incredibly complicated (Droppo *et al.*, 1997). Pollutants are absorbed on the surface of SPM by various mechanisms, including mobility, bed loadation, suspension, and resuspension, and subsequently carried downstream, resulting in significant water quality degradation. The most important elements impacting chemical migration in water are the amount (concentration), quality (surface activity), and composition of SPM (Horowitz, 2008).

1.2 Problem statement

Water is essential for us, especially in regional economic development (Sim *et al.*, 2018) and plays a crucial role in industrial, domestic, agricultural, aquaculture, hydroelectric power generation and the environment as a water source (Mei, Carr and Weng, 2017). River basins in Malaysia usually have been shared by two or more states, and the issues regarding water disputes are common. Recently, Penang is currently having a problem with the water authority due to the transboundary of the Muda River. The controversy about water disputes overuse of the Muda River started between two inter-states Kedah and Penang due to the government of Kedah's logging of the Ulu Muda

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Forest Reserve. The total area of logging at Ulu Muda Forest is 25,000 hectares, equivalent to 15.3% of the total Ulu Muda water catchment area will be destroyed and at the same time will affect the water quantity and water quality in Penang (Jaseni, 2020). Therefore, the Perai River is an alternative water resource to Penang and a backup plan for a new water intake.

In addition, the continuous growth of commercial and industrial activities has resulted in a high population growth rate in Perai. The study area's population grows year after year as a result of its attractive setting. Rising living standards and industry growth have resulted in and will continue to result in greater water use, as well as increased waste discharge into natural waterways and the sea. (Ayub *et al.*, 2004). Therefore, it would increase the potential for heavy metals pollution. From the previous study also by Ayub et al. (2004) the study area which is the Perai river is heavily contaminated by industrial and commercial waste. The untreated wastewater may contain harmful materials and high pollution levels, poisoning the stream and destroying the aquatic ecology in the process. As a result, thousands of dead fish have been discovered in the Perai river, including catfish and spotted scats, which are thought to be the result of untreated water dumped into the river by a neighbouring plant.

Bed loads, which are the main source and sink for heavy metals and play a large role in the transit and storage of potentially hazardous metals, are the main problem in the river system aside from that. These bed loads likely contained heavy metal. Based on these study by (Burton, Phillips and Hawker, 2006; Durán, Sánchez-Marín and Beiras, 2012; Alonso Castillo *et al.*, 2013), the study of the overlying water column has also offered more important strategies for a better understanding of the early identification and partitioning dynamics of heavy metals than the bed loads have due to discontinuities

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and changes in water flows (Alonso Castillo *et al.*, 2013). On the other hand, heavy metals have also been transported using suspended loads or suspended particles. Hou et al. found that more than 90% of the heavy metal burden in aquatic systems is derived from suspended particles and bed loads, with just a minor amount of free metal ions remaining dispersed in water. (Amin *et al.*, 2008; Zheng *et al.*, 2008; Zahra *et al.*, 2014) The issue of heavy metals conveyed by suspended particles and silt in the river motivated this investigation. Therefore, it is useful to research how heavy metals are distributed in silt and suspended particles.

1.3 Objectives

This study aims to obtain the current pollution level in terms of heavy metals in the Perai river, Seberang Perai, Penang. The study is carried out to achieve the following two main objectives:

a) To identify the heavy metals in suspended loads and bed loads

b) To study the relationships between heavy metals in the suspended load, bulk sample, and bed loads at the Perai River

1.4 Scope of study

The study focused only on four metals which is mercury (Hg), aluminium (Al), zinc (Zn), and iron (Fe). According to a literature review, these heavy metals were considered common in the area. The study also focused on the Perai River, which will determine whether it is suitable for future water intake in Penang.

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1.5 Significance of the study

Water contamination and degradation are a major concern in developing countries, aggravated by increasing anthropogenic activity. It is posing a risk to the functionality and usage of current natural water supplies. This can be linked to the worldwide trend of increased industrialization, resource exploration, and diversification of national development goals (Kithiia, 2011).

The justification for this study is that pollution of water resources is one of the key reasons for freshwater scarcity along the Perai river, prompting the need for freshwater sources and supplies to be conserved. Humans and organisms are both endangered by heavy metal contamination. Availability of freshwater supplies for domestic usage is also impacted by heavy metal pollution.

