# SPATIAL AND TEMPORAL ANALYSIS OF HEAVY METALS DISTRIBUTION IN SUNGAI PERAI

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**SCHOOL OF CIVIL ENGINEERING**
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# SPATIAL AND TEMPORAL ANALYSIS OF HEAVY METALS DISTRIBUTION IN SUNGAI PERAI

by

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I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

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# ABSTRAK

Logam berat adalah komponen umum di permukaan air, namun kepekatannya berubah secara dramatik. Kajian ini bertujuan untuk menentukan taburan logam berat di Sungai Perai untuk mengenal pasti kawasan dengan kepekatan logam berat yang tinggi dan menilai analisis temporal logam berat di Sungai Perai dalam hubungan antara kepekatan logam berat dan kesan pasang surut. Sungai Perai dikelilingi oleh kawasan perindustrian, dan itulah sebabnya ia dipilih sebagai kajian kes. Kepekatan logam berat ditentukan menggunakan ICP-OES, sementara perisian ArcGIS Pro digunakan untuk menghasilkan peta taburan spasial dan Microsoft Excel digunakan untuk menganalisis nilai kepekatan logam berat. Berdasarkan kajian, taburan logam berat di Sungai Perai menunjukkan bahawa nilai kepekatan besi yang tinggi dikesan pada P1, P2 dan P3 semasa air surut dan air pasang. Kepekatan tembaga yang tinggi dilihat pada P2, P4, P9 dan P10 semasa air surut dan P12 semasa air pasang. P1, P2 dan P3 telah menunjukkan kepekatan zink yang tinggi semasa air surut dan sementara itu, P2 telah menunjukkan kepekatan tinggi semasa air pasang. Kepekatan plumbum yang tinggi diperhatikan pada P1 semasa air surut dan P13 dan P14 semasa air pasang. Terakhir, mangan menunjukkan kepekatan tinggi pada P5 semasa air surut dan P2, P4, P5, P6 dan P7 untuk air pasang. Untuk analisis temporal, untuk besi, titik persampelan yang tidak mematuhi Kelas IV berada pada P9 semasa air surut dan P10 semasa air pasang. Untuk tembaga, semasa air pasang, lokasi pengambilan sampel yang tidak mematuhi Kelas IV adalah P7 dan P12. Kemudian untuk zink, titik persampelan yang tidak mematuhi Kelas IIA adalah pada P4 semasa air surut. Terakhir adalah mangan, semasa air pasang titik persampelan yang tidak mematuhi Kelas IV berada di P2 dan P7.

# ABSTRACT

Heavy metals are common components on the surface water, however their concentrations were dramatically changed. This study aims to determine the spatial distribution of heavy metals in Sungai Perai to identify the areas with a high concentration of heavy metals and evaluate the temporal analysis of heavy metals in Sungai Perai in the correlation between the concentration of heavy metals and the tidal effects. Industrial areas surround Sungai Perai, and it is the reason it was selected as the case study. The concentration of heavy metals was determined using ICP-OES, while ArcGIS Pro Software was used to generate spatial distribution maps and Microsoft Excel was used to analyze the concentration value of heavy metals. Based on the study, the spatial distribution of heavy metals in Sungai Perai has shown that high concentrations of iron are detected at P1, P2 and P3 during low tide and high tide. A high concentration of copper was spotted at P2, P4, P9 and P10 during the low tide and P12 during the high tide. P1, P2 and P3 have shown a high concentration of zinc during the low tide and meanwhile, P2 has revealed a high concentration during the high tide. A high concentration of lead is noticed at P1 during the low tide and P13 and P14 during the high tide. Lastly, Manganese has shown a high concentration at P5 during the low tide and P2, P4, P5, P6 and P7 for the high tide. For temporal analysis, for iron, the sampling points that do not comply with Class IV are at P9 during low tide and P10 during high tide. For copper, during high tide, the sampling locations which do not comply with Class IV are P7 and P12. Then for zinc, the sampling points that do not comply with Class IIA is at P4 during low tide. Lastly is Manganese, during high tide the sampling points that do not comply with Class IV are at P2 and P7.

## TABLE OF CONTENT

**LIST OF TABLES**

## LIST OF FIGURES

## LIST OF ABBREVIATIONS

| | |
|---|---|
| AFS | Atomic Fluorescence Spectrometry |
| ASS | Atomic Absorption Spectrometry |
| BOD | Biochemical Oxygen Demand |
| Cd | Cadmium |
| COD | Chemical Oxygen Demand |
| Cr | Chromium |
| Cu | Copper |
| EF | Enrichment Factor |
| $Er^i$ | Risk Of Individual Metal |
| Fe | Iron |
| GFAAS | Graphite Furnace Atomic Absorption Spectrometry |
| ICP-AES | Inductively Coupled Plasma-Atomic E mission Spectrometry |
| ICP-AES | Inductively Coupled Plasma Atomic Emission Spectrometer |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometer |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectroscopy |
| IDW | Inverse Distance Weighting |
| Igeo | Geoaccumulation Index |
| Mn | Manganese |
| Pb | Lead |
| RI | Ecological Risk Index |
| TOC | Total Organic Carbon |
| Zn | Zinc |
| P1 | Point 1 |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background Study

Sungai Perai is 24 kilometer long and it is known as the longest river in Pulau Pinang. Sungai Perai has provided source of fresh water for daily use as well as transportation and trading route for settlers and people who resided along the riverbanks prior to the founding of Penang in 1786 (Tern, 2018). According to a study by Mok (2018), along the Sungai Perai, there were a number of rich peat swamp and wetlands which provide home for more than 150 plant species, 125 bird species and 35 fish species. Originally, Sungai Perai was seen to be in good condition. However, the river became contaminated during the fast industrial development as a result of its role as the disposal point for hazardous waste by irresponsible individuals and factory companies (Mok, 2017). The water quality of the river has been classified as Class III, indicating that it is contaminate and requires treatment.

