ASSESSMENT OF HEAVY METAL POLLUTION WITHIN DOWNSTREAM OF PERAK RIVER BASIN USING QUAL2K MODELLING

NUR AINA BINTI MOHD ROSLAN

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by

NUR AINA BINTI MOHD ROSLAN

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Name of Student: Nur Aina binti Mohd Roslan

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

Signature:

Date : 4 August 2021

Endorsed by:

_____
(Signature of Supervisor)

Name of Supervisor: Sr. Dr. Abdul Hakim Salleh

Date: 5/8/2021

Approved by:

_____
(Signature of Examiner)

Name of Examiner: Dr. Nik Azimatolakma Awang

Date: 6/8/2021

(Important Note: This form can only be forwarded to examiners for his/her approval after endorsement has been obtained from supervisor)

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ABSTRAK

Kajian penyelidikan ini telah dilakukan untuk menilai status kualiti air berdasarkan parameter fisio-kimia yang dipilih serta jumlah kepekatan logam berat untuk memahami scenario kualiti air di Hilir Sungai Perak. Empat jenis ujian telah dilakukan di makmal iaitu ujian Jumlah Pepejal Terampai (TSS), kekeruhan, Jumlah Nitrogen Kjeldahl (TKN) dan logam berat mealului analisis daripada ICP-OES. Jumlah Pepejal Terampai (TSS), kekeruhan, dan Jumlah Nitrogen Kjeldahl (TKN) terhadap sampel air yang diuji berada dalam lingkungan 30.67 hingga 742 mg/L, 21.55 hingga 87 NTU dan 0 hingga 4.928 mg/L. Kepekatan 19 jenis logam berat dalam kajian ini telah diuji menggunakan mesin Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Turutan unsur logam berat dalam samel air adalah seperti yang berikut, Ca > Mg > Cu > Fe > Pb > Mn > Sr > V > Ti > Mo > Tl > Ni > As > Sb > Be > Co > Cr > Li > Cd. Permodelan menggunakan Qual2K telah dilakukan untuk melihat tahap taburan pencemaran. Enam jenis logam berat telah dipilih untuk dijadikan parameter untuk mengukur Jumlah Beban Harian Maksimum (TMDL). Enam jenis logam berat tersebut adalah Cd, Cu, Fe, Mn, Ni and Pb. Melalui pengiraan TMDL, pengurangan beban pencemaran terhadap kesemua logam berat berjaya mencapai sasaran kualiti air yang ditetapkan. Hasil daripada pengiraan untuk TMDL adlaah 1.8533 kg/day.

ABSTRACT

This research study has been conducted to assess status of the water quality based on the selected physio-chemical parameters as well as the concentration of heavy metals in order to understand the present scenario of water quality of the downstream of Perak River. Four tests were conducted to assess the water quality, which are Total Suspended Solid (TSS), turbidity, Total Kjeldahl Nitrogen (TKN) and heavy metals by ICP-OES. The total suspended solid (TSS), turbidity, and total kjedahl nitrogen (TKN) of tested water samples is in the range of 30.67 to 742 mg/L, 21.55 to 87 NTU and 0 to 4.928 mg/L respectively. The concentration of 19 heavy metals have been analysed using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) machine. The concentration of heavy metals were in the order of Ca > Mg > Cu > Fe > Pb > Mn > Sr > V > Ti > Mo > Tl > Ni > As > Sb > Be > Co > Cr > Li > Cd. The modelling of dispersion of heavy metals along the downstream of heavy metals were made using Qual2K. Six heavy metals, which are Cd, Cu, Fe, Mn, Ni, and Pb, have been chosen as the parameters for Total Maximum Daily Load (TMDL) calculation. From the calculation of TMDL, load pollution reduction was observed to meet the targeted water quality standard for all chosen heavy metals. The value of TMDL obtained from the analysis was 1.8533 kg/day.

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CHAPTER 1

INTRODUCTION

1.1   Heavy Metal Pollution in River Basin

Rivers play an important part in the ecosystems as rivers provide water supplies for commercial, residential and recreational purposes, irrigation in agriculture, transportation as well as drainage channels for surface water (Chin and Ng, 2016; Low et al., 2016). However, the river's water quality has declined gradually each year due to adverse factors, such as high population density, life stock farming, aquacultures, construction works i.e. land clearing and transportation of construction and waste material, sewage discharge and inappropriate waste management measures causing river pollution (Chin and Ng, 2016; Shan et al., 2020). The number of polluted rivers in Malaysia has gradually increased for the past 20 years. Nearly 17 out of 186 rivers in Malaysia have been classified as contaminated and hazardous (unfit) for human use in 2008 (Salam et al., 2019). It is also appears that about 38.6% and 8.6% of rivers in Malaysia are classified as severely polluted and polluted in 2012 (Poon et al., 2016). If the river water in Malaysia is further polluted, river pollution will become a severe problem in Malaysia, which will affect the sustainability of the water resources in fulfilling the water demand (Rezania et al., 2016). River contamination can also affects the life of living organisms and plants, as well as the economy (Afroz and Rahman, 2017).

