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STUDY ON SEDIMENT QUALITY USING HEAVY METALS FROM RIVER SEDIMENT

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DECLARATION

I declare that this thesis entitled "title of the thesis" is the results of my own research except as cited in the references.

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ABSTRACT

The study of sediment analyses the various elements, sources, and kinds of sediment, focusing on the effects of heavy metal contamination and the dynamics of natural rivers. Analytical methods that improve our comprehension and aid in environmental preservation include microwave digestion and ICP-OES. Grain size distribution and heavy metal concentration are the main subjects of this study being conducted in Kelantan to evaluate the features of the sediment. The objectives are to analyses the grain sizes in the sediment, measure the concentrations of heavy metals, and compare the levels of heavy metals with different fractions of the grain size. The study contributes to understanding sediment quality and potential environmental impacts, guiding effective management strategies This study conducted in Kelantan employs rigorous methods to investigate sediment characteristics. It uses techniques such laboratory sieving, loss on ignition, microwave digestion, enrichment factor and geoaccumulation index and ICP-OES analysis to analyses grain size distribution, texture, organic matter, and heavy metal concentrations from samples taken from seven different locations. The objective of the study is to offer thorough understandings of sediment quality and possible environmental effects. Significant patterns can be seen when analyzing the amounts of heavy metals in sediment samples and comparing the grain sizes (32µm–63µm and <32µm). The content of cadmium varies; 32µm–63µm had lower levels than <32µm. Except for <32µm in the Buloh River, the majority of chromium content is still below 100. The greater copper values in <32µm are a result of fractured rocks. Sediment composition affects iron content, whereas mineralization and river currents affect manganese amounts. Around 32 µm is where nickel accumulates the most, and lead distribution is similar at all diameters. The amount of zinc varies depending on location and size. The Kelantan study conducted a thorough analysis of the grain size distribution and heavy metal concentration of the sediment, finding intricate connections that are important for ongoing research and environmental management.

ABSTRAK

Kajian sediment menganalisis pelbagai elemen, sumber, dan jenis sediment, dengan tumpuan kepada kesan pencemaran logam berat dan dinamika sungai semulajadi. Kaedah analisis yang meningkatkan pemahaman kita dan membantu dalam pemeliharaan alam sekitar termasuk pencernaan gelombang mikro dan ICP-OES. Taburan saiz butiran dan kepekatan logam berat adalah subjek utama kajian ini yang dijalankan di Kelantan untuk menilai ciri-ciri sediment. Objektifnya adalah untuk menganalisis saiz butiran dalam sediment, mengukur kepekatan logam berat, dan membandingkan tahap logam berat dengan fraksi saiz butiran yang berbeza. Kajian ini menyumbang kepada pemahaman kualiti sediment dan impak alam sekitar yang berpotensi, memandu strategi pengurusan yang berkesan. Kajian ini dijalankan di Kelantan menggunakan kaedah-kaedah yang teliti untuk menyelidiki ciri-ciri sediment. Ia menggunakan teknik-teknik seperti ayakan makmal, kehilangan terbakar, pencernaan gelombang mikro, faktor pengkayaan dan indeks geoakumulasi dan analisis ICP-OES untuk menganalisis taburan saiz butiran, tekstur, bahan organik, dan kepekatan logam berat dari sampel yang diambil dari tujuh lokasi berbeza. Objektif kajian adalah untuk memberikan pemahaman yang mendalam tentang kualiti sediment dan kesan alam sekitar yang mungkin. Corak yang signifikan dapat dilihat semasa menganalisis jumlah logam berat dalam sampel sediment dan membandingkan saiz butiran (32μm–63μm dan <32μm). Kandungan kadmium berbeza; 32μm–63μm mempunyai tahap yang lebih rendah daripada <32μm. Kecuali untuk <32μm di Sungai Buloh, kebanyakan kandungan kromium masih di bawah 100. Nilai tembaga yang lebih tinggi dalam <32μm adalah hasil daripada batuan yang retak. Komposisi sediment mempengaruhi kandungan besi, manakala mineralisasi dan arus sungai mempengaruhi jumlah mangan. Sekitar 32 μm adalah tempat di mana nikel paling banyak terkumpul, dan taburan plumbum serupa pada semua diameter. Jumlah zink berbeza bergantung kepada lokasi dan saiz. Kajian Kelantan menjalankan analisis menyeluruh terhadap taburan saiz butiran dan kepekatan logam berat dalam sediment, menemui hubungan yang rumit yang penting untuk penyelidikan berterusan dan pengurusan alam sekitar.

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LIST OF ABBREVIATIONS

C	CARBON
O	OXYGEN
TI	TITANIUM
FE	IRON
NI	NICKEL
ZN	ZINC
AS	ARSENIC
NB	NIOBIUM
AG	SILVER
CD	CADMIUM
SN	TIN
HG	MERCURY
PB	LEAD
CA	CALCIUM
MG	MAGNESIUM
NA	SODIUM
CR	CHROMIUM
MN	MANGANESE
CO	COBALT
ICP-OES	INDUCTIVELY COUPLED PLASMA-OPTICAL EMSSION SPECTROMETER
OM	ORGANIC MATTER
GPS	GLOBAL POSITIONING SYSTEM
UMK	UNIVERSITI MALAYSIA KELANTAN

LIST OF SYMBOLS

α	Alpha
%	Percentage
µ	micro

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Sediment encompasses solid materials moved and settled by wind, water, or ice, encompassing diverse particles like sand, silt, clay, organic matter, and chemical precipitates. This geological component accumulates in varied environments such as rivers, lakes, oceans, and glaciers. Its significance lies in shaping Earth's surface, as sediment undergoes continuous processes of erosion, transport, and deposition. (Koltermann and Gorelick 1996). Deposition is the process by which silt builds up in a variety of habitats, including lake bottoms, riverbeds, and coastal regions, as a result of the conveying medium losing energy. Sediment layers have the potential to lithify into sedimentary rocks over time, providing important information about the geological and environmental history of Earth. Although the specific definition of "sand" varies, in the language of English-speaking geologists, it usually refers to mineral grains larger than silt but smaller than 1 or 2 mm. Conversely, "silt" is typically linked to deposits that have both mineral particles and organic stuff in them. It is noteworthy to mention that there is not much agreement among former or present experts in the field about this definition of silt, which has to do with organic content. Within the geological community, the disciplinary or geographical concerns might influence how sediment particles are classified, especially the differences between sand and silt. (Wentworth 1922).

Numerous investigations have used advanced analytical instruments to look into the presence of heavy metals in river sediments. Results consistently show that accumulated heavy metals from various sources of pollution are stored in sediment found in rivers, lakes, and marshes. Heavy metal deposition in aquatic sediments is a result of anthropogenic activities such agricultural operations, urban runoff, and industrial discharges. Significant ecological effects of this contamination could include decreased water quality and aquatic life. (Sakai, Kojima et al. 1986). The elements to be investigated are Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. This is to determine the ecological risk levels of heavy metal pollution (Pb, Cu, Cr, Cd, Fe, Mn) in the sediment of the river. (Fajri 2020).

1.2 Problem Statement

Studying sediment quality in both unexplored and previously explored areas, as well as small and large river areas in the Kelantan River. In this study, it will ensure that the sediment content in each sediment is good and does not impact the environment. Additionally, this study will investigate sediment quality using heavy metal elements to determine the mineral and metal content present in the sediment.

1.3 Objectives

1. To determine the grain size distribution of sediment at the selected location in Kelantan.
2. To determine the heavy metals contents of the sediments and compare grains size 32um-63um and less than 32um.
3. Determine the pollution level by using enrichment factor and geoaccumulation index.

1.4 Scope of Study

This study will investigate sediments containing heavy metals to ensure sediment quality is good. To determine sediment quality, it is crucial to observe and understand the processes and results obtained from the physical and chemical characteristics of the sediment, such as particle size distribution, organic matter, microwave digestion, and ICP-OES. This is further supported by ICP-OES data indicating whether the heavy metal content in the sediment is high or low. Within the scope of this study, samples will be collected from different areas, all located within the state of Kelantan, including Airchanal (Airchanal River), Kampung Gemang (Ketil River), Kampung Satan (Satan River), Gua

Musang (Ketil River), and Lojing (Ber River, Ber Spring Steam/outlet, and Ber Spring Confluence). In determining the level of pollution and sediment quality, enrichment factor and geoaccumulation are suitable methods for identifying sediment quality.

1.5 Significances of Study

In term of environmental health, it is essential to comprehend the existence, dispersion, and effects of heavy metals in sediment in order to evaluate the condition of aquatic ecosystems. These metals have the ability to build up in sediment, which can have an impact on aquatic environments' flora and fauna and possibly upset ecological balance and biodiversity. Provides updates sediment heavy metal data are formulated in part by the results of studies conducted on heavy metals in sediment. Determining acceptable limits and guidelines for the preservation of aquatic ecosystems is made easier with the aid of contamination assessment levels. *Long-Term Impact Assessment*, Tracking the concentrations of heavy metals in sediment over time is useful for determining trends and long-term impacts. Predicting future effects and making educated decisions about environmental remediation and conservation are made easier with the help of this data.

CHAPTER 2

LITERATURE REVIEW

2

2.1 Sediment

Although the specific definition of "sand" varies, in the language of English-speaking geologists, it usually refers to mineral grains larger than silt but smaller than 1 or 2 mm. Conversely, "silt" is typically linked to deposits that have both mineral particles and organic stuff in them. It is noteworthy to mention that there is not much agreement among former or present experts in the field about this definition of silt, which has to do with organic content. Within the geological community, the disciplinary or geographical concerns might influence how sediment particles are classified, especially the differences between sand and silt. (Wentworth, 1922),(Zhang et al., 2021). Sediment encompasses solid materials moved and settled by wind, water, or ice, encompassing diverse particles like sand, silt, clay, organic matter, and chemical precipitates.(Najafi et al., 2021). This geological component accumulates in varied environments such as rivers, lakes, oceans, and glaciers. Its significance lies in shaping Earth's surface, as sediment undergoes continuous processes of erosion, transport, and deposition. (Koltermann & Gorelick, 1996). Lithification is the process by which sediment layers are compressed and cemented together over time to create sedimentary rocks. Numerous types of rocks, including sandstone, shale, and conglomerate, are formed as a result of this process. Sedimentary rocks can include fossils and hints about the past, and they frequently offer insightful information about Earth's history.(Bathurst, 1980),(De Vleeschouwer et al., 2023)

Figure 2.1:Common sediment in river.