Internationally, the environmental pollution by related industries or food through effluent discharge has given a warning to animals and plants and can eventually endanger human life quality (Olaniyi, Ibrahim. Raphael, Odoh. Nwadiogbu, 2012). In Malaysia, industrialisation has resulted in environmental problems such as air, soil and water pollution (Al-Shami et al., 2011). The discharge of untreated urban and industrial waste into rivers and oceans pollutes the environment (Wan Abdullah et al., 2020). Anthropogenic activities are contributors to toxins in the marine biological system that are highly toxic (A. Ismail et al., 2016). Examples of anthropogenic activities are abandoned boats on the watershed, agricultural activities and untreated wastewater (Dibofori-Orji et al., 2019). Then, the important natural process for environmental pollution is soil and rock weathering and natural disasters such as earthquakes and flooding (Wang, Duan & Wang, 2020).

Even in a low concentration, natural and mainly anthropogenic heavy metals in the environment may cause bioaccumulation in aquatic species (Al-Shami et al., 2011). The definition of bioaccumulation refers to the rise in contaminant concentrations in marine species due to absorption from the surrounding ecosystem contaminant bioaccumulation is aided by a variety of sources of exposure (Blasco, 2016). Urbanization, deforestation, irrigation and drainage of wetlands all negatively affect the aquatic ecosystem (Al-Shami et al., 2011). After that, unlike other contaminants, heavy metals are not biodegradable and can accumulate in sediments over time and metals contamination in sediments can be harmful towards the marine species (Tang et al., 2008).

Heavy metals are part of an ill-defined group of metallic components (Singh et al., 2011). Heavy metals are needed in different amounts by living organisms and the example of heavy metals that requires by humans are iron, cobalt, copper, manganese, molybdenum and zinc (Singh et al., 2011). Even at a low concentration, heavy metals affect human health including neurological diseases and cancers (Fraser et al., 2011). Heavy metals such as mercury, arsenic, cadmium and lead are commonly found in marine species especially fish and seafood, from coastal areas affected by industrial effluent (Wan Abdullah et al., 2020). Heavy metals toxicity in humans has also been linked to severe health issues that worsen over time, impacting organs such as the heart, kidneys, brain, liver and others (Renu et al., 2021).

## 1.2 Problem Statement

Over the last few decades, contamination of the natural environment caused by rapid industrial growth has become a severe problem, especially heavy metals pollution in the aquatic system (Wan Abdullah et al., 2020). There are many studies about spatial and temporal analysis of heavy metals distribution in the most past year. In Hong Kong, a study was conducted at Victoria Harbour, a major port situated in the southeastern part of the Pearl River Estuary. As a result, in the subsurface sediments of the harbour's central region were discovered in high concentration of Cu (Tang et al., 2008). Then, in Italy, there was a study had been carried out at Naples on urban soils. Naples is a heavily populated city, it is situated near the sea and being a part of one of the most heavily populated regions in the world (Imperato et al., 2003). The outcome from this study is that human activity in the Naples urban area has resulted in a high concentration of Cu, Pb and Zn in urban soils (Imperato et al., 2003).

Furthermore, a study was also performed at Liaodong Bay, the Bohai Sea in China on its surface marine sediments. Liaodong Bay is situated closed to the interior sea in China and the northeast of the Bohai Sea. It is the most populous country globally, established economy, culture, education and the most influential scientific and technological force and manufacturing base (Liu et al., 2017). The result from this study is the land-based contaminants discharged were the primary cause of Cd and Az contamination in Liaodong Bay sediment (Liu et al., 2017). In Hong Kong, there was another study about spatial and temporal analysis of heavy metals contamination in sediments of a mangrove swamp. Mangrove sediments are diminished and serve as either sources or sinks of heavy metals as they are in other coastal marshes (Tam and Wong, 1995). Consequently, heavy metals pollution has not been a major issue in the Sai Keng mangrove ecosystem.

Heavy metals are common components of the earth's surface however their geochemical processes and biochemical composition were dramatically changed and they have been polluted by indiscriminate living organisms (Singh et al., 2011). The fact that anthropogenic activities are increasing remarkably in developing countries and still have not been controlled effectively led to heavy metals pollution such as mining, urban construction, drainage and irrigation (Yan et al., 2018). As a result, the emission of heavy metals and their environmental actions have brought concern worldwide (Yan et al., 2018). One of the most chronic contaminants is heavy metals. This is because they would not degrade and accumulate in the food web resulting in potential risk to human health and environmental imbalance (Dibofori-Orji et al., 2019). Even though certain of these heavy metals are essentials as micronutrients, their high concentrations in the food chain may trigger toxicity and environmental impacts and threaten aquatic ecosystems and also their users (Shanbehzadeh et al., 2014).