Contamination of heavy metals is one of the causes of river pollution. Heavy metals come from various anthropogenic activities such as commercial and industrial, sand mining operations, smelting, and coal burning (Esmaeilzadeh et al., 2019). Heavy metals will continuously accumulate through these activities and finally be deposited in the environment especially in water and soil to an unknown concentration. Moreover,

heavy metals can also seep into sediments and build up in terms of toxicity which has an irreversible impact on contaminating underground aquifers and drinking water wells, and thus affecting consumers' health (Salam et al., 2019). Rock weathering can also contribute to heavy metal pollution in the environment via natural phenomena. Nevertheless, portions of metal released are in minute quantities, and rarely affect the river water quality as much as anthropogenic activities (Haris et al., 2017). Most of the rivers in Malaysia are polluted with heavy metals due to inappropriate land use, affecting the quality of river water (Othman et al., 2018). A study made on the water quality of the Johor River shows that its water quality index (WQI) falls under Class IV due to uncontrolled sand mining and industrial activities along the Johor River (Liang et al., 2020).

1.2   Problem Statement

Perak River covers about 70% of the state of Perak. The river flows from the upper region of Perak state, near the Thai border and passed through several towns before emptying into the Straits of Malacca. As the economic growth of the country is rising, human activities such as manufacturing, construction and industrial are overgrowing in the development area surrounding the river. All of the human activities caused the effluent coming from those activities to affect the river's water quality. Heavy metal pollution is one of the problems that arise. The investigation of current water quality of the downstream Perak River basin is important to record and track changes of any heavy metal contamination with the aim to control and monitor the dispersion of pollution from the source. Heavy metals present in the Perak River might came from the weathering of soils and rocks as well as from human activities such as aquaculture, domestic wastewater discharge and agriculture run-off. Thus by accessing the source of metal

element, further analysis on the risks as well as the steps to minimize the impact of heavy metal contamination on the environment and human health. The modelling of heavy metals from the investigation will be applied by using Qual2K model in order to obtain the distribution of heavy metal concentration along the downstream of Perak River.

1.3   Objectives

The objectives of this research study are listed as follows:

1. To analyzes the water quality based on selected parameters (TSS, Turbidity, TKN and Heavy Metals)

2. To map the dispersion and mobility of pollution based on selected water quality parameters by applying the Qual2K modelling.

3. To calculate the total daily maximum loading of pollutants released into the river catchment.

1.4   Scope of Study

The scope of study area is limited towards evaluating the level of pollution within the downstream of Perak River Basin. The water quality model, which is Qual2K, is used in the study to demonstrate the degree of pollution along the downstream of Perak River Basin. The analysis that is involved in the study are limited to total suspended solids (TSS), turbidity, total kjedahl nitrogen (TKN) and heavy metals by ICP-OES analysis. The studied parameters were then applied into the Qual2K model to observe and compare the intensity of pollution along the downstream part of Perak River.

CHAPTER 2

LITERATURE REVIEW

2.1   Perak River Basin

In Peninsular Malaysia, Perak River Basin is the second-longest river after the Pahang River, and the river covers the state land for almost 70 per cent (Mohammed Abdus Salam et al., 2019). The flow of the river originates from the border of Perak-Kelantan-Thailand at the upper region of Perak State. It ends in the Straits of Malacca with an approximate length of 400 km, with catchment area of 14900 km^2 (Wakif et al., 2020). The main tributaries of the Perak River are Pelus River, Bidor River, Kinta River and Batang Padang River, which are located near the main cities of the Perak State (Hanif et al., 2015). The Perak River is the primary source of water supply for the state population, as the amount of water channeled to the residents of the Perak State are nearly 1774 million liters per day (Hanif et al., 2015; Wakif et al., 2020).