(Mr rooter plumbing et al, 2019)

Sediment classification by origin categorizes sediment into four primary types, which are as lithogenous sediment, hydrogenous sediment, biogenous sediment and comogenous sediment. (Ozerova et al., 2023). Lithogenous sediment is Rocks on land weather both physically and chemically to produce sediments. Natural forces like wind, water, and ice carry them, and they are subsequently deposited in diverse settings. Lithogenous sediments consist of particles such as clay, silt, and sand. The majority of the Earth's surface is composed of these common sediments. (Schnurrenberger et al., 2003). Hydrogenous sediments, also known as authigenic or chemical sediments, encompass a diverse range of materials that form directly from seawater through chemical processes. These sediments are distinct from lithogenous (land-derived) or biogenous (biologically produced) sediments.(Li & Schoonmaker, 2003). River sediments classified as "biogenous" come from the detritus of living things that formerly graced the river's ecology. Organic debris like shells, bones, and other hard components of creatures that live in or close to rivers make up these sediments. sediments with a high concentration of the skeletal remains of both microscopic and macroscopic species, as well as organic production remnants. Calcareous biogenous sediments, siliceous biogenous sediments, and phosphatic biogenous sediments are the three main types into which they can be divided. (Balasubramanian, 2017). Sediments that are discovered on Earth's surface and have alien origins are referred to as cosmogenous sediments. These elements originate from space and are not from Earth. They originate from cosmic sources, including meteorites, dust particles from interplanetary travel, and other objects that enter Earth's atmosphere and land on the planet's surface. (Balasubramanian, 2017).

2.1.1 Natural River

The dynamic structure of river systems is responsible for the scarcity of totally straight rivers. Although certain rivers may seem straight for short distances, meandering is common due to topography's intrinsic unpredictability, sediment movement, and erosional forces. The balance between erosion and deposition, interactions with geological structures, and sediment deposition are what cause river bends and curves. The restriction that a river's straight length usually cannot be more than ten times its breadth draws attention to the way rivers naturally seek a balance between depositional and erosional processes, resulting in winding routes. The ever-changing interaction of natural forces impacting river form is reflected in its dynamic nature.(Leopold & Langbein, 1966). To generate and implement knowledge about rivers, it is important to classify the forms and processes of rivers. Organising rivers according to characteristics like hydrology, geomorphology, or biological processes makes predictions and generalisation easier, which promotes efficient management. Nonetheless, arguments over the uniformity of processes in various spatial contexts emerge because rivers are intricate biophysical systems. For instance, dividing rivers into perennial and intermittent categories based on their hydrological trends. The dispute in science centres on whether these classifications are universally applicable, since the interplay of biophysical processes in rivers can differ greatly depending on geological, climatic, and geographical conditions.(Tadaki et al., 2014)

A natural river is a stream that has been shaped by natural processes without much human interference. Natural rivers create a variety of features such meanders, riffles, and pools as they follow the course determined by topography, erosion, and sedimentation.(Wohl & Merritts, 2007) The idea emphasizes how catchment, banks, and bed work in perfect harmony to create the dynamic interaction between flows and sediment movement in natural rivers. The orderly configuration determined by natural processes is reflected in the channel and floodplain form's systematic distribution. Stressing unrestrained transitory behaviour draws attention to the river's adaptability, which enables it to react to changes in its surroundings. River ecosystem resilience and ecological balance depend on maintaining these natural processes.(Newson & Large, 2006).

2.1.2 Heavy Metal

The pollution caused by heavy refers to high levels of heavy metals found in aquatic environments, mostly as a result of industrial and human activity. The release of heavy metals into aquatic environments is caused by anthropogenic sources such as mining operations, aviation deposition, sewage and industrial wastewater discharges, and the burning of fossil fuels.(Zhang et al., 2011). The term "heavy metal pollution" refers especially to the specific heavy metals or elements that pollute aquatic ecosystems. Lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), zinc (Zn), copper (Cu), nickel (Ni), and arsenic toxicity (As) are some of the heavy metals that are most frequently monitored and cause concern because they can contaminate aquatic environments.(Vallius & Leivuori, 2003). Various analytical methods are used to determine the presence and concentration of heavy metals in sediment. Some of the commonly employed techniques include Atomic Absorption Spectrometry (AAS),Inductively Coupled Plasma Mass Spectrometry (ICP-MS),Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Fluorescence (XRF), Sequential Extraction Procedure (SEP), Cold Vapor Atomic Absorption Spectrometry (CV-AAS) and Colorimetric Methods.(Zhang et al., 2011).

2.2 Grain size process

In sedimentology, grain particle size distribution (PSD) study is essential because it provides information on the properties of the sediment. Grain sizes and kinds are accommodated by a variety of techniques, including sieving, laser diffraction, and sedimentation. The type of sediment determines selection, guaranteeing precise findings for a range of environmental and geological research.(Jaijel et al., 2021) The purpose of this manual sifting procedure is to isolate particular size fractions of interest, which will make future analysis easier. It is a crucial stage in the study of sediment because it enables more focused inquiries into the features and attributes of sediment across various size ranges.(Blott & Pye, 2012). Further laboratory tests, such as mineralogical characterization, chemical testing, or other size-specific evaluations, can also be performed on the isolated sediment fractions. The information gathered from this procedure provides important new understandings of the dynamics of sedimentation, patterns of erosion, and environmental processes in aquatic environments. In general, manual sieving is a basic method in sediment analysis that gives scientists a thorough grasp of the makeup and distribution of sediment particles within a given size range. (Jaijel et al., 2021).

2.3 Organic matter

This process governs the recycling of inorganic carbon, nutrient dynamics, carbonate dissolution, and organic carbon flux within marine sediments. It determines the burial of organic matter in sediment, influencing CO_2 removal and oxygen input to the atmosphere. Quantitative models have been developed to understand these complex interactions, guiding our comprehension of global-scale carbon and nutrient cycling in marine environments.(Arndt et al., 2013). Organic matter (OM) preservation is influenced by a number of recognized parameters, although the underlying mechanisms are not fully understood. Only a portion of the microbial, enzymatic, and mineral interactions involved in the breakdown of OM has been studied. This knowledge gap compromises the validity of OM-related proxies by making it more difficult to accurately analyses past and present carbon cycles. Gaining a deeper comprehension of these mechanisms is essential to improving our understanding of the biogeochemical processes on Earth, guaranteeing more accurate assessments of carbon fluxes, and strengthening the validity of proxies in paleoenvironmental reconstructions.(Zonneveld et al., 2010)

2.4 Microwave digestion

A standard in both inorganic and organic analysis, microwave-assisted sample preparation increases productivity by shortening the time needed for digestion and increasing analytical precision.(Nóbrega et al., 2012). In trace heavy metal analysis, microwave digestion has gained a lot of traction, particularly prior to instrumental detection by methods like AAS, ICP-AES, and ICP-MS. Many sample types, such as sediments, soils, mushrooms, dust, vegetables, wheat, and botanical samples, are used with this technique. Among its benefits are low-volume digestion, the ability to analyse small samples, and a decrease in method sensitivity problems brought on by dilution. By reducing the amount of chemicals used and potential risks, the closed system improves safety while still being economical and effective it can handle over ten samples in an hour. Depending on the sediment samples, several acid mixes are used, including HCl-HNO3, HNO3-H2SO4, HCl-HNO3-H2SO4, HCl-HNO3-HClO4, and HCl-HNO3-H2O2.(Tuzen et al., 2004).

2.5 Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The study aimed to evaluate river sediment samples for their trace metal adsorption capacity and assess metal mobility under diverse environmental conditions. The chemical forms or speciation of elements in sediment, not just their amounts, influence their behavior in natural systems.(Alomary & Belhadj, 2007). Two extraction methods were rigorously assessed, along with total digestion procedures, to determine comprehensive trace metal content. Analysis employed an inductively coupled plasma optical emission spectrometer (ICP-OES), providing precise quantification and insights into trace metal distribution and potential mobilization in river sediments.(Botes & Van Staden, 2005). ICP-OES operates by ionising and excitation sample atoms in a high-temperature plasma that is produced from argon gas. Next, the light that each element emits is distributed and detected. ICP-OES simultaneously measures element concentrations by comparing this emission to standards, providing accuracy for a range of applications, including materials analysis and environmental science.(Olesik, 1991). Element concentrations such as Pb, Cd, Cr, Cu, Zn, Fe, and Mn.