The weathering of rocks and soil, the release of municipal and industrial trash into waterways, and anthropogenic activities are just a few ways heavy metals reach the environment. The increased level of heavy metals in the soil will cause a rise in the concentration of heavy metals in crops, which will also result in a considerable rise in the concentration of heavy metals in the human diet. In order to assess the level of contamination in the Perai River, it was justified to investigate the concentrations of heavy metals in bed loads and suspended loads. Therefore, it will support future water intake decision-makers in making informed decisions.

From the laboratory analysis, we can obtain the concentration of heavy metals in bed load and suspended loads through the ICP test. Hence, the findings of this study will act as a guide for future research in this area.

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1.6 Thesis outline

Chapter 1: Introduction – General description of the study that includes the problem statement, objectives to achieve and scope of work to be carried out.

Chapter 2: Literature Review -This chapter's content discusses previous research on the importance of heavy metals in suspended loads and bed loads. This chapter's content discusses earlier studies that were involved in the investigation into the sources of heavy metals and the effects of their presence in river systems on various aspects of the environment, including human health.

Chapter 3: Methodology - Describing each step that was taken throughout the earlier investigation. The study region is introduced in this chapter, followed by a description of the sample analysis. This chapter will also cover the study area, sampling techniques, and data analysis methods.

Chapter 4: Results and Discussion - The results of the study are discussed in this chapter including the assessment level of concentration of heavy metals in suspended loads and bed loads base on the standard by National Water Quality Standard (NWQS) and Ministry of Health (MOH), as well as to study the relationships between heavy metals in the suspended load, bulk sample, and bed loads at the Perai River

Chapter 5: Conclusion and Recommendation - This chapter concludes the findings of this study and provides suggestions to mitigate the problem in the Perai River.

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CHAPTER 2

LITERATURE REVIEW

2.1 Heavy metals

2.1.1 Accumulation of heavy metals in river

Pollution levels in the water, such as rivers and lakes, can be determined by pollutants in the water (Morata *et al.*, 2019). Research on water pollution and the reasons that contribute to it, as well as the areas prone to pollution in the surrounding river sections, is usually required for the water quality assessment (Yan *et al.*, 2015). Water quality in rivers has been declining worldwide (Schwarzenbach *et al.*, 2010; Lintern *et al.*, 2018), and Malaysian river systems are no exception. The Department of Environment has been constantly monitoring the Perai River due to its low water quality standards.

Due to their availability at trace concentrations (ppb to less than 100 ppm) in a variety of environmental matrices, heavy metals are also classified as trace elements (Kabata-Pendias, 2010). Temperature, phase association, adsorption, and sequestration are physical factors impacting their bioavailability. Additionally, chemical parameters including octanol/water partition coefficients, complexation kinetics, speciation at thermodynamic equilibrium, and lipid solubility are important. Other significant biological feature include species traits, trophic interactions, and physiological and biochemical adaptation (Tchounwou *et al.*, 2012).

Heavy metals are harmful to the environment and people's health because of their toxicity and mobility (Kamaruzaman *et al.*, 2017; Raznisyafiq *et al.*, 2021). Heavy metal contamination is an issue in developing countries, say (Akcay, Oguz and Karapire, 2003; Olivares-Rieumont *et al.*, 2005; Wang *et al.*, 2010; Li *et al.*, 2012). Heavy metals such as aluminium, cadmium, copper, iron, lead, manganese, nickel, selenium, and zinc exist there because they cannot be eliminated from the environment or broken down (Selvi *et al.*, 2019).

Several factors, such as river flow, slope gradient and length, particle size, erosion, and deposition, impact the transit of suspended particles and deposits in the riverbed. In rivers, heavier loads can be carried by strong flows whereas lighter loads, like fine silt, can be carried by low flows. Figure 2.1 depicts the size-dependent distribution of mineral and organic colloids in aquatic environments. In suspended bed load systems, two main parts can be distinguished. The particulate fraction (diameter > 0.2 m) sinks fast to the bed bed loads, whereas the colloidal fraction (diameter 0.2 m) stays suspended longer and may help transfer adsorbed organisms across significant distances (Blo *et al.*, 2002). Surface area, settling speed, and deposition rate of suspended bed load can all be calculated.