According to a newspaper report by Ismail (2020), the Pulau Pinang State Government is considering Sungai Perai as a potential alternative source of raw water supply to suit the requirements of the people. Although Sungai Perai's water capacity is insufficient to meet the overall requirements of the people, it can serve as a future source of extra raw water supply for Pulau Pinang. Next, from a newspaper article reported by Othman (2021), there were thousands of fish that died in the Sungai Perai. It was thought that the untreated wastewater discharges from nearby factories were to blame. In most past studies, research on the spatial and temporal analysis of heavy metals distribution had been done in many countries. However, heavy metals studies for Malaysia rivers are uncommon, especially in Sungai Perai. Due to this reason, this study is conducted to provide information regarding this matter.

## 1.3 Objectives

The objectives of this study are as follows:

i. To determine the spatial distribution of heavy metals in Sungai Perai in order to identify the areas with a high concentration of heavy metals.

ii. To evaluate the temporal analysis of heavy metals in Sungai Perai by correlating the concentration of heavy metals and the tidal effects.

## 1.4 Scope of Works

This study is carried out along Sungai Perai and the primary aim of this study are to determine the spatial distribution and temporal analysis of heavy metals from the effluents of industrial area. However, this study only focuses on the heavy metals that have a higher concentration and does not comply with the conditions for National Water Quality Standards for Malaysia which are iron, copper, zinc, lead and manganese. The study started with water sampling of the Sungai Perai. The sampling of the water samples was done during the dry season and it was done twice, once during low tide and once during high tide. There were 15 sampling locations that had been selected and all points were mixed source points. Then, the equipment used to test the elements of heavy metal presence in the Sungai Perai was Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The temporal analysis of heavy metals in Sungai Perai was being analyzed by using a graph that generated using Microsoft Excel software. Lastly, a geographic information system is used to analyze the spatial distribution of heavy metals in Sungai Perai and the analysis was conducted by using ArcGIS Pro.

## 1.5 Structure of Thesis

There are five chapters in this thesis. Chapter one, a short introduction for background study, problem statement, objectives and scope of works are discussed. After that, for chapter two a literature review on the overview of heavy metals, effects of heavy metals, wastewater characteristics, past study on heavy metals, heavy metals analysis, statistical analysis and spatial distribution of heavy metals had been done. Then, chapter three explained the methodology used in this study: heavy metals analysis using ICP-OES, spatial distribution analysis of heavy metals using ArcGIS Pro and statistical analysis of heavy metals using Microsoft Excel software. Next, chapter four presented the results of the heavy metals analysis, the spatial distribution and the temporal trends of heavy metals. Lastly, a summary of the results and recommendations for the future study for chapter five.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview of Heavy Metals

Metals and their substances with an atomic density greater than four ± 1 g/cm$^3$ are commonly referred to as heavy metal pollutants (Qiu et al., 2021). Because of their biological toxicity and non-degradability, heavy metal pollution in water has become a rising global issue because it poses a danger to public health and natural ecosystems (Yang et al., 2021). The discharge of untreated municipal and industrial waste have polluted the rivers and oceans (Wan Abdullah et al., 2020). Toxic heavy metals are transported into the environment through natural and anthropogenic activities, mostly industrial activities and fuel combustion (Albayrak and Pekgöz, 2021). Toxic elements are most often incorporated into foods by interaction with the environmental (Wan Abdullah et al., 2020).

The health of lake ecosystems worldwide is seriously threatened by anthropogenic activities such as mining, urban construction, drainage and irrigation (Liao et al., 2019). The anthropogenic activities have the potential to alter the spatial distribution of aluminium, bacterial and archaeal communities, the geochemical fraction of phosphorus and sediment metabolism functions (Y. Long et al., 2021). Toxic elements such as mercury, arsenic, cadmium and lead are commonly found in marine species, particularly fish and seafood from the coastal areas affected by industrial discharge (Wan Abdullah et al., 2020). Even at low concentrations, cadmium, lead, nickel and copper are harmful to marine species (Wan Abdullah et al., 2020). Those heavy metals can build up high concentrations in the gills and muscles (Wan Abdullah et al., 2020). Rather than being released into the marine environment as a single entity, heavy metals and other contaminants are released in a complex form (Wan Abdullah et al., 2020).

Following are the tables that show Malaysia's National water quality standard and the uses for every classes.

Table 2.1: National water quality standard for Malaysia (DOE, 2009)

| Parameter | Unit | Class | | | | |
|---|---|---|---|---|---|---|
| | | I | IIA/IIB | III | IV | V |
| Al | mg/L | Natural levels or absent | - | (0.06) | 0.5 | Levels above IV |
| As | mg/L | | 0.05 | 0.4(0.05) | 0.1 | |
| Ba | mg/L | | 1.00 | - | - | |
| Cd | mg/L | | 0.01 | 0.01*(0.001) | 0.01 | |
| Cr (IV) | mg/L | | 0.05 | 1.4(0.05) | 0.1 | |
| Cr (III) | mg/L | | - | 2.5 | - | |
| Cu | mg/L | | 0.02 | - | 0.2 | |
| Ca | mg/L | | - | - | - | |
| Mg | mg/L | | - | - | - | |
| Na | mg/L | | - | - | 3 SAR | |
| K | mg/L | | - | - | - | |
| Fe | mg/L | | 1 | 1 | 1(Leaf)5(Others) | |
| Pb | mg/L | | 0.05 | 0.02*(0.01) | 5 | |
| Mn | mg/L | | 0.1 | 0.1 | 0.2 | |
| Hg | mg/L | | 0.001 | 0.004(0.0001) | 0.002 | |
| Ni | mg/L | | 0.05 | 0.9* | 0.2 | |
| Se | mg/L | | 0.01 | 0.25(0.04) | 0.02 | |
| Ag | mg/L | | 0.05 | 0.0002 | - | |
| Sn | mg/L | | - | 0.04 | - | |
| Zn | mg/L | | 5 | 0.4* | 2 | |