2.6 Enrichment factor and geoaccumulation index

To evaluate the level of elemental pollution in environmental samples, especially sediments, two metrics are used the enrichment factor (EF) and the geoaccumulation index (Igeo). An element of interest's concentration is normalised in relation to a reference or background element that is steady, immobile, and unaffected by human activity in order to determine the EF (Looi et al., 2019). It is employed to evaluate the degree of metal enrichment, with distinct categories denoting differing levels of enrichment. In contrast, the geoaccumulation index, or (Igeo), compares the present concentration of a metal with its pre-industrial concentration in order to assess the degree of contamination in sediments. Diverse (Igeo) values denote different degrees of contamination, from completely uncontaminated to highly contaminated. (Abdullah et al., 2020)

The enrichment factor (EF), which is divided into several categories to represent different levels of enrichment, is used to evaluate the degree of metal enrichment. $EF < 2$ indicates depletion to mineral enrichment, $2 \leq EF < 5$ indicates moderate enrichment, $5 \leq EF < 20$ indicates significant enrichment, $20 \leq EF < 40$ indicates very high enrichment, and $EF > 40$ indicates extremely high enrichment. The classification of enrichment factor is based on the calculated value. (Abdullah et al., 2020). Sediment pollution is assessed using the geoaccumulation index (Igeo), which is divided into many categories to represent different contamination levels. The geoaccumulation index is classified according to its calculated value: $Igeo < 0$ denotes uncontaminated to moderately contaminated, $0 \leq Igeo \leq 1$ indicates moderately contaminated, $1 \leq Igeo \leq 2$ indicates moderately to strongly polluted, $2 \leq Igeo \leq 3$ indicates strongly polluted, $3 \leq Igeo \leq 4$ indicates strongly to extremely polluted, and $Igeo > 4$ indicates extremely polluted. (Looi et al., 2019)

CHAPTER 3

MATERIALS AND METHODS

3

3.1 Materials

A variety of instruments are needed for sample collection and storage in the sediment quality research. Vehicles such as proton persona, proton kelisa and ford raptor and standard tools like a scoop, plastic bags, aluminium foil, GPS, and a storage box were used for the sample collection trip. Laboratory equipment and apparatus, such as an oven, microwave digestion apparatus, a furnace, laboratory sieves, a micropipette, beakers, centrifuge tubes, crucibles, scales and ICP-OES, are necessary to ascertain the heavy metal content in sediment. To evaluate the heavy metal concentration in sediment using ICP-OES, solid samples were converted into liquid form using hydrochloric acid (HCl), nitric acid HNO_3, hydrogen peroxide H_2O_2, and hydrofluoric HF.

3.2 Methods

3.2.1 Sampling of sediment

Sampling of sediment was conducted in the state of Kelantan at 7 different locations in October 2023, namely Airchanal River, Satan River, Buluh River, Kentil River, Ber River, Ber Spring Steam/outlet, and Ber spring Confluence. Each sample taken was placed in a plastic bag, sealed, and stored in a box for further processing. Each selected area was marked using the Global Positioning System (GPS) on location map to determine the location, as shown in figure 3.2.

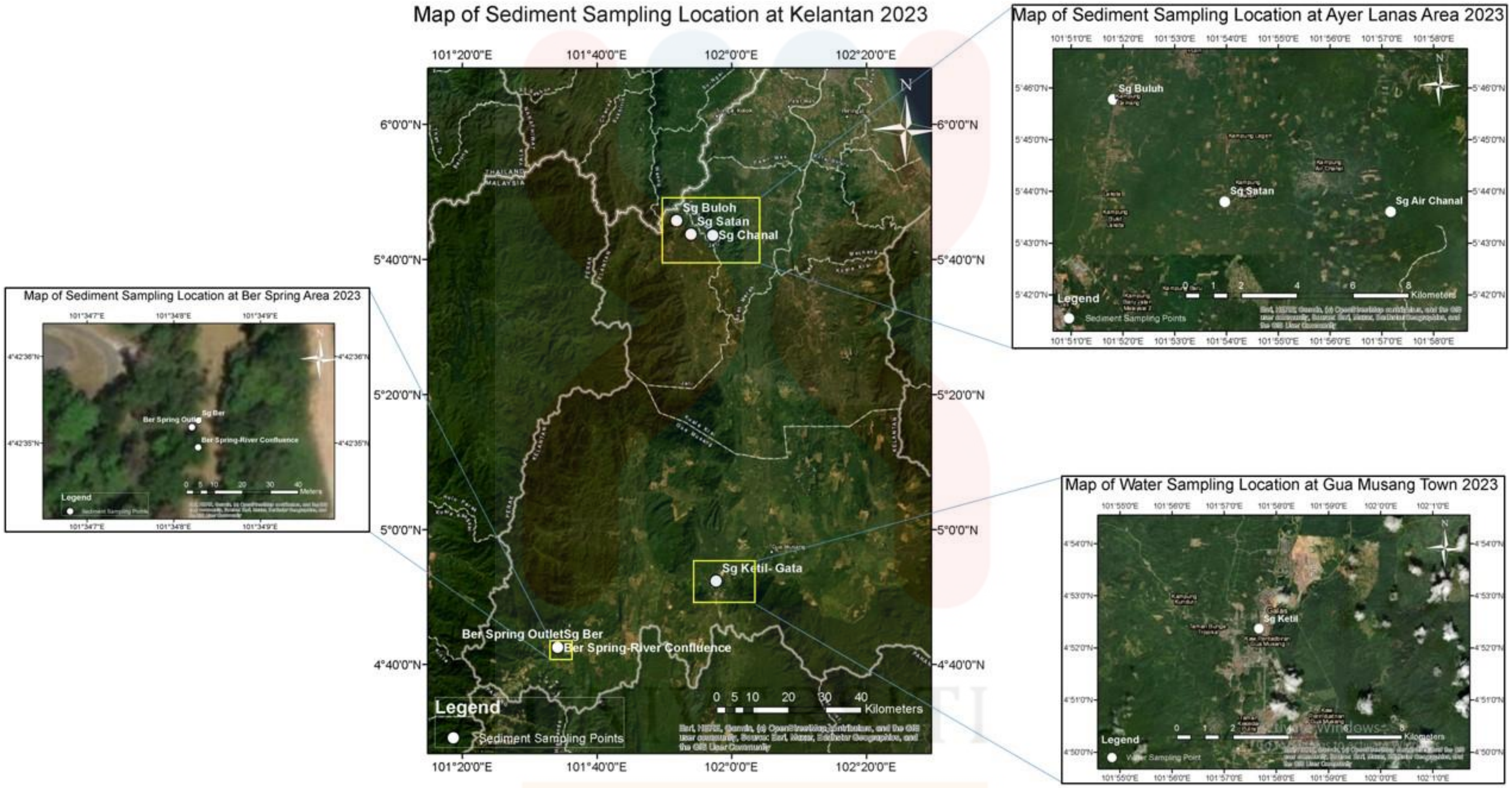

Figure 3.2: sampling location in Kelantan sediment

3.3 Sediment physical characteristics determination

3.3.1 Grain size distribution and texture

For this process, a standard laboratory sieve set was used to separate the collected sediment to different grain size above 4 mm, 2 mm – 4mm, 1mm- 2mm, 850µm-1mm, 740µm-630µm, 540µm-630µm, 450µm-540µm, 320µm-450µm, 240µm-320µm, 125µm-240µm, 63µm-125µm, 32µm-63µm, <32µm. The collected sediment was poured onto a sieve set with descending grain sizes from top to bottom, then shaken manually with closed lid until all sediment grains were separated. The separated grains were then weighed accordingly and recorded for grain size distribution and texture analysis.

3.3.2 Organic Matter

In the process, it requires a dried sample weighing 0.2 g to be placed in the furnace. Before carrying out this process, the crucible must be cleaned before being placed in the oven at a temperature of 105°C for 12 hours. After 12 hours, the crucible was allowed to cool before inserting the sample. The sample will be placed in the crucible and then returned to the oven at a temperature of 105°C for a day. After a day has passed, remove the crucible and sample, then allow them to cool before placing them in the furnace at a temperature of 550°C for 6 hours. After 6 hours, remove the sample from the furnace and allow it to cool before weighing. Record the weight before and after, and calculate the percentage of organic matter in the sediment using formula (3.3.2).

$$\textbf{Loss on ignition 100\%} = \frac{sample\ weight\ before\ heating - sample\ weight\ after\ heating}{sample\ weight\ before\ heating} \times 100\% \qquad (3.3.2)$$

3.4 Sediment heavy metal determination

3.4.1 Microwave digestion

An essential method in analytical and environmental chemistry, microwave digestion is frequently used to carefully prepare sediment samples for examination. Specialised tools are needed to start this process, such as a microwave digestion system with a microwave cavity, temperature control, and pressure control. Crucial components also include an analytical balance for accurate sediment sample weighing and Teflon or quartz jars that were selected based on their suitability for microwave digestion.

Before sediment is taken to ICP OES, it will undergo several processes to transform it into a liquid form. In this process, 0.2g of sediment will be weighed and placed into a microwave digestion with a mixture of chemicals, namely HNO_3, HCl, H_2O_2, and HF, and then subjected to microwave digestion for 2 hours with 260˚C temperature. Afterward, all samples will be removed, and 0.5 moles HNO_3 solution will be added to produce the sample in liquid form. Subsequently, the sample will be taken to ICP OES to identify the heavy metals present in the sediment.

3.4.2 Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES)

There was a methodical process involved in the analysis of heavy metals in soil and sediment samples. Grain size variability was minimised by grinding and sieving the 32 µm-63µm fraction to a particle size of <32 µm after it was oven-dried at 105 °C. The samples were kept cold. The reference material was not dried in an oven to prevent the loss of volatile compounds. The concentrations of each element were calculated based on dry weight and adjusted for moisture content. microwave digestion used for change solid to liquid sample. After the process sample was bring to ICP-OES analysis for check content heavy metal in sediments.

3.5 Enrichment factor and geoaccumulation index

In this study, sediment quality will be measured and assessed using the enrichment factor and geoaccumulation methods to ensure that metal concentrations in sediment are of good quality and do not pose environmental hazards. In this method, calculations will be conducted to determine metal concentrations and assess pollution levels in sediment. The formula for the enrichment factor (3.5.1) and the formula for the geoaccumulation index, using 1.5 as a correction factor for changes in mineral content in the Earth's crust (3.5.2), will be employed.

$$EF = \frac{[(C/R)]sample}{[(C/R)]background} \tag{3.5.1}$$

$$Igeo = log2\,\frac{C_n}{1.5} \times B_n \tag{3.5.2}$$

CHAPTER 4

RESULTS AND DISCUSSION

4 Physical Characteristics of Kelantan Fluvial sediment

The sediment samples were collected from various areas in Kelantan, i.e., Airchanal River, Satan River, Buluh River, Ketil River, Ber River, Ber Spring Steam/outlet, and Ber Spring Confluence, as shown in figure 4.1. The collected sediment exhibits diverse physical characteristics. These sediments vary in colour, including dark, brown, orange, and others, as depicted in table 4.2. Furthermore, the sediments have different odours, such as earthy, faecal, and muddy smells.