Changes in river discharge from one season to the next can impact the mobility and concentration of metals. In a river system, metals are transmitted in dissolved form and adsorb to the surface of suspended particulate matter (Bibby and Webster-Brown, 2006). River movement is crucial for the transportation of metal. Fine material, as opposed to large particles, is better suited to transferring metals at low river flows because it can better control metal migration. A larger volume of water carrying a significant amount of silt increases in the overall metal burden. Compared to the load when the flow is high, there are many more metals in the river system when the flow is low (Gallo *et al.*, 2006).

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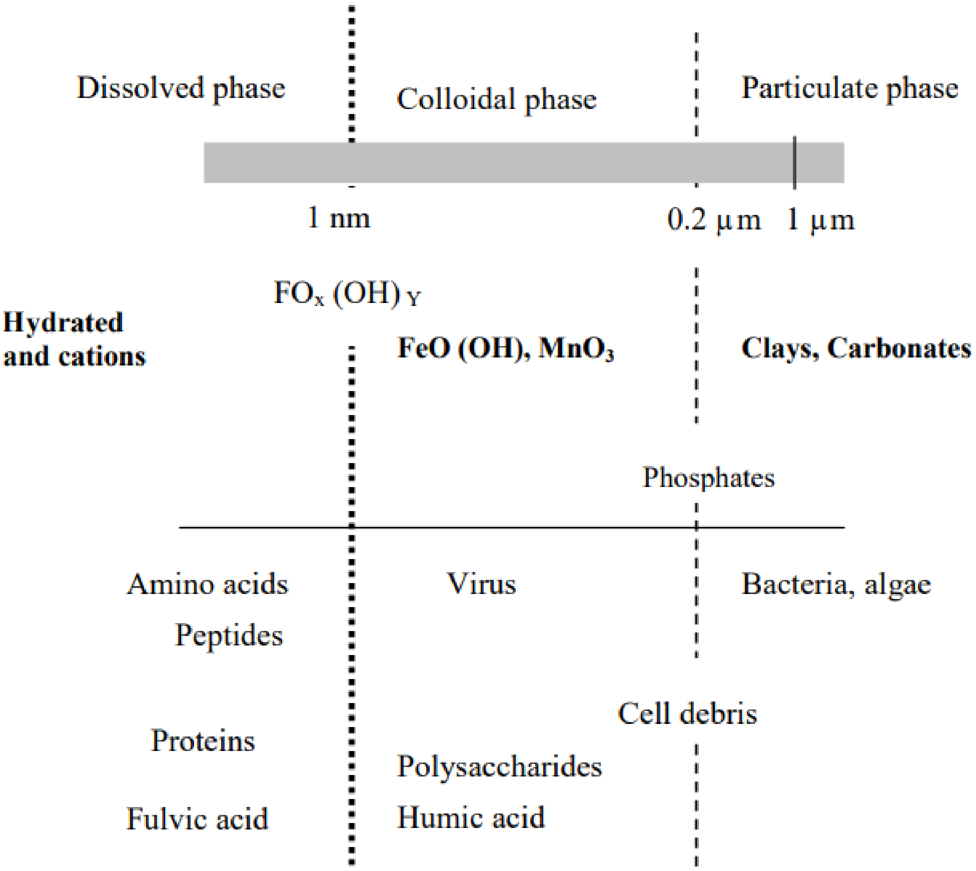

Figure 2.1 Distribution of mineral and organic colloids as a function of size in aquatic systems (Buffle and Leppard, 1995)

Concentrations of heavy metals have risen due to anthropogenic activities and negligent home sewage discharge (smelting, which releases arsenic, copper, and zinc; pesticide applications, which releases arsenic; and fossil fuel combustion, which releases nickel and selenium). Runoff or aerial deposition transports these concentrations into freshwater habitats (Gall, Boyd and Rajakaruna, 2015; Masindi and Muedi, 2018). For instance, lakes, rivers, and reservoirs become the primary water supply for all living organisms. Additionally, river water is dispersed and absorbed anthropogenic pollution, which directly affects aquatic life and human health (by drinking water) (Wee *et al.*, 2016).