Table 2.2: Water classes and uses

| Class | Uses |
|---|---|
| Class I | Conservation of natural environment.<br>Water Supply I – Practically no treatment necessary.<br>Fishery I – Very sensitive aquatic species. |
| Class IIA<br><br><br>Class IIB | Water Supply II – Conventional treatment required.<br>Fishery II – Sensitive aquatic species.<br><br>Recreational use with body contact. |
| Class III | Water Supply III – Extensive treatment required.<br>Fishery III – Common, of economic value and tolerant species; livestock drinking. |
| Class IV | Irrigation |
| Class V | None of the above. |

## 2.2 Effect of Heavy Metals

Heavy metals concentration is beyond safety requirements in many rivers and groundwater. Heavy metal contamination has become more severe due to rapid global economic development, birth rate and increased industrialization (Qiu et al., 2021). Environmental changes have the most impact on the water, which is the most direct and sensitive factor (Alifujiang et al., 2021). Examples of human activities that contribute to landscape changes and pollution are agriculture, forestry, mining, water storage and diversion (Gardes et al., 2020). The toxicity of heavy metals has negative impacts on the quality of life and health of animals, such as reducing breeding success and increasing mortality rates (Albayrak and Pekgöz, 2021).

Via bioaccumulation or biomagnification in food chains, heavy metals are highly persistent and non-biodegradable, negatively impacting organisms' growth and behaviour. Heavy metals can be consumed by direct inhalation, swallowing or skin contact, posing health risks to humans and wild animals. For example, lead (Pb) can affect the immune function and nervous system, cadmium (Cd) inhibits growth and fertility in organisms and then for trace elements such as zinc (Zn) and chromium (Cr) have toxic effects at high concentrations (Xia et al., 2021). Another example effect of lead is it can have a severe adverse impact on children's blood and brains (Yang et al., 2021).

When heavy metals migrate, as they travel up the food chain and humans consume them, they can cause symptoms ranging from mild to severe illnesses. An example of a disease for mild symptoms is tiredness and nausea; meanwhile, severe illness is cancer (Yang et al., 2021). Since heavy metals are non-biodegradable, they remain in the environment for a longer time and pose long-term health threats by producing reactive oxygen species (Renu et al., 2021). Reactive oxygen species trigger several injuries such as hepatic injury, renal injuries, cardiovascular system disorders and inflammation-related diseases. Antioxidants can neutralisze or prevent the harmful effects of reactive oxygen species, thus reducing the risks. Toxic effects caused by heavy metals can occasionally interrupt this process.

## 2.3 Past Studies on Heavy Metals

Several studies have investigated the nature of intertidal sediment in Liaodong Bay, including heavy metals, organic contaminants and sediment particle characteristics. Surface sediment monitoring data were used in an integrated study to describe the spatial distributions and temporal patterns of heavy metals in the Liaodong Bay over ten years from 2004 to 2013. Five types of pollutants were measured: Hg, Cd, Pb, As and Cu. The most widespread pollutants were Hg, Cd and As. Cu and Pb pollution levels were low in both areas and levels. Over the las ten years, the amount of Cd in the environment has been steadily declining and As has followed a similar pattern. Emissions from various sources were also investigated to determine the potential causes of metal emissions. Cd and As differences could be caused by the dramatic descending of wastewater (Liu et al., 2017).

In a study, the impact of Chinese industrialization and urbanization on soil environmental quality was examined. Soil samples were collected from Jiangsu Province and Cd, Pb, Cr, Cu, Zn, Hg and As were evaluated. The spatial variability composition, spatial distribution pattern and pollution degree are also being assessed. In Jiangsu Province, the mean values of Hg, Cd, Pb, Cr, Cu and As were all greater than the background values. Cr and As amounts represented severe pollution, while medium pollution was represented by Cu, Zn, Cd and Pb levels. Hg was not a source of pollution meanwhile Cr and As were minor pollutants. The most considerable influence on the spatial variability of heavy metal emissions was industrialization. Natural and anthropogenic activities impacted Cr, Cu, Zn and As while Cd and Pb were predominantly influenced by the latter (Wang et al., 2020).

In 1999, a study of surface and subsurface soil Cu, Cr, Pb and Zn concentrations in the Naples city urban area were assessed. To explain the metals spatial distribution, contour maps were developed. Cu, Pb and Zn concentrations in soil were compared at twelve sites from the 1974 sampling. Most surface soils from the urban region, and the eastern industrial zone had Cu, Pb and Zn concentrations that far exceeded the Italian Ministry of Environment's standards for soils in public, residential and private areas. Cr levels were never found to be excessive and Cu tends to settle in soils along railway and tramway tracks. Cr and Cu are mostly inorganic primarily in soil, whereas Pb is mostly found as residual mineral phases. Cu, Pb and Zn levels have risen dramatically since 1974, with a higher accumulation in soils from roadside fields (Imperato et al., 2003).