During the sampling process, several factors influence the smell, colour, and shape of each sediment. For example, rain carries additional materials through the current that prevails. There are also areas with less pleasant smells such as the smell in the Satan River and spring steam/outlet. This is because both rivers have a somewhat similar smell like mud and human faces. This happens because the Satan River area is a residential area inhabited by Satan village residents for a long time, making human daily activities occur. For the smell of sediment in the spring steam/outlet, it occurs due to changes in the chemical composition caused by heat. This occurs when exposed to high temperatures, organic matter in the sand can undergo decomposition or degradation. This process can produce unpleasant-smelling compounds, such as sulfur gas that smells like rotten eggs or methane gas. All these sediments have been identified in terms of size using laboratory sieves to facilitate the identification of heavy metals and organics present in each sediment.

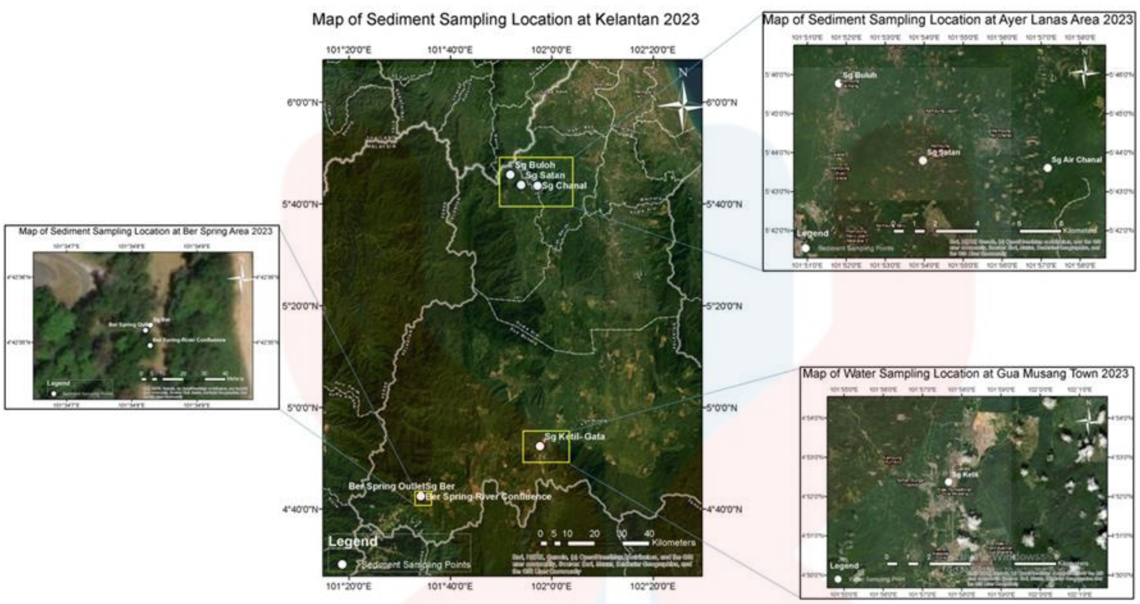

Figure 4.1: Map of sediment sampling location at Kelantan

Sample	Colour	Odour
Airchanal river	Dark	Earthy
Satan river	Brown	faecal
Buloh river	Brown	Muddy
Ketil river	Orange	Muddy
Ber river	Brown	Earthy
Ber spring steam/outlet	Brown	Rotten egg
Ber spring confluence	Dark	Earthy

Table 4.2 colour and odour each sample

4.1.1 Grain size distribution of sediment

An essential stage in sediment analysis is the manual screening of dried sediment to separate out particular size fractions, especially those as small as 32µm. A set of laboratory sieves with increasingly lower mesh sizes, ranging from 4mm to 32 µm, are used in this manual sieving process. The dried sediment sample is carefully placed onto the top sieve, and the sediment is separated according to size using a mixture of tapping, shaking, and hand shaking or, if one is available, a sieve shaker. The material that goes through each sieve is gathered in a pan underneath the sieves, and each sieve holds particles within a certain size range., as illustrated in Figure 4.1.1

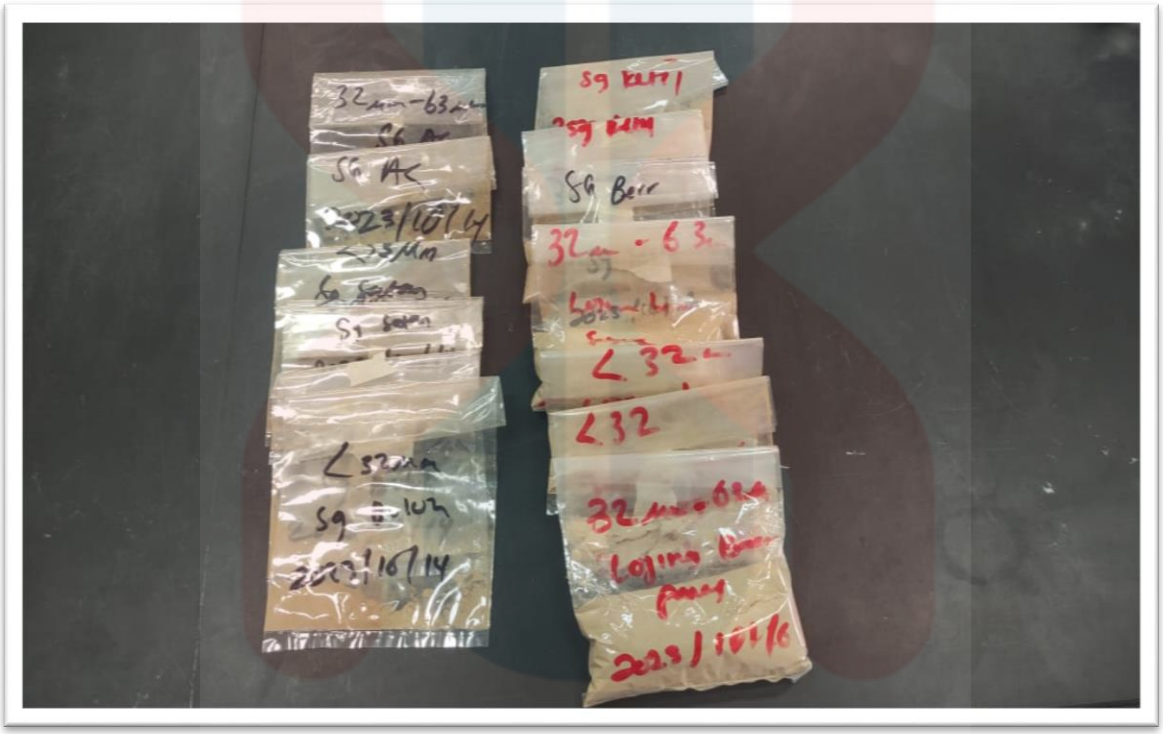

Figure 4.1.1: After grains size distribution sample Buloh River and Ber spring steam/outlet

4.1.2 Organic matter of Kelantan sediment

The tables, which are sorted by grain size, give information on the amount of organic matter present in sediment samples that were taken from several rivers in Kelantan. Sediment, which consists of diverse decomposing plant and animal remains and other organic materials, must contain organic stuff. The percentage of organic matter in the samples was estimated using the Loss on Ignition (LOI) method. For each river sample, the weight of the crucible, the weight before igniting, the weight after ignition, and the estimated loss on ignition percentage are shown in Table 4.1.1(a), which concentrates on silt with a grain size between 32µm and 63µm. For example, the sediment from the Airchanal River showed a 11.96% loss on ignition, meaning that organic matter accounted for 11.96% of the initial weight. Similar data is shown in Table 4.1.1(b), which concentrates on sediment whose grain size is smaller than 32µm. Here, the composition of biological stuff is examined at a finer particle level. For instance, the statistics show that the organic matter concentration of silt from the Airchanal River that has grains smaller than 32µm is 11.6%. The percentage of the starting weight that is lost after burning off organic materials during ignition is known as the Loss on Ignition percentage. Increased percentages suggest that the silt contains more organic stuff. Because it affects microbial activity, sediment stability, and nutrient cycling in aquatic habitats, organic matter in sediment has ecological significance. (Zhang et al., 2020)

Sample	Weight crucible (g)	Weight before (g)	Weight after(g)	Loss on ignition %
Airchanal river	21.02	0.25	0.2201	11.96%
Satan river	21.87	0.25	0.2324	7.04%
Buloh river	21.08	0.25	0.2432	2.72%
Ketil river	21.36	0.25	0.2445	2.2%
Ber river	21.48	0.25	0.2322	7.12%
Ber spring steam/Outlet	21.58	0.25	0.2310	7.6%
Ber spring confluence	21.26	0.25	0.2405	3.8%

Table 4.1.2(a) organic matter of grain size 32µm-63µm at Kelantan sediment

Sample	Weight crucible (g)	Weight before (g)	Weight after(g)	Loss on ignition %
Airchanal river	20.60	0.25	0.2210	11.6%
Satan river	24.27	0.25	0.2440	2.4%
Buloh river	22.10	0.25	0.2304	7.84%
Ketil river	19.75	0.25	0.2406	3.76%
Ber river	21.28	0.25	0.2202	11.92%
Ber spring steam river	21.42	0.25	0.2306	7.76%
Ber spring confluence river	21.14	0.25	0.2321	7.16%