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The global occurrence concentration ranges of aluminium, arsenic, copper, iron, and zinc in freshwater habitats are between 0.1 and 0.2 mg L-1, 12–2 g L-1, 0.005–30 mg L-1, 0.5–50 mg L-1, and 0.01–0.05 mg L-1, respectively, according to statistics from the World Health Organization (WHO) (Herschy, 2012). In addition, the investigations also showed that natural freshwater habitats had occurrence concentrations of cadmium, lead, manganese, nickel, and selenium that are less than 1 g L-1, 5 g L-1, 0.1 mg L-1, and 0.02 mg L-1, respectively.

Bed load, a crucial element of riverine ecosystems, serves as a source and sink for heavy metals (Pejman *et al.*, 2015; Huang *et al.*, 2019). Most heavy metals that enter rivers instantly settle in the bed load, which is far more concentrated in the bed load than in the river's water body (Shyleshchandran, Mohan and Ramasamy, 2017; Liu *et al.*, 2018). When physicochemical or hydrological circumstances change, heavy metals in the bed load may desorb or resuspend, generating secondary pollution in the water body (Liang *et al.*, 2015; Kouidri *et al.*, 2016). Benthic creatures are directly impacted by the build-up of heavy metals in bed load, and many other organisms are indirectly impacted via the food web (Krasnići *et al.*, 2013; Fu *et al.*, 2014).

2.1.2 Heavy metals in bed loads

One of the river's main constituents is bed load. Sand and other organic and inorganic particles that are precipitated as a result of weathering and biological activity make up the bed load. As a result, the form was loose and unconsolidated. The main source and repository of heavy metals in the aquatic environment is bed load, and bed loads are essential for the movement and storage of potentially dangerous metals (Yan *et al.*, 2009; Gao and Chen, 2012). The distribution of heavy metals in the sand close to

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populated areas can be used to assess the dangers of discharging human waste and provide proof of anthropogenic effects on ecosystems (Demirak *et al.*, 2006). Determining the bed load's quality is, therefore, an essential step in figuring out a result, determining the quality of bed load is a crucial step in determining the danger of man-made pollution in aquatic systems.

Because of their ability to absorb dissolved metals, bed loads are regarded to be the most sensitive indicator of trace metals. They can also be a non-point source of trace metals by releasing them into water column when they undergo physio-chemical changes (Karbassi *et al.*, 2007; Sharma and Subramanian, 2010). Due to their prolonged residence time and potential to document the history of contamination in aquatic ecosystems, assessment of bed bed load quality is frequently regarded as the most crucial step in identifying the anthropogenic input of trace metals in the aquatic environment (Tuna *et al.*, 2006).

Different mechanisms, such as changes in pH and redox potential, bed load resuspension, and the movement of contaminated benthic biota into the surrounding water, can cause heavy metals bound in bed loads to be released (Darvish *et al.*, 2012; Zhao *et al.*, 2014). The introduction of runoff from agricultural and nearby coastal lands as well as riverine fluxes are examples of anthropogenic activities that contribute to the spread of heavy metals in river systems. Other natural processes include rock weathering and riverbed erosion (GUVEN and AKINCI, 2008; Hosono *et al.*, 2010; Wang *et al.*, 2010). Bed load is the ultimate sink for heavy metals, yet it is not indestructible (Hsu *et al.*, 2016).

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Bed load metal deposition has negative environmental effects on both river water quality and nearby inhabitants. For instance, many freshwater invertebrates depend on bed load for feeding and are vulnerable to toxic metal bioaccumulation. Numerous top-of-the-food-chain animals, such as birds, fish, and humans, could be put in danger by this bioaccumulation. Additionally, a significant risk to nearby consumers is posed by the remobilization of metals from agricultural areas into crops during the reclamation of the metal-contaminated river and stream bed loads (Demirak *et al.*, 2006). Over 99 percent of pollutants are maintained in bed loads, which act as significant sinks and carriers for toxins in aquatic ecosystems, while less than one percent of pollutants are dissolved in water throughout the hydrological cycle (Filgueiras, Lavilla and Bendicho, 2004).