Al-Mur et al., (2017) had studied the distributions of heavy metals in four sediment cores from the Red Sea near Jeddah. Every core's depth-resolved parts were examined for Cr, Mn, Fe, Cu, Zn and Pb. The results revealed high concentrations of Mn, Cu and Pb heavy metals. According to this study's findings, heavy metals concentrations in the core sediments were much higher in the top 15 cm. Metal levels are likely to be elevated in the upper 15 cm of core sediments that reflect recent years, due to discharge from industrial activities such as fertilizer use and sewage waste. The concentration of heavy metals in core sediments appears to be rising towards the Downtown area and has risen in recent years. The findings indicate that anthropogenic sources of Zn, Cu and Pb pollution may affect certain areas.

## 2.4 Analysis Methods

### 2.4.1 Heavy Metals Analysis

Sediment samples were freeze-dried and then ground in an agate grinder until fine particles were collected to study metal concentrations. The concentrations of major and trace elements in sediment samples were determined using the nitric acid and perchloric acid digestion process. In a heating block, around 0.2 g of ground sediment samples were digested with a mixture of 6 ml nitric acid and 1.5 ml perchloric acid at 50 °c for 3 h, 100 °c for 1 h, 125 °c for 1 h, 150 °c for 3 h, 175 °c for 2 h and 190 °c until fully dry. The remaining then was dissolved with 10 mL of 5% (v/v) nitric acid and heated for 1 hour at 70 °c. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV) was used to evaluate the major and trace elements in the solutions (Tang et al., 2008).

In September of each year, surface sediment samples (0-2 cm) were collected with a grab sampler according to the method GB17378.3 (2007) “The speciation for the marine monitoring-part 5: sediment analysis”. Since most metals were correlated with fine grains, sediment samples were freeze-dried, gently disaggregated with a pestle and mortar, and sieve after returning to the lab. Five contaminants were measured which were

Hg, Cd, Pb, As and Cu. The concentrations of Pb, Cd, Cu and As were calculated by digesting the samples (0.1-0.5 g) on an electric heating plate at 180-200 °c with a mixture of concentrated HNO (5 ml) and HClO4 (2 ml). Atomic absorption spectrometry (ASS) and certain cases such as low concentrations and graphite furnace atomic absorption spectrometry (GFAAS) were used to test Pb, Cd and Cu. Atomic fluorescence spectrometry (AFS) was used to evaluate the As concentrations. The concentration of Hg was determined using a direct mercury analyzer (DMA80, Milestone) based on EPA method 7473 (Liu et al., 2017).

The sediment samples were microwave digested with mixed concentrated acids of HF-HNO3-HClO4 for element concentration analysis. An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to measure the concentrations of Al, Ca, Fe, K, Mg, Mn, P and Zn. Meanwhile, an inductively coupled plasma mass spectrometer (ICP-MS) was used to determine Cd, Cr, Cu, Ni and Pb concentrations. The ICP-MS (Agilent 7700x) was used to assess the Pb isotope rations in the digestion solution (206Pb/207Pb and 208Pb/206Pb (Zhu et al., 2019).

Adjustments were made during field sampling to account for actual conditions around the sampling points. Surface soil samples were taken from the top 0-20 cm layer, mixed and bagged. Natural air drying, grinding and screening are used to prepare soil samples. The Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004) was used for further research. Graphite furnace atomic absorption spectrophotometry was used to determine the content of Cd and Pb. While atomic fluorescence spectrometry was used to determine the content of As and Hg and flame atomic absorption spectrophotometry was used to determine the content of Cr, Cu and Zn. The analysis method was tested with first-class national soil reference materials (GBW series) (Wang et al., 2020).

The soil samples were dried at room temperature and then ground through a 100-mesh nylon sieve after significant impurities were removed to determine the concentrations of heavy metals.  A crucible was used to store each soil sample (around 0.5 g) and 10 mL of HCl. The crucible was put in the oven for 12 h to oxidize organic matter. The solution was then reduced in volume by heating it on an electric hot plate at about 95 °c. HNO3, HF and HClO4 were added after cooling and the crucible was covered and heated at 120 °c for 2 hr. The crucible was then exposed and continually heated until the solution was nearly dry and the fumes had dissipated. The crucible was gently heated after adding HNO3 and deionized water to dissolve the residue. A flame atomic absorption spectrometer (FAAS) was used to determine the concentrations of Cu, Zn, Pb, Cr, Ni and Mn. In contrast, a graphite furnace atomic absorption spectrometer (GFAAS) was used to determine the concentration of Cd and an inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the concentration of V (Ruiz-Fernández et al., 2019).

### 2.4.2 Statistical Analysis

There are several types of statistical analysis to measure the concentrations of heavy metals. To see if there were any significant differences in particle sizes and metal concentrations among the sediment samples obtained at different sampling times and various sampling sites, Tang et al., (2008) had used one-way ANOVA and a student t-test. Metal correlations in harbour sediments were discovered using a Pearson correlation. All statistical analyses were performed with a 95 percent confidence interval ($p<0.05$) as the critical stage. SPSS for Window Release 10.1 was used to conduct the statistical analyses.