Table 4.1.2(b): organic matter of grain size <32µm at Kelantan sediment

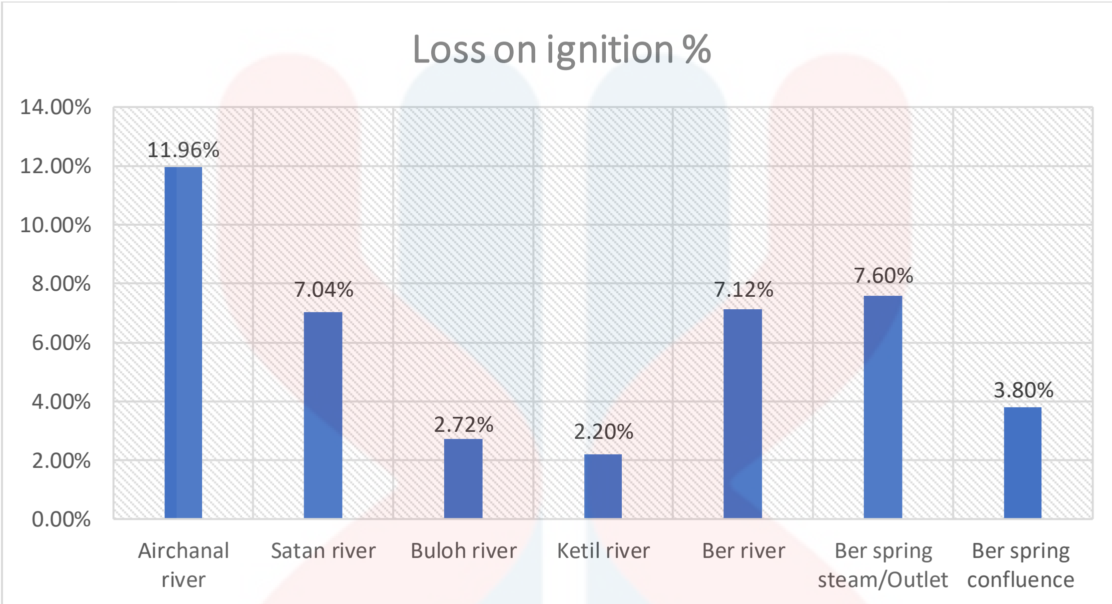

Figure 4.1.3(a) organic matter of grain size 32µm-63µm at Kelantan sediment

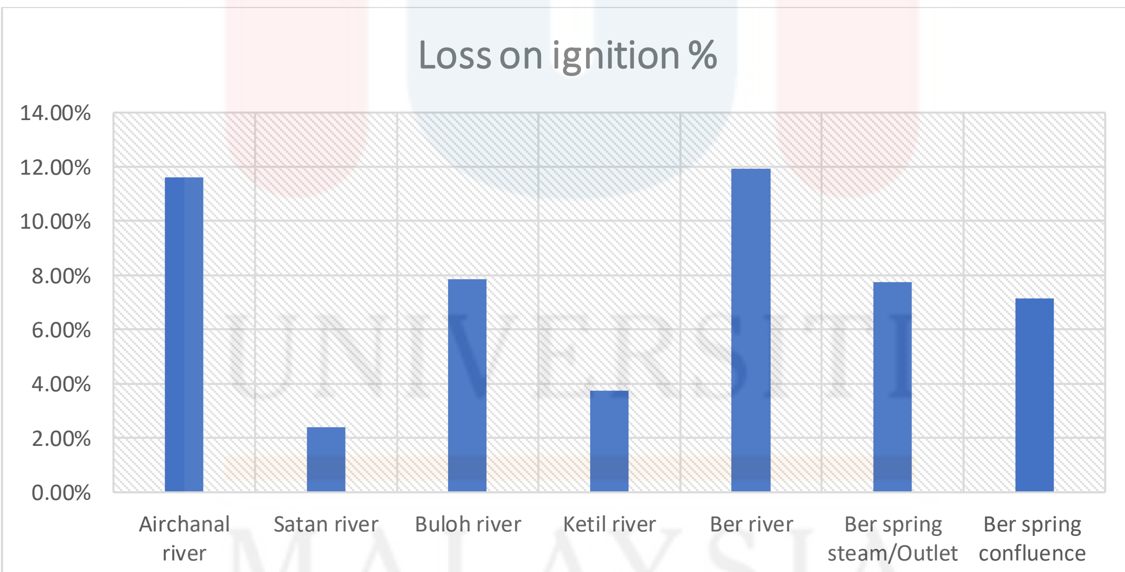

Figure 4.1.3(b) organic matter of grain size <32µm at Kelantan sediment

4.2 Heavy metal contents and compare of the sediments and grain size 32µm-63µm and less than 32µm.

Before sediment is taken to ICP OES, it will undergo several processes to transform it into a liquid form. In this process, 0.2g of sediment will be weighed and placed into a microwave digestion with a mixture of chemicals, namely HNO_3, HCl, H_2O_2, and HF, and then subjected to microwave digestion for 2 hours. Afterward, all samples will be removed, and 0.5 moles HNO_3 solution will be added to produce the sample in liquid form. Subsequently, the sample will be taken to ICP OES to identify the heavy metals present in the sediment, referring to table 4.2.

SEDIMENT SAMPLE	AirChanal River		Buloh River		Satan River		Ketil River		Ber River		Ber Spring Steam/outlet		Ber spring Confluence	
Grain Size	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm
Cd	0.429	0.81	0.448	0.442	0.379	0.726	0.273	0.692	0.527	0.475	0.618	0.568	0.251	0.157
Cr	60.887	89.33	66.176	162.24	71.601	72.43	55.297	68.946	50.458	57.328	49.938	59.278	54.199	63.713
Cu	39.693	41.502	12.146	20.372	32.584	40.734	18.663	23.956	11.972	15.859	11.533	16.694	14.772	19.779
Fe	36934.458	45576.288	22410.372	31937.65	40101.327	31045.142	26279.032	34984.052	23644.434	27208.775	21592.474	25330.644	24327.2	30445.153
Mn	951.181	586.033	549.01	624.746	1531.357	907.232	0.727	0.403	433.052	517.594	417.549	558.092	426.697	468.04
Ni	34.035	25.977	20.214	62.816	22.258	40.901	13.892	20.193	16.071	19.267	17.506	23.355	17.216	23.501
Pb	66.69	74.519	54.211	75.437	53.453	63.684	29.707	56.061	49.754	53.723	53.132	58.671	52.741	52.802
Zn	115.195	89.54	58.245	85.557	75.19	104.889	48.721	66.684	48.87	52.981	46.226	57.868	49.776	54.801

Table 4.2 heavy metal contents of the sediment and grain size 32µm-63µm and <32µm

After obtaining data from ICP-OES for heavy metals with a grain size analysis, it indicates that Cadmium present in the 32µm-63µm range shows a slight difference compared to 32µm, where it exhibits a lower cadmium content compared to 32µm. Cadmium found in the 32µm-63µm range demonstrates a lower cadmium concentration compared to 32µm, which shows higher readings than 32µm-63µm. This occurrence is due to the larger sediment size of 32um, which influences the readings. As shown in figure 4.2.1.

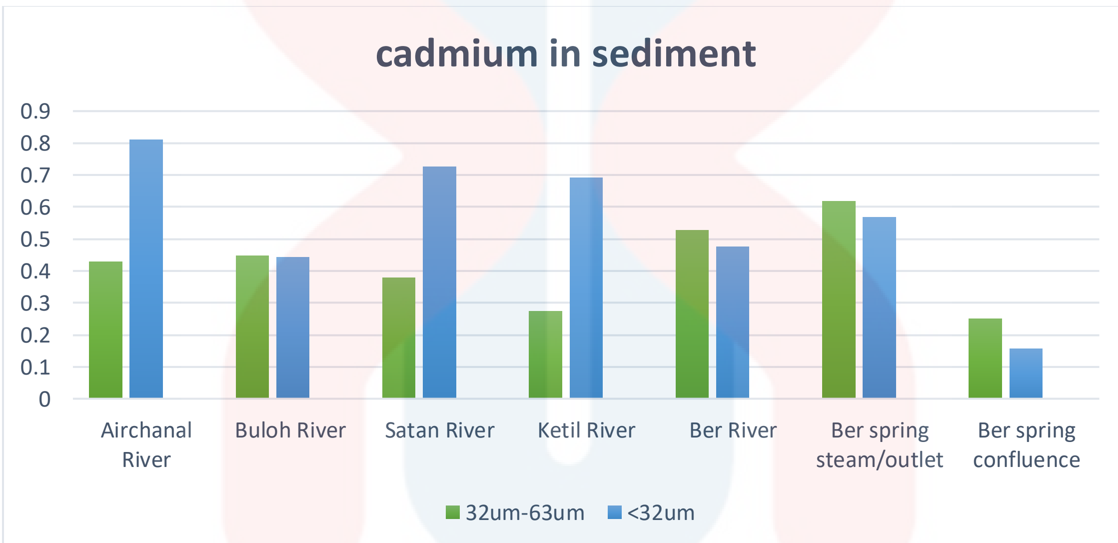

Figure 4.2.1: concentration of cadmium in sediment grain size 32µm-63µm and <32µm

According to the data obtained in 4.2.2, the total amount of chromium in the sediment does not exceed 100 for the 32µm-63µm and <32µm sizes, with only one size exceeding 100, which is <32µm in Buloh River with a total of 162.24 ppm. This can be explained by the Buloh River environment as it contains many small rocks and sand that do not originate from there.(Li et al., 2015) This phenomenon occurs due to the transportation by water and currents, which bring in other particles such as rocks and sand, causing the sand there to mix with the sand carried by the currents.