It's possible that contaminated bed load does not always contain heavy metals. As a result, contaminants may desorb from the particles and release them into the aqueous phase in response to changing environmental conditions. Although they can be a long-term exposure source for ecosystems, heavy metal-contaminated bed loads pose a short-term threat to biodiversity (Ghosh *et al.*, 2011). However, there are a variety of chemical forms of heavy metals that can be found in bed loads, each having a unique set of physical and chemical characteristics in terms of chemical interactions, mobility, biological availability, and potential toxicity (Singh *et al.*, 2005; LIU *et al.*, 2008; He *et al.*, 2011).

On the other hand, the mineralogy, size, and dispersion of the bed loads impact the concentration of pollutants deposited in bed loads. Minerals like Fe and Mn oxides tend organic molecules like carbohydrates could absorb trace elements (Filgueiras, Lavilla and Bendicho, 2004). As adsorption capacity rises with smaller particle sizes, absorbed trace metals can be released back into the water body because the entire process

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is reversible and regulated by pH and redox potential (Kashem and Singh, 2001; Filgueiras, Lavilla and Bendicho, 2004; Jain, 2004).

When metals are bonded to mineral surfaces and linked to carbonates, Fe-Mn oxides, organic matter, sulphides, and the lattice of refractory crystalline minerals like silicates, they interact with the bed load matrix through a number of binding mechanisms (Gleyzes, Tellier and Astruc, 2002; Fytianos and Lourantou, 2004; Gao and Li, 2012). The composition of the bed load particles, the characteristics of the compounds that are adsorbed, and the prevailing physicochemical conditions all influence and govern the accumulation and mobility of heavy metals in bed loads, even when low concentrations of heavy metals are present in the surrounding water column (Sahuquillo, Rigol and Rauret, 2003; Christophoridis, Dedepsidis and Fytianos, 2009; Gao and Li, 2012).

Heavy metal concentrations in bed loads vary depending on particle bed location, heavy metal deposition, particle size, and the presence or absence of organic content in the bed loads. Because bed loads serve as key reservoirs for pollutant-heavy elements, they have been utilised to track pollution in aquatic ecosystems (Salomons *et al.*, 1987). Several studies have demonstrated that bed loads in rivers can accumulate heavy metals from the water column, acting as sinks for metals transported in by feeder streams (Harding and Whitton, 1978). The capacity of bed loads to absorb and retain pollutants, on the other hand, is determined by their composition. The adsorption capacity of heavy metals is proportional to their surface area and surface characteristics (Filgueiras, Lavilla and Bendicho, 2004).

On the other hand, these bed load quality indicators either set a qualitative threshold or focus on a single metal's ecological risk assessment. Heavy metal pollution,

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on the other hand, usually takes the form of complex combinations in the environment. Therefore, metal pollution's synergistic impacts, rather than individual metal effects, may be of greater significance. In worst-case circumstances, the potential negative effects of hazardous substances (such as heavy metals) in the same medium can be presumed to be cumulative (Neff, Stout and Gunster, 2005).

On the other side, it might be easier to detect temporal changes in dissolved or suspended metals. The assessment of trace metal distribution across several phases in an aquatic environment should therefore serve as the foundation for an efficient water management programme (Davide *et al.*, 2003). It is not enough to determine the total amounts of metals in bed loads to anticipate to mobilize these elements. The chemical form of trace metals, which affects their mobility, bioavailability, and toxicity to organisms, has a significant impact on how they behave in the environment (Davide *et al.*, 2003; Tuzen, Sari and Soylak, 2004; Bacon and Davidson, 2007)

2.1.3 Heavy metals in total suspended loads

One of the criteria used to detect pollution in water is total suspended loads. This parameter's concentration number can be used as a benchmark for measuring the level of pollution present. Large suspended load values will have an impact on the environment in these waters. Suspended load concentrations can be determined in the lab using a variety of procedures used by numerous environmental analysts, one of which is the Gravimetric method. The value of suspended load in relatively shallow water environments such as coastal locations can vary based on numerous factors such as coastline topography, river flow to the coast, seawater tides, and currents (Wibisana, Soekotjo and Lasminto, 2019).