Then, Zhu et al., (2019) used a one-way ANOVA (Fisher test, p b 0.05) to describe the significant variations in heavy metal concentrations and different variables in the sediments. The association of heavy metals with other parameters in the sediments was determined using linear regression analysis. PCA is a technique for screening multiple variables in a complex system and it was used in this study to classify the causes of heavy metals in the sediments based on relationships between variables with different geochemical properties. The software packages SPSS 19.0 and Origin 2017 for Windows were used to conduct all statistical analyses in this study.

After that, Al-Mur et al., (2017) used SAS JMP Pro 10 for the statistical and correlation analysis. Researchers used linear regression analysis to compare heavy metal concentrations in sediment cores to determine the relationship between heavy metals. For Cr, Mn, Fe, Cu, Zn and Pb, the correlations between the elements were analyzed using all depth samples (n=25) in each core.

In Sigmastat, the heavy metal concentrations were statistically analyzed using analysis of variance by Pichtel et al., (1997). The Student-Newman-Keuls Method was used to check the difference between means when large F-values were obtained.

Lastly, SPSS (11.5 package version) was used by Liu et al., (2017) to process the statistical data. To classify the populations, concentration levels, means, medians, lower and upper quartiles for each heavy metal were determined. This software was used to construct frequency histograms using the Kolmogorov-Smirnov test. Non-parametric statistics were used because the concentration values were not normally distributed. The pattern was identified using the Mann-Kendall non-parametric test, which statistically evaluated whether there was a monotonic upward or downward trend of correlations over time. A monotonic upward trend meant that the variable increased steadily over time, but the trend may be linear or not. The spatial distributions were mapped using Super map software (Super map Deskpro 6) and the temporal variations of contaminants were analyzed using a scatter diagram using origin8. Finally, the over standard rates were calculated using the first-class standard values.

### 2.4.3 Spatial Distribution Analysis

The spatial distribution of heavy metals in the soils of Jiangsu Province was determined using ordinary kriging interpolation based on the specification of the variation function. The spatial distribution trends of the seven heavy metals in the soil displayed both zonal and concentrated patterns. Each heavy metal element had a large content area, showing that human activities in this area negatively impact soil heavy metal content. Cd, Cr, Cu and Zn had similar spatial distribution trends, with concentrations distributed zonally along the Yangtze River and in isolated areas around Taihu Lake. The areas with high levels of these five heavy metals were found to be consistent with urban development trends after comparing the spatial distribution findings with the land-use map of Jiangsu Province (Wang et al., 2020).

On a national scale, the spatial distribution of aquatic heavy metal emissions in 1 km x 1 km grids cannot be effectively visualized as a picture. As a result, the spatial characteristics of aquatic heavy metal emissions in 2010 were demonstrated using the kernel density plot. A kernel density model is a non-parametric approach for estimating a variable’s probability density function that displays the spatial distribution of relative emissions rather than absolute values. The map’s colours reflect the probability density of aquatic heavy metals emissions measured using a kernel density model. The kernel density map was used to identify hotspots and spatial gradient distribution. Hg, Cd, Pb and As had pretty similar spatial distributions but Cr(VI) were not identical (Huang et al., 2019).

ArcGIS 10.2 was used to map the distribution of sampling points. The maps representing the spatial distribution of As and heavy metals and HPI and HEI in shallow groundwater of Dongting Lake were created using ArcGIS and the inverse distance weighting (IDW) method with the power parameter set to 2. To create spatial distributions of contaminants, IDW in ArcGIS was used. Since Co and Cd elements were unidentified in the wet season and Cr elements were unidentified in the dry season, their distribution characteristics were not included in the analysis. Natural causes such as soil and mineral content of rocks and anthropogenic activities influenced the distribution of heavy metals in groundwater, resulting in varying distribution characteristics in different areas and under other environmental conditions (X. Long et al., 2021).

Eight heavy metals were detected and analyzed using Geographic Information System (GIS) technology in samples collected from manure, 10 cm depth surface soil, 50 cm depth subsoil, surface water and cow drinking water from a dairy farm in Dulbert Mongolian Autonomous County, Daginq City, Heilongjiang Province, China. Using GIS inverse distance weighted interpolation and the pollution index process, heavy metals' spatial distribution analysis were carried out. In the Supplementary Material, the three-dimensional spatial distribution of inverse distance weighted (IDW) interpolation of As and other heavy metals in soil samples were depicted. Various heavy metals migrated in different ways, resulting in different spatial distributions (Qi et al., 2020).

Khodami et al., (2017) aimed to determine the spatial and temporal distribution of heavy metals in the sediments of Bayan Lepas Free Industrial Zone of Penang, Malaysia. Metals were examined and their spatial distribution was assessed using GIS mapping. The GIS was used to assess spatial variation in heavy metal concentrations in the Keluang River and Bayan Lepas coastal region. The ArcGIS 10.3 (ESRI) software package was used to create all of the maps. The inverse distance weighting (IDW) method in GIS was used to interpolate each metal with a corresponding coordinate sample (XY) extracted from the database file. To assess heavy metal contamination in sediments, a variety of indices have been used. Metal contamination was evaluated using the enrichment factor (EF), geoaccumulation index (Igeo), risk of individual metal ($Er^i$) and ecological risk index (RI).