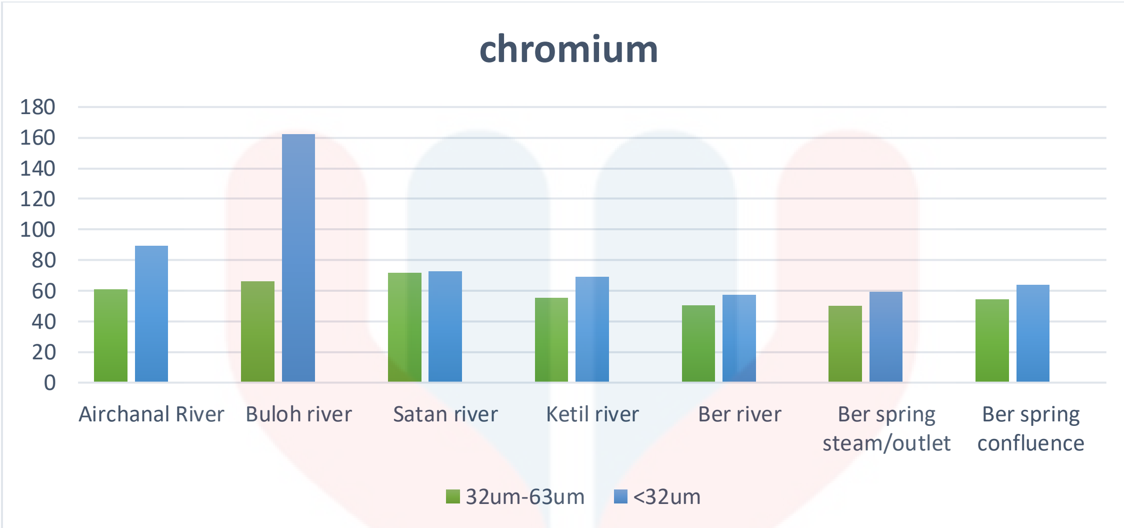

Figure 4.2.2: concentration of chromium in sediment grain size 32µm-63µm and <32µm

Referring to the data presented in 4.2.3, it has shown a difference between the sizes 32µm-63µm and <32µm, where the amount of copper in the <32µm size is higher compared to the 32µm-63µm size. The total amounts for the <32µm size in Airchanal River and Satan River are 41.502 ppm and 40.734 ppm, respectively. This is attributed to the presence of many fractured rocks in those areas, which significantly influences the copper mineral content in the <32µm size.

In contrast, the 32µm-63µm size shows lower values, specifically in Ber River and Ber Spring Stream/outlet. This is influenced by a less effective weathering process, resulting in a lower production of copper. Additionally, not only does the pH in the soil affect the mineral content in the sand, but microbial activities can also impact copper processing. (Yin et al., 2012)

Figure 4.2.3: concentration of copper in sediment grain size 32µm-63µm and <32µm

Iron is a mineral fraction derived from rocks that will affect sand to ensure the iron content in the sand is either high or low. Referring to the figure 4.2.4 below, it has shown variations according to size, where the size 32um-63um is slightly lower compared to <32µm. This ensures that the 32µm-63µm size has other particles that make the iron content in the sand lower compared to the <32µm size.

However, Satan River shows high iron content with a total of 40101.327 ppm. This is because the 32µm-63µm size has smaller particles that influence the high iron content. In contrast, the <32µm size has shown high iron content, such as in Airchanal River, which is 45576.288 ppm. This occurs because Airchanal River has many rocks such as Granite, Hornfels, Limestone, Mudstone, Sandstone, and Aplite. Leading to the natural weathering process of rocks like This has caused the soil and water to contain high iron, resulting in the sand having a high iron content.

Figure 4.2.4: concentration of iron in sediment grain size 32µm-63µm and <32µm

Referring to the figure 4.2 (i), it has shown normal levels for Airchanal River, Buloh River, Ber River, Ber Spring Stream, and Ber Spring Confluence, which are 951.181 ppm, 549.01 ppm, 433.052 ppm, 417.549 ppm, and 426.697 ppm for the 32um-63um size and <32um size are 586.033 ppm, 624.746 ppm, 517.594 ppm, 558.092 ppm, and 468.04 ppm. This is in contrast to Satan River and Ketil River, which have high and low values. Satan River has a high manganese content with values of 1531.357 ppm and 907.232 ppm for the 32µm-63µm size and <32µm size. This occurs because the area has natural mineralization containing minerals. This allows manganese to be released when rocks break, resulting in a high manganese content in that area. On the other hand, Ketil River has a low manganese content, namely 0.727 ppm and 0.403 ppm for the 32um-63um size and <32µm size.

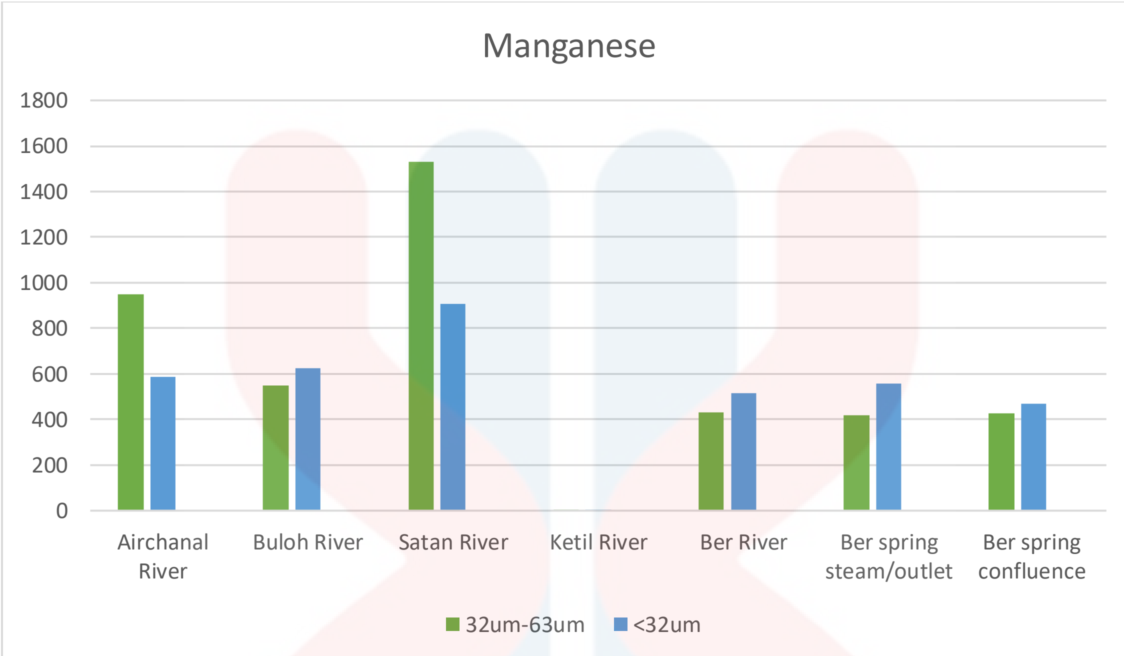

Figure 4.2. (i): concentration of Manganese in sediment grain size 32µm-63µm and <32µm

The observations from figure 4.2(ii) highlight a significant difference in the <32µm fraction, particularly noticeable in Buloh River and Satan River, where the nickel readings in sediment are 62.816 ppm and 40.901 ppm, respectively. This pronounced difference suggests that smaller particle sizes, represented by <32µm, play a crucial role in nickel accumulation within the sediments. There are multiple reasons for the greater nickel content in the fraction smaller than 32 µm. First of all, there are more sites for nickel adsorption in smaller particles since they have a higher surface area per unit mass. This is especially crucial in places where the water contains a lot of nickel, such Sungai Buloh and Sungai Satan. Because the waterborne nickel binds to the finer particles more effectively, the concentration in the <32µm fraction is higher. (Yusoff et al., 2022) Additionally, because of their larger surface area and stronger specific surface contacts, the smaller particles might be more reactive and have a greater propensity to adsorb nickel. This might be a factor in the elevated nickel readings in the <32µm fraction that have been seen.

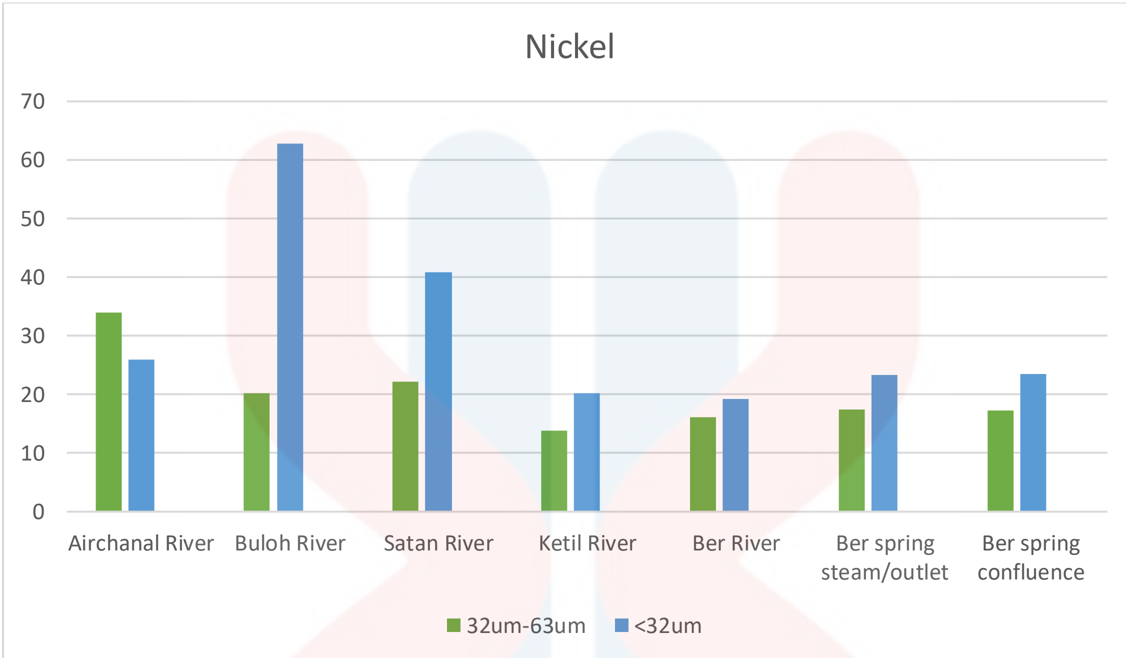

Figure 4.2(ii): concentration of Nickel in sediment grain size 32µm-63µm and <32µm

The variation displayed in figure 4.2(iii) indicates that the size <32µm is greater than the range of 32µm–63µm. Because lead has stuck to the silt, the size <32µm has more lead because the figure readings indicate this. The lead content of the Spring Confluence is the same, registering values of 52.741 ppm and 52.802 ppm for the 32µm–63µm and <32µm diameters, respectively.