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Because a large portion of urban and industrial areas contain regions with artificially created impermeable areas, such as roads, parking lots, and rooftops, the amount of runoff that does not undergo any treatment processes is greater than the amount that is absorbed into the surface during rainfall. Rainfall-runoff has been identified as a substantial non-point source of heavy metal contamination, and studies have consistently shown that water quality is deteriorating. Suspended loads management and monitoring are essential due to non-point sources of particulate matter that travel through rainfall-runoff and accumulate large concentrations of pollutants (Jeong *et al.*, 2020).

The suspended particle load in urban runoff is a substantial pollutant that degrades the clarity of the water in receiving bodies of water. Since heavy metals and other contaminants highly attracted to particles, stormwater treatment systems almost always include a particle separation process. Suspended loads, a performance measure that is often employed in urban stormwater planning and analysis, is based on this theory. Though research has questioned the efficacy of utilising suspended load as a reliable indicator in stormwater, it is common practise to quantify suspended load concentrations to characterise the suspended particles in the runoff.

Dissolved load, suspended loads, and bed load are heavy metals that consist of the three groups of heavy metals in the aquatic system. The dissolved phase has a lower concentration than the suspended loads phase, even though it is regarded to be more damaging to aquatic life and humans. Because of their large surface area and reactivity, floating particles readily absorb the dissolved heavy metals. Because of this, emphasis has been paid more to heavy metals in the suspended load phase than in the dissolved phase (Zhang *et al.*, 2014).

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Additionally, before being exported to the ocean, heavy metals in the fluvial environment are largely conveyed by suspended particles in the aquatic system and sink there. According to the past research, more than 90% of loads are transported in suspension, with the bed load at estuaries making up less than 10% and frequently than 1% of the total load delivered by a river to the ocean. In addition, heavy metals tend to collect in suspended loads in river water due to their proximity to water, and the primary way that heavy metals accumulate in bed loads is by the deposition of suspended particles that have been exposed to metal ions. Surface bed silt was contaminated due to the interrupted water flow. This is a key mechanism for ecological worries about heavy metals at the bed load-water interface. As a result, numerous countries have carried out substantial research on heavy metals in suspended loads, their impacts on the fluvial ecosystem, and their fluxes to the ocean (Zeng *et al.*, 2019).

This redistribution mechanism is crucial because it controls the mobility and toxicity of trace metals in estuaries and coastal waters. In addition, physical mixing and the biogeochemical processes that take place in transitional waters have an impact on the chemical composition of the suspended particles in rivers. The chemical composition of suspended loads also correlates with the chemical or mineralogical compositions of the surrounding soils or bed loads, which are the system's primary sources of suspended loads (Beltrame, De Marco and Marcovecchio, 2009).

Because of particle/solute interactions, flocculation, coagulation, and the bed location of particle-bound trace metals, estuaries can act as effective filters for suspended loads and trace metals. Additional processes that impact the behaviour of trace metals in estuaries include re-suspension of bed loads, metal desorption from particles, metal diffusion from bed load pore water to overlying water, mobilisation of Fe and Mn in

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reducing bed loads, and sorption in low salinity and high turbidity zones. Due to the highly dynamic nature of the estuary environment, heterogeneous reactions, and hydrodynamic time scales, estuarine chemistry is particularly challenging. As a result, there is no set pattern to the behaviour of trace metals in estuaries.

In order to better understand natural variability and lay the groundwork for differentiating between natural and anthropogenic loads, it is essential to explore the whole range of estuary types, across the full spectrum of climates, flow regimes, geomorphology, and biological communities.

2.2 Sources of heavy metals pollution

Both natural and man-made sources of heavy metals enter river systems, and as they move from one level to the next, they are distributed to bed loads and biota. The quantity and mobility of metals in the rocks that make up the river's catchment area regulate the trace metal level of the water in the river, and the abundance of metals in those rocks determines the trace metal level of the river water (Masindi and Muedi, 2018).