### 2.5 Spatial Distribution of Heavy Metals

The heavy metals concentration on the sediments has differed significantly between the sample locations but not significantly during the four sampling times (ANOVA, $p > 0.05$). This was because the sediments in Victoria Harbour are extremely mixed due to physical processes such as tidal effects and human disturbances. So, the 210Pb dating method was the only way to successfully build the chronology for sediment core B4. Significant temporal variations in heavy metals concentration were found in core B4 sediment, particularly for Cu and Zn, showing changes have metals input to the harbour over the last few decades. In the sediment core, the trend for Cu was quite similar to the trend for Zn, and there was a significant correlation between the two metals ($p < 0.05$). This suggests that the two metals are likely to come from the same sources of industrial emissions and other inputs. The Pb profile has a somewhat different trend than the Cu and Zn profiles (Tang et al., 2008).

Liu et al., (2017) created a GIS map to show the spatial distributions of heavy metals pollutions in Liaodong Bay sediment in typical years, to explain the spatial characteristics of heavy metals. Within ten years, Cd and As contents show significant decreases. For these two metals, three maps were created, each corresponding to a different year to monitor the distribution variations over time. Between 2007 and 2012, both the magnitudes and ranges of Cd pollution decreased considerably. In 2012, Cd concentrations in most areas were less than 0.32 mg/kg except for Jinzhou Bay, where the average Cd concentration was 0.74 mg/kg, which was greater than the other locations. When compared to Cd, As contamination was more widespread, occurring even in the centre of Liaodong Bay in 2007. With concentrations of 36.6 mg/kg, Taiping Bay and Jinzhou Bay stations were found to be relatively heavily contaminated. In 2009, Hg concentrations were higher from Jinzhou Bay to Huludao City than in other regions. Jinzhou Bay was the most heavily contaminated location, with an average value of 0.1 mg/kg. Only a few sampling locations in Taiping Bay and Jinzhou Bay were marginally polluted with Cu and Pb, respectively.

A study about the spatial distribution of heavy metals in Naples city’s urban soils in Italy was done by Imperato et al., (2003). All data for Cu, Cr, and Zn are included meanwhile for Pb, the two biggest values measured in soil samples obtained at the city's boundaries are eliminated to improve the presentation of geochemical anomalies. The eastern section of the city, which corresponds to areas of heavy industry and numerous oil refineries as well as combustible reserves are found, has high concentrations of all metals. Copper appears to accumulate in soils next to railway lines and tramways, primarily along the east coast. The concentrations of lead in the city varied. However, there is significant Pb contamination of soils from the city centre and industrial eastern and western districts. The most polluted soils are found near highways and busy streets. Low Pb levels are only found in soils in the city’s northwest area, which is distinguished by a higher elevation (150 m above sea level).

The maximum concentration of cadmium in surface water was found at station 3, whereas the lowest concentration was found at station 1 along the studied area. August had the highest Cadmium concentration in terms of geographical variation. A one-sample t-Test showed a statistically significant difference in nickel spatial variation for the months of August and September ($p > 0.05$) and there was no statistically significant difference ($p > 0.05$) in Iron concentration between August and October, however October had the highest concentration in surface water. One-sample t-Test revealed a statistically significant difference ($p = 0.05$) geographically for lead. Lead was not identified in stations 1, 2, or 5 throughout the month of October. In terms of location, the month of September had the greatest mean lead concentration. In August, copper was not discovered in stations 2, 3, 4, and 5, while in October, copper was not detected in station 1. The maximum concentration was found in October, while the lowest was found in August (Dibofori-Orji et al., 2019).

## 2.6 Temporal Analysis of Heavy Metals

Cu, Pb, and Zn were found in the highest concentrations in the middle region of the harbour, with mean concentrations of 173, 44.3, and 171 mg/kg, respectively. The different urban conditions in the territory could explain the large geographical variance of metals. The proximity of the location to the most intensively populated areas likely caused the significant concentrations of heavy metals (Cu, Pb, and Zn) discovered in the middle (B2 and B3). These areas have a high population density, high traffic density and are located near the old industrial zones. In contrast, B1 sediments with lower metal concentrations are found in high tidal flushing, low population density and little anthropogenic activity. In the central and western areas of the harbour, there was a significant concentration of heavy metals, particularly Cu, which was 20 times greater than the baseline value. Cu concentrations in surface sediments also exceed Hong Kong's Upper Chemical Exceedance Level and could threaten aquatic life (Tang et al., 2008).

The temporal variations of each heavy metal concentrations were examined using an intuitional tendency chart and the Mann-Kendall test was used to determine statistically the trend of the median concentrations during the previous ten years by Liu et al., (2017). The changes in Hg, Cu, and Pb were too minor and the Mann-Kendall test revealed no apparent tendency for variation. Despite some significant changes between years, there was a slightly decreasing trend in Hg values during the last ten years. Cd showed a clear decreasing trend from 2004 to 2013, with median values dropping nearly thrice from 0.62 in 2005 to 0.18 in 2012. Between 2007 and 2009, the rate of decline was the highest. Cd concentrations varied only slightly before and after this time. From 2006 to 2013, As in Liaodong Bay sediment showed a very dramatic declining trend. The pace of decline was rapid, and the median As concentration in 2006 was roughly 6 times higher than the median value is 2013, indicating that As pollution in the Liaodong Bay had been drastically reduced during the previous 8 years. There were no obvious variations in Pb and Cu concentrations for ten years, with only minor fluctuations between years.