Lead can interact with different sized sediment particles when it is present in the water. In this instance, the particles smaller than 32 µm have a higher surface area relative to their mass, which increases their ability to adsorb lead ions. Consequently, the figure results for silt containing particles smaller than 32µm show a greater lead level.

The lead distribution in sediment for particles smaller than 32µm and those between 32µm and 63µm is comparable, according to the lead concentration for the Spring Confluence, which is constant across the two size fractions. This consistency implies that lead is dispersed uniformly among the various sizes of sediment particles in the Ber spring Confluence.

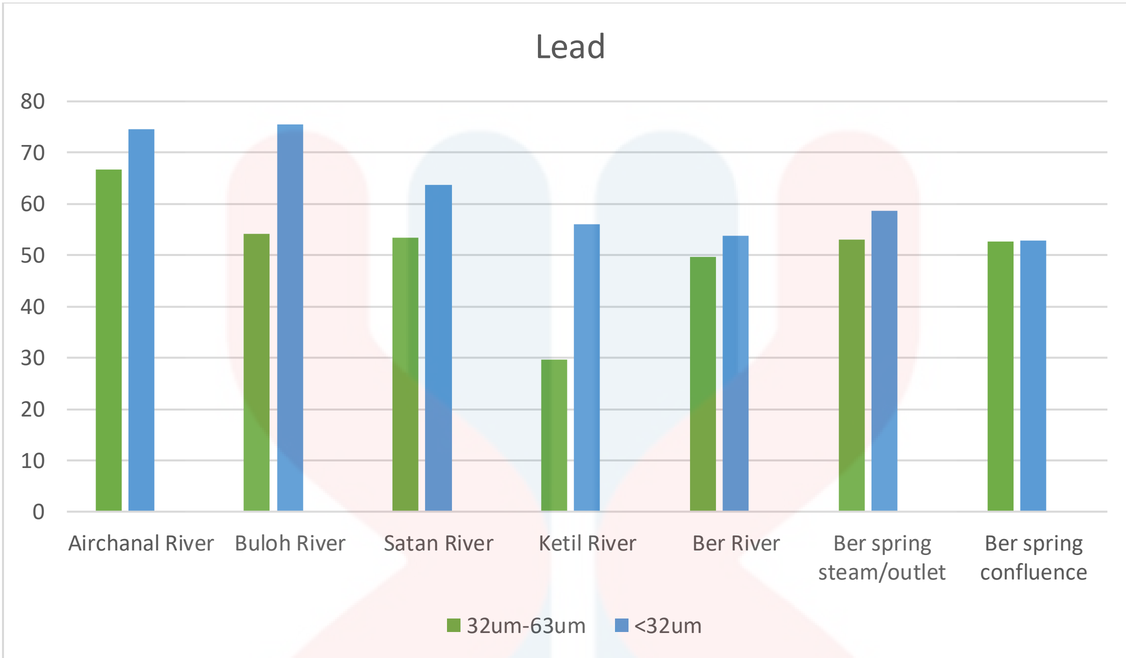

Figure 4.2 (iii): concentration of Lead in sediment grain size 32µm-63µm and <32µm

Referring to figure 4.2 (iv), it has been shown that zinc in the <32µm fraction is more abundant compared to the 32µm-63µm fraction. As illustrated in the figure, the <32µm size indicates more precise data regarding zinc content. For instance, the Satan River has shown that the zinc content in the 32µm-63µm size is 75.19 ppm, while the <32µm size indicates a higher zinc content of 104.889 ppm. In contrast, the Airchanal River has demonstrated high zinc content in the 32µm-63µm size, while the <32µm size has shown lower zinc content. This occurs because particles in the 32µm-63µm size range have more zinc compared to the <32µm size, as particles in the 32µm-63µm range tend to have a higher zinc concentration, leading to their isolation.

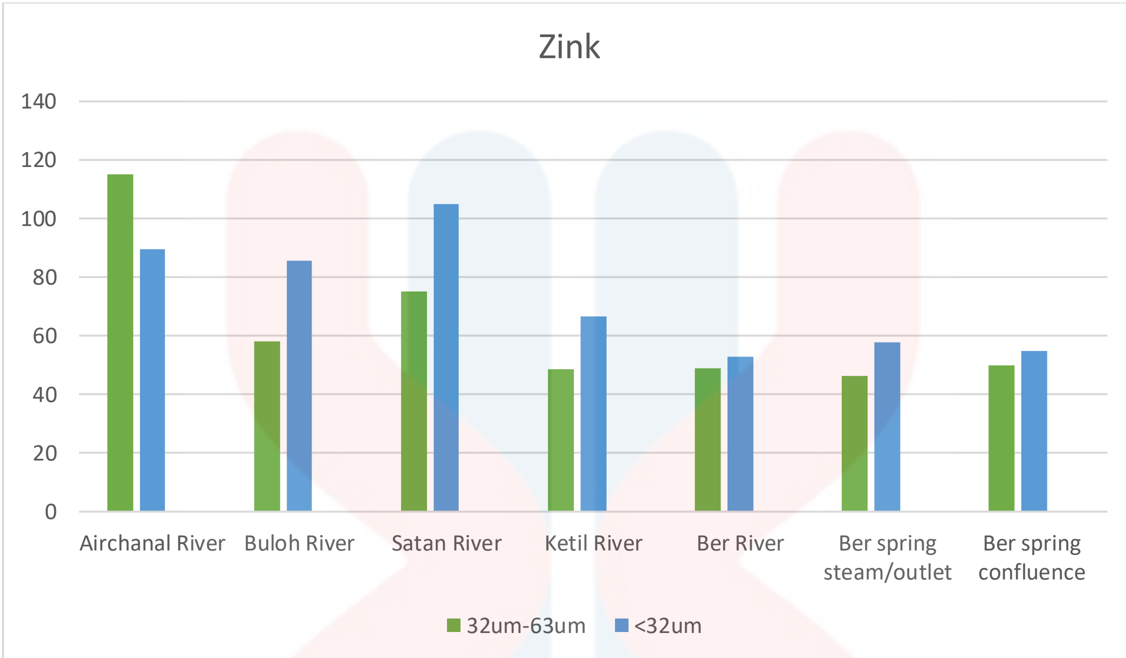

Figure 4.2. (iv): concentration of Zink in sediment grain size 32µm-63µm and <32µm

4.3 Determine the pollution level by using enrichment factor and geoaccumulation index.

After obtaining data from ICP-OES regarding the heavy metal content in sediment to determine the heavy metal pollution level using the enrichment factor and geoaccumulation index. The enrichment factor assesses the level of enrichment of a particular element or mineral in sediment. An enrichment factor value greater than 1 indicates enrichment, while a value less than 1 indicates depletion. Geoaccumulation assesses the level of contamination of a particular element or mineral in sediment. A positive value indicates contamination, and a negative value indicates the natural background level.

In Table 4.3(a), the level of metal enrichment is depicted, where the average level of metal enrichment is <5 EF, categorized as a moderate level for Zn, Fe, Ni, Mn, Cd, Cr, and Cu elements. This indicates that the pollution level is moderate and not hazardous. In contrast, Pb has shown a significant pollution level due to the considerable enrichment of Pb content. Meanwhile, the geoaccumulation index has indicated a low pollution level for Fe, Ni, Mn, Cd, Cr, and Cu elements, and the existing mineral content is natural. However, it is different for Pb and Zn elements, which have shown a slightly higher pollution rate, i.e., >5.

Elements such as Cr, Cu, Fe, Mn, Ni, and Zn have shown low enrichment, where these six elements only have mineral enrichment <2 which is not harmful to the environment and does not lead to pollution. This is due to geological and local environmental conditions that can also play a role in influencing the distribution and impact of mineral elements (Triandiza et al., 2021). In contrast, elements Cd and Pb have high enrichment >5. This is because these elements have toxic properties and are easily influenced by temperature and pH, leading to high enrichment. However, this high enrichment has the potential for pollution (Wang et al., 2017).

A moderate pollution accumulation index occurs in the Airchanal River, Buloh River, and Satan River for the element Pb. This happens because these areas are inhabited by village residents, allowing them to engage in activities that can contribute to an increase in Pb levels. This is also influenced by geological characteristics and environmental conditions that result in high lead mineral content. (Zulkafflee et al., 2022). Other elements such as Zn, Cr, Cu, Cd, Fe, Ni, and Mg have shown low pollution levels, where the average metal content for each element is <1. This is because these areas are not contaminated with human activities that could lead to high metal content in each element.