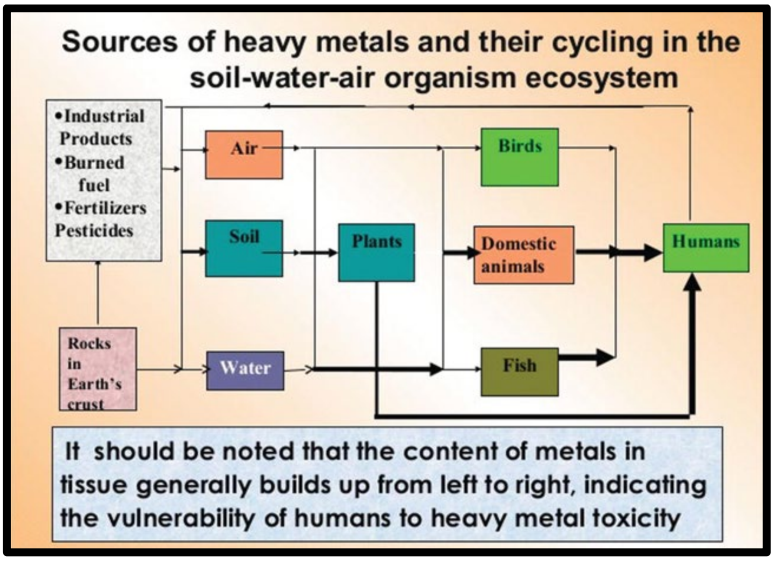

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Figure 2.2 Sources of heavy metals and their environmental cycle (Brady and Duncan, 1994)

2.2.1 NATURAL PROCHAPTER 2CESS

Numerous investigations have uncovered numerous heavy metal natural sources. Heavy metal emissions occur naturally in a range of unusual environmental situations. These emissions can come from a variety of sources, including volcanic eruptions, sea-salt sprays, forest fires, rock weathering, biogenic sources, and wind-borne soil particles. In addition, metals can be discharged into other environmental compartments by natural weathering processes, releasing them from their endemic spheres. Hydroxides, oxides, sulphides, sulphates, phosphates, silicates, and organic molecules are just a few of the many different forms that heavy metals can take. The heavy metals lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn), and copper (Cu) are the most often discovered ones (Cu). Although the heavy metals described above can be present in humans and other mammals in very small concentrations, The aforementioned heavy metals are present in humans and other mammals in minimal concentrations, posing substantial health hazards(Herawati et al., 2000).

Soil erosion, especially rock weathering, and the dissolving of water-soluble salts are natural sources. Metals that occur naturally in aquatic ecosystems flow through them without causing harm. They move on their own, unaffected by human activity. Growing public concern about the possible accumulation of heavy metals and other toxins in agricultural soils has been fuelled by deteriorating environmental conditions and a growing reliance on agrochemicals.

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2.2.2 Anthropogenic process

Pollutants are released into various environmental compartments by industries, agriculture, wastewater treatment, mining and metallurgical operations, and runoffs. For a number of metals, it has been discovered that anthropogenic usage of heavy metals outweighs natural fluxes. The majority of the metals found in wind-blown dust come from commercial locations. Anthropogenic sources that significantly contribute to the contamination of the environment with heavy metals include insecticides, which release arsenic, lead, copper, and zinc, smelting, which releases nickel, vanadium, mercury, selenium, and tin, and burning fossil fuels, which releases nickel, vanadium, mercury, and tin. The routine production of goods to satisfy the demands of a big population has been found to cause human activities to contribute more to environmental damage (He, Yang and Stoffella, 2005).

Land use is the term for how people use terrestrial space for things like commerce, habitation, recreation, conservation, and governmental functions. The idea of land use has a significant impact on how human communities develop. Patterns of societal evolution and land use have had an impact on regional and global ecosystems from prehistoric times. Current development patterns, the characteristics of the natural environment, and the outcomes of prior development attempts all influence future development potential and the necessity to repair or restore environmental resources. The term "land usage" describes how humans use lands and its resources. These areas' physical features result from many years of interaction between people and the environment.