2.2   River Pollution

River pollution occurs when contaminants are released into the natural environment, usually due to human activities. Water contamination is caused by a variety of sources of chemicals and pathogens, as well as physical parameters. Contaminants may also include organic and inorganic substances. Due to urbanization and modernization, river water pollution has become a serious concern in Malaysia and threatening the sustainability of water resources. In 2017, out of 477 rivers monitored, the Department of Environment (DOE) found that only 219 rivers (46%) were classified as clean, 207 rivers (43%) were identified as slightly polluted and, 51 rivers (11%) were classified as polluted (Lee Goi, 2020).

2.2.1 Point Source and Non-point Source

A point source is an identifiable source of pollution where pollutants are discharged through a pipe or a drain. Contaminants in the water may came from different discharges from industrial, agriculture, or sewage treatment plants. The pollutants released from these sources may contain harmful solvents, petroleum, pesticides and heavy metals. The accumulation of contaminants from the point source can end up in the water supply stream if not treated properly. Pollution from point sources is easier to control than pollution from non-point sources. The contaminated water has been gathered and transported to a single point, where any water treatment facilities can treat the water.

Non-point source, on the other hand, is the combination of pollutants from various types of sources in an area. The non-point source is difficult to identify and control. Despite significant advances in the construction of modern sewage treatment plants, non-point sources are still responsible for a considerable portion of water pollution problems. Non-point sources are usually associated with the land use and land activity in the surrounding area of pollution. For example, runoff is the primary source of non-point pollution in urban areas where rainfall runoff is discharged as stormwater (Ongley et al., 2010). The pollutants in stormwater often include sediments and debris, dust, oil and grease and toxic chemicals from industrial areas. Another source of non-point pollution is from agriculture activities. In areas where crops and landscaping are conducted, these activities may carry soil, fertilizers, pesticides that contain bacteria and microorganisms that can be hazardous to human health and aquatic life.

2.3   Water Quality Standards

The water quality standard is first developed by the Water Quality Act 1965, followed by the Federal Water Pollution Control Act 1972, with more adjustments by the Clean Water Act in 1977, 1982 and 1987 (Department of Environmental Conservation, 2016). At each state, territorial, authorized tribal or federal law provides a water quality standard (WQS) approved by the United States Environmental Protection Agency (USEPA). The WQS must meet the desired state of a water body and the methods that will be used in order to accomplish the required condition (United States Environmental Protection Agency, 2020). The authority can utilize water bodies for public water supplies, recreation, fishing, agriculture and home to aquatic organisms from the execution of water quality standards. Therefore, establishing the water quality standard functioned to protect public health and marine life in the water bodies and ensure a level of water quality that is acceptable for its intended use.

2.3.1   Water Quality Index, WQI

A water quality index demonstrates the overall water quality based on different water quality parameters at various locations and times. The index provided understandable information on the water quality data and classified the river into its classes and status of water quality. Different countries use different type of water quality index according to the authorities of the country such as the Canadian Water Quality Index (CWQI), Oregon WQI, British Columbia WQI and National Sanitation Foundation WQI) (Arman et al., 2013; Suratman et al., 2015).

2.3.2   Interim National Water Quality Standards, INWQS

In Malaysia, the Department of Environment (DOE) introduces the Interim National Water Quality Standard (INWQS). The INWQS considers six different parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved oxygen (DO), total suspended solid (SS), pH value and ammoniacal nitrogen (NH_3-N). The formula applied in calculating the WQI for the INWQS is shown in Equation 2.1 (DOE, 2014; Suratman et al., 2015). The calculated WQI is then used to categorize the quality of river water are shown in Table 2.1 to Table 2.4.

$$WQI = 0.22 * SIDO + 0.19 * SIBOD + 0.16 * SICOD + 0.15 * SIAN \qquad (2.1)$$
$$+ 0.16 * SISS + 0.12 * SIpH$$

Table 2.1   Water Quality Standards for Heavy Metals (DOE, 2014)