SEDIMENT SAMPLE	Sg Air Chanal		Sg Buloh		Sg Satan		Sg ketil		Sg Ber		Ber Spring Steam/outlet		Ber spring Confluence	
Grain Size	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm
Cd	2.86	5.4	2.99	2.95	5.86	4.84	1.82	4.61	3.51	3.17	4.12	3.79	1.67	1.05
Cr	0.4349	0.6380	0.4726	1.1588	0.5114	0.5173	0.3949	0.4924	0.3604	0.4094	0.3567	0.4234	0.3871	0.4550
Cu	0.5837	0.6103	0.1786	0.2995	0.4791	0.5990	0.2744	0.3522	0.1760	0.2331	0.1696	0.2455	0.2172	0.2908
Fe	0.5862	0.7234	0.3557	0.5069	0.6365	0.4927	0.4171	0.5553	0.3753	0.4318	0.3427	0.4020	0.3861	0.4832
Mn	1.00	0.6168	0.5779	0.6576	1.6119	0.9549	0.0007	0.0004	0.4558	0.5448	0.4395	0.5874	0.4491	0.4926
Ni	0.4253	0.3247	0.2526	0.7852	0.2782	0.5112	0.1736	0.2524	0.2008	0.2408	0.2188	0.2919	0.2152	0.2937
Pb	6.669	7.4519	5.4211	7.5437	5.3453	6.3684	2.9707	5.6061	4.9754	5.3723	5.3132	5.8671	5.2741	5.2802
Zn	1.5359	1.1938	0.7766	1.1407	1.0025	1.3985	0.6496	0.8891	0.6516	0.7064	0.6163	0.7715	0.6636	0.7306

Table 4.3.1(a): pollution level in sediment by using enrichment factor

SEDIMENT SAMPLE	AirChanal river		Sg Buluh		Sg Satan		Sg ketil		Sg Ber		Ber Spring Steam/outlet		Ber spring Confluence	
Grain Size	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm	32µm-63µm	<32µm
Cd	0.516	1.432	0.578	0.559	0.337	1.275	-0.136	1.205	0.812	0.662	1.042	0.920	-0.257	-0.934
Cr	-2.30	-2.18	-2.18	-0.886	-2.066	-2.05	-2.439	-2.121	-2.571	-2.387	-2.586	-2.339	-2.468	-2.235
Cu	-1.403	-1.339	-3.111	-2.365	-1.688	-1.366	-2.492	-2.131	-3.132	-2.727	-3.186	-2.652	-2.829	-2.408
Fe	-1.9406	-1.6371	--2.6620	-2.1500	-1.8216	-2.1909	-2.4320	-2.0185	-2.5838	-2.3815	-2.7150	-2.4851	-2.5428	-2.2196
Mn	-0.583	-1.281	-1.376	-1.189	0.103	-0.651	-10.93	-11.787	-1.718	-1.461	-1.770	-1.352	-1.739	-1.606
Ni	-1.817	-2.207	-2.569	-0.933	-2.430	-1.581	-3.110	-2.571	-2.900	-2.638	-2.777	-2.361	-2.801	-2.3522
Pb	2.152	2.312	1.853	2.33	1.833	2.085	0.985	1.902	1.729	1.84	1.824	1.967	1.813	1.815
Zn	0.034	-0.329	-0.949	-0.394	-0.581	-0.101	-1.207	-0.754	-1.202	-1.086	-1.281	-0.959	-1.176	-1.037

Table 4.3.1(b): pollution level in sediment by using geoaccumulation index

Element	<2	2 ≤ EF < 5	5 ≤ EF < 20	Average conc. In earth crust
Cd	-	/	-	0.2
Cu	/	-	-	70
Cr	/	-	-	200
Zn	/	-	-	80
Fe	/	-	-	50000
Mn	/	-	-	1000
Ni	/	-	-	100
Pb	-	-	/	16

Figure 4.3.2(a): pollution level in sediment by using enrichment factor

Element	0 (unpolluted)	0-1 (unpolluted to moderately polluted)	1-2 (moderately polluted)	Average conc. In earth crust
Cd	/	/	-	0.2
Cu	/	-	-	70
Cr	/	-	-	200
Zn	/	/	-	80
Fe	/	-	-	50000
Mn	/	-	-	1000
Ni	/	-	-	100
Pb	-	-	/	16

Figure 4.3.2(b): pollution level in sediment by using geoaccumulation index

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5 Conclusions

The goal of the Kelantan study was to thoroughly evaluate the particle size distribution, heavy metal concentrations, and sediment properties at a particular site. contrasting the concentrations of heavy metals in sediment fractions that were less than 32µm and those that were between 32µm and 63µm.

In conclusion, the research conducted in Kelantan advances our knowledge of the distribution of heavy metals and the dynamics of sediment in the chosen area. Predicting the behaviour of sediments is based on determining physical parameters like grains size distribution and texture and organic matter. The evaluation of heavy metal concentrations highlights possible environmental consequences, requiring continued surveillance. Microwave digestion and ICP-OES processes assist in identifying the heavy metal content in sediment to determine the sediment quality present in each studied area. The complex link between sediment properties and heavy metal retention is highlighted by the comparison of various grain size fractions. Enrichment factor and geoaccumulation index are also used to identify the heavy metal content in sediment, where these heavy metals may or may not affect the river environment. In this study, the sediment quality can be said to be uncontaminated, and the condition of the sediment is good and uncontaminated Overall, the results have consequences for the sustainable use of aquatic ecosystems in the area as well as environmental management. In order to preserve and improve the environmental quality of the researched area, ongoing research and monitoring programmers are essential.

5.1 Recommendations

Integration of Sediment Monitoring Programmers, to record temporal variations in sediment characteristics and heavy metal concentrations, it is advised to establish long-term sediment monitoring programmers. Consistent sampling and examination will yield an extensive dataset for evaluating patterns and pinpointing plausible origins of fluctuations. Source Identification to determine the precise manmade and natural sources influencing the amounts of heavy metals in sediments, carry out source apportionment studies. Comprehending the origins will facilitate efficient methods of mitigating pollution and advance environmentally sound land use practices. Sediment Transport Dynamics to comprehend the flow of heavy metals in the water system, look at sediment transport dynamics. This involves analyzing patterns of sedimentation and erosion as well as the variables affecting the movement of sediment, in order to forecast possible effects later on. Finally, we hope that this study can be extended to remote and unexplored areas in order to assess sediment quality in areas of interest. This can help understand sediment quality in a particular location to preserve the environment from contamination by human activities that contribute to the degradation of river life and its surroundings.

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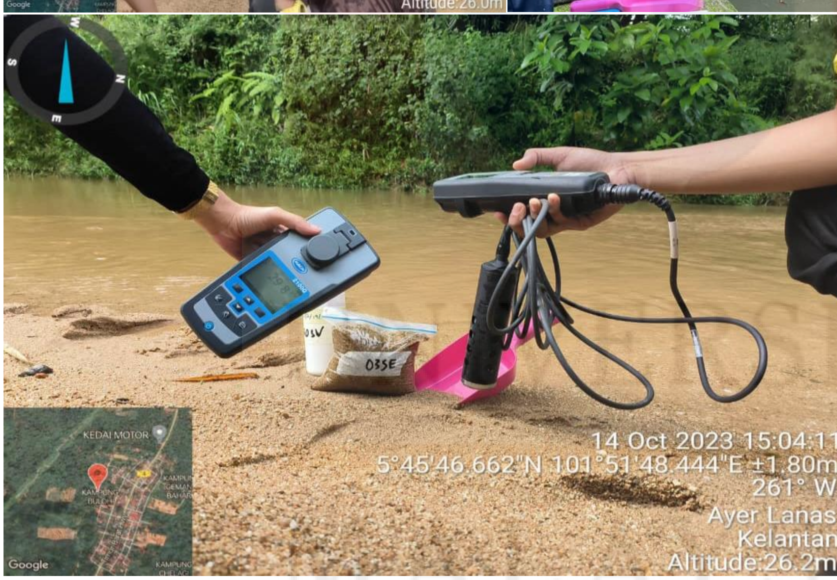
APPENDIX A

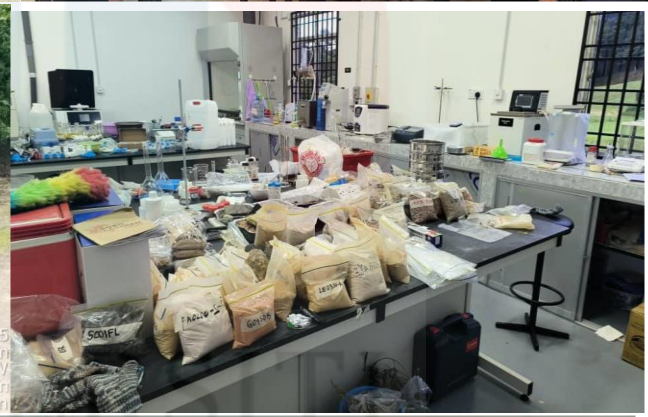

14 Oct 2023 15:04:32
5°45'46.722"N 101°51'48.504"E ±1.30m
232° SW
Ayer Lanas
Kelantan
Altitude:26.0m
Google


KEDAI MOTOR
Google
O3SE
14 Oct 2023 15:04:11
5°45'46.662"N 101°51'48.444"E ±1.80m
261° W
Ayer Lanas
Kelantan
Altitude:26.2m

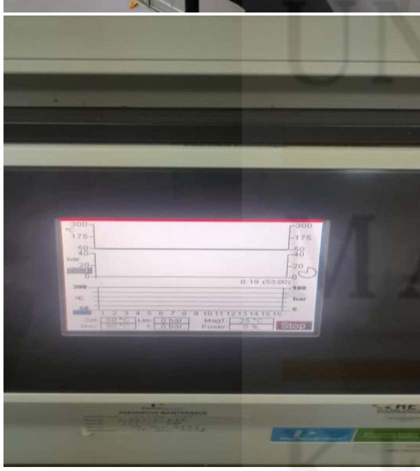
APPENDIX B


16 Oct 2023 15:09:09
4°52'22.452"N 101°57'40.122"E ±2.00m
268° W
Jalan Bukit Chupak
Kampung Gata
Gua Musang
Kelantan
Altitude:106.3m


14 Oct 2023 12:43:05
216° SW
Kelantan
Altitude:69.5m




LABORATORY SAFETY



APPENDIX C