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Using a range of physical, chemical, and biological criteria, (Giri and Qiu, 2016) claim that water quality is an assessment of the use of water for a number of purposes, including drinking, industrial, agricultural, recreational, and habitat purposes. Water quality is important to all life on Earth; hence it is of interest to a wide spectrum of scientists, researchers, and managers of water resources. The water's quality is impacted by the place, time, weather, and pollution sources (Giri and Qiu, 2016). Due to the existence of point and non-point sources (NPS), it is difficult to maintain the quality of the water. NPS pollution is a natural occurrence, hence it cannot be completely eliminated. However, human activities can greatly impact on how quickly pollution is produced at the source, which is a problem. NPS pollution is an ongoing natural occurrence that will never completely go away. Finding activities that significantly worsen water quality and developing management plans to address problems are difficult when dealing with non-point source pollution. On the other hand, human action has the potential to significantly affect the rate of pollution at the source. The following elements were included in Browne's 1989 definition of NPS contamination:

- Non-point sources are pervasive, extend over extensive areas and "background-contaminate" natural lands as a result of or in response to human activity.
- Land use, geological, and hydrological factors can affect non-point source pollution, which can change daily or annually. Society only influences issues related to land management.
- The hydrological cycle involves the production and movement of non-point sources. Deteriorated soil particles are transported by surface runoff from permeable places. Additionally, it transfers and absorbs pollutants that are

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dumped in impermeable spaces. Contaminants from septic tanks and landfills are carried by groundwater.

- Urban runoff contains suspended particles, metals, bacteria, aerobics, nutrients, and lipids. Vehicles, the use of fertilisers and pesticides, animal manure, construction work, and road pickling are a few examples of

Due to changes in land use brought on by urbanisation, industrialisation, and agriculture, which can impact runoff quality and quantity, watershed surface characteristics can also change. Indicators of both land use and water quality are related to determine the effect of changes in land use on water quality (Buck, Niyogi and Townsend, 2004; Baker, 2005; Li *et al.*, 2008; Giri and Qiu, 2016). All of this research found a strong relationship between land use and water quality indicators. In general, watersheds with larger proportions of human activity and economic development tend to have higher levels of water pollution, whereas watersheds with lower proportions of human activity and economic development tend to have better water quality. Due to the vast region and challenging monitoring, information of such connections at a watershed scale throughout seasons is currently insufficient (Rodrigues *et al.*, 2018).

The contamination of river waterways seriously endangers the public's health in Malaysia. In Malaysia, the Department of Environment (DOE) is in charge of monitoring river water quality. The DOE (2018) claims that the monitoring programme for Peninsular Malaysia started in 1978. In 1985, the monitoring programme was expanded to include Sabah and Sarawak; in 1998, the Island's Marine Water Quality Monitoring Program was added. Currently, 233 coastal and estuarine monitoring stations have been built in 73 islands across all of Malaysia. There are 86 sites for the DOE's island

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monitoring programme (2018). The four subcategories of these islands are marine parks, protected islands, holiday islands, and development islands. The monitoring program also includes in-situ measurements of water quality parameters including pH, temperature, dissolved oxygen, turbidity, conductivity, and salinity. Laboratory evaluations of parameters like Escherichia coli, cadmium, copper, mercury, and lead are also included. Four to six times a year are selected for sampling. Important data on the water quality conditions of many water bodies are obtained through this monitoring activity.

Emissions from industry, agriculture, and transportation affect SPM concentrations (Harrison *et al.*, 2003; Atafar *et al.*, 2008; Park and Dam, 2008). When there is industrial activity, the levels of heavy metals such As, Cd, Cu, and Zn increase in the environment (Park and Dam, 2008). Direct release of polluted gas into the atmosphere results in the creation of dust as it interacts with other airborne particles. While some of the dust enters the river by air precipitation or rainfall and settles on roads, farms, and other surfaces, other portions enter the river and contribute to the SPM cycle in the fluvial ecosystem. In addition to industrial waste, sewage that has been contaminated by industrial output is thrown directly into the river through the outlets, worsening the SPM contamination in the river.

Furthermore, automobile exhaust emissions are a significant cause of SPM build-up. Similar to how industrial gas is released, so is automobile exhaust. High concentrations of Cu, Zn, and Pb are heavy metals linked to urban mobility (Harrison *et al.*, 2003); in Beijing road dust, and traffic-related exhaust emissions are responsible for 34.47 percent of the heavy metal content (Men *et al.*, 2018). Heavy metal deposition in the soil is facilitated by the use of chemical fertilisers and pesticides in agriculture (Atafar