Between October 2012 and September 2014, research was conducted in Woji Creek to determine the spatial and temporal distribution and pollution of heavy metals. Pb > Ni > Fe > Cd > Cu was the sequence of heavy metals dominance in Woji by Dibofori-Orji et al., (2019). The one-sample t-Test revealed a statistically significant difference in cadmium geographically for the month of October ($p < 0.05$), but not for the other months or the temporal concentration ($p > 0.05$). The presence of nickel in station 4 was not detected in water samples taken in August and September. Temporally, the results of a single sample t-Test revealed no statistically significant differences across the stations ($p > 0.05$). When one sample t-Test was done, the results of iron concentration showed no statistically significant difference ($p > 0.05$) in the surface water over time. However, in the month of September, there was a statistically significant difference ($p < 0.05$) in the temporal data. Station 5 had the highest mean concentration of temporal data. A statistically significant difference ($p = <0.05$) in the temporal data for lead was also found at station 3 by one sample t-Test. The investigation found that the sediment in the study area has a low degree of heavy metal contamination.

# CHAPTER 3

# METHODOLOGY

## 3.1 Introduction

In this chapter, the methods and materials used to achieve the study's objective will be described. Figure 3.1 shows the procedure of carrying out the research.

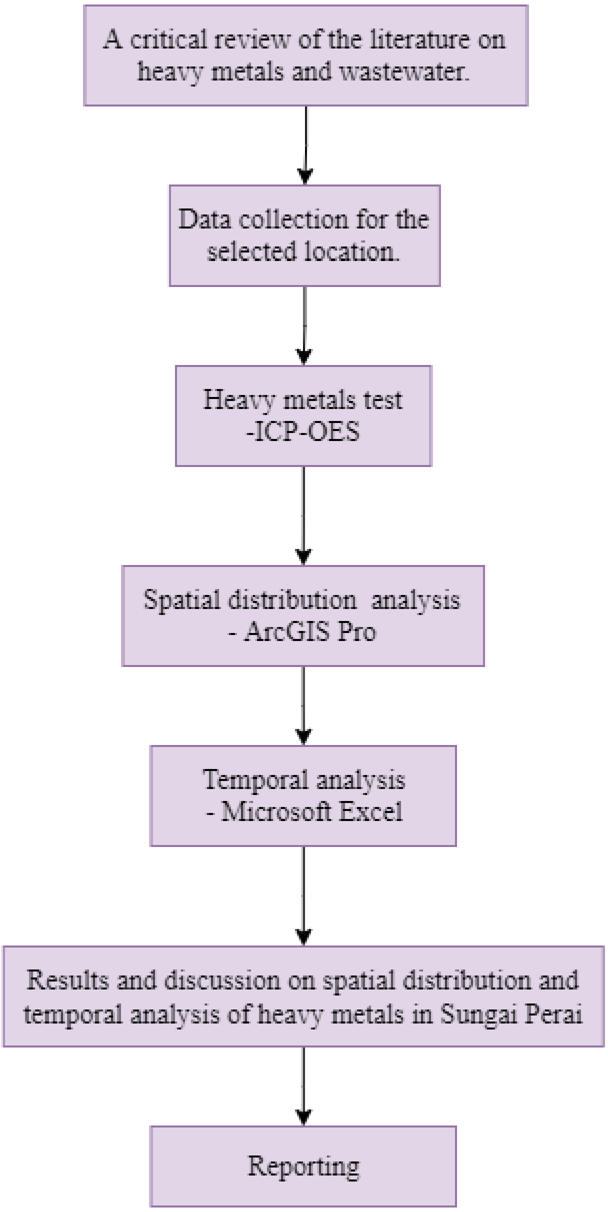


Figure 3.1: Flowchart of the study

## 3.2 Sample Collection

Penang State's mainland section is known as Seberang Perai. Seberang Perai Utara, Seberang Perai Tengah and Seberang Perai Selatan are the three administrative districts that make up Penang Mainland. Seberang Perai has an estimated population of 818, 197 people and occupies 751 $km^2$ (in the year 2010). Sungai Perai is the main river in the Malaysia state of Penang. It also separates Butterworth from the Perai and Seberang Jaya suburbs as Butterworth's mother flow. The 24-kilometre Sungai Perai flows through commercial, agricultural and residential areas, linking to numerous tributaries and the Sungai Muda. According to a study by Mok (2018), along the Sungai Perai, there were a number of rich peat swamp and wetlands which provide home for more than 150 plant species, 125 bird species and 35 fish species.

A preliminary study was conducted on the sampling locations areas and the sampling was done on $3^{rd}$ and $4^{th}$ May 2021. The water samples of effluent from the study area were obtained during the dry season in 2021. The location of the sampling points along the Sungai Perai as shown in Figure 3.2 and Table 3.1. There are 15 sampling points in total along the Sungai Perai where the sampling of the water samples was done twice, once during low tide and once during high tide. Tides start in the oceans and flow to the coasts, where they present themselves as a continuous rise and fall of the sea surface. High tide occurs when the largest section of the wave reaches a specific spot, whereas low tide refers to the lowest part of the wave. There are two tidal cycles in most coastal locations across the world, which means there are two tides and two high tides. 15 samples were collected on the same day for each tidal effect. A water bucket with a long handle was used to collect the samples of river water. The data was recorded on-site by using YSI Hanna Instrument-via immersing the probe in the water samples. The pH,