Parameter	Unit	Class				
		I	IIA/IIB	III#	IV	V
Al	mg/l		-	(0.06)	0.5	
As	mg/l		0.05	0.4(0.05)	0.1	
Ba	mg/l		1	-	-	
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	-	-	
Hardness	mg/l		250	-	-	
Ca	mg/l		-	-	-	
Mg	mg/l		-	-	-	
Na	mg/l		-	-	3 SAR	
K	mg/l		-	-	-	
Fe	mg/l	N	1	1	1 (Leaf) 5 (Others)	
Pb	mg/l	A	0.05	0.02*(0.01)	5	
Mn	mg/l	T	0.1	0.1	0.2	
Hg	mg/l	U	0.001	0.004(0.0001)	0.002	
Ni	mg/l	R	0.05	0.9*	0.2	
Se	mg/l	A	0.01	0.25(0.04)	0.02	
Ag	mg/l	L	0.05	0.0002	-	
Sn	mg/l		-	0.004	-	
U	mg/l	L	-	-	-	
Zn	mg/l	E	5	0.4*	2	L
B	mg/l	V	1	(3.4)	0.8	E
Cl	mg/l	E	200	-	80	V
Cl$_2$	mg/l	L	-	(0.02)	-	E
CN	mg/l	S	0.02	0.06(0.02)	-	L
F	mg/l		1.5	10	1	
NO$_2$	mg/l	O	0.4	0.4(0.03)	1	A
NO$_3$	mg/l	R	7	-	5	B
P	mg/l		0.2	0.1	-	O
Silica	mg/l	A	50	-	-	V
SO$_4$	mg/l	B	250	-	-	E
S	mg/l	S	0.05	(0.001)	-	
CO$_2$	mg/l	E	-	-	-	IV
Gross-α	Bg/l	N	0.01	-	-	
Gross-β	Bg/l	T	1	-	-	
Ra-226	Bg/l		< 0.1	-	-	
Sr-90	Bg/l		< 1	-	-	
CCE	µg/l		500	-	-	
MBAS/BAS	µg/l		500	5000(200)	-	
O&G (Mineral)	µg/l		40 ; N	N	-	
O&G (Emulsified Edible)	µg/l		7000 ; N	N	-	
PCB	µg/l		0.1	6(0.05)	-	
Phenol	µg/l		10	-	-	
Aldrin/Dieldrin	µg/l		0.02	0.2(0.01)	-	
BHC	µg/l		2	9(0.1)	-	
Chlordane	µg/l		0.08	2(0.02)	-	
t-DDT	µg/l		0.1	(1)	-	
Endoslufan	µg/l		10	-	-	
Heptachlor/Epoxide	µg/l		0.05	0.9(0.06)	-	
Lindane	µg/l		2	3(0.4)	-	
2,4-D	µg/l		70	450	-	
2,4,5-T	µg/l		10	160	-	
2,4,5-TP	µg/l		4	850	-	
Paraquat	µg/l		10	1800	-	

Table 2.2   Water Quality Standard for physicochemical parameter (DOE, 2014)

Parameter	Unit	Class					
		I	IIA	IIB	III	IV	V
NH$_3$-N	mg/l	0.1	0.3	0.3	0.9	2.7	> 2.7
BOD	mg/l	1	3	3	6	12	> 12
COD	mg/l	10	25	25	50	100	> 100
DO	mg/l	7	5 – 7	5 – 7	3 – 5	< 3	< 1
pH	-	6.5 - 8.5	6 – 9	6 – 9	5 – 9	5 – 9	-
Colour	TCU	15	150	150	-	-	-
Electrical Conductivity	μS/cm	1000	1000	-	-	6000	-
Floatables	-	N	N	N	-	-	-
Odour	-	N	N	N	-	-	-
Salinity	%	0.5	1	-	-	2	-
Taste	-	N	N	N	-	-	-
TDS	mg/l	500	1000	-	-	4000	-

Table 2.3   Interim National Water Quality Standard (INWQS) for physicochemical parameter (DOE, 2014)

Parameter	Unit	Class				
		I	II	III	IV	V
NH$_3$-N	mg/l	< 0.1	0.1 – 0.3	0.3 – 0.9	0.9 – 2.7	> 2.7
BOD	mg/l	< 1	1 – 3	3 – 6	6 – 12	> 12
COD	mg/l	< 10	10 – 25	25 – 50	50 – 100	> 100
DO	mg/l	> 7	5 – 7	3 – 5	1 – 3	< 1
pH	-	> 7	6 – 7	5 – 6	< 5	> 5
TSS	mg/l	< 25	25 – 50	50 – 150	150 – 300	> 300
WQI	-	< 92.7	76.5 – 92.7	51.9 – 76.5	31.0 – 51.9	> 31.0

Table 2.4   Classes and status of water quality based on INWQS (DOE, 2014)

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

2.4   Total Maximum Daily Load (TMDL)

One of the implemented approaches to manage the quality of river water in Malaysia is the total maximum daily load (TMDL). TMDL functioned to determine the possible amount of contaminants that a water body can received without adversely affecting the recommended water quality standards (Salvai & Bezdan, 2008; USEPA, 2001). TMDL is often used as a planning mechanism for water quality conservation in affected water bodies. The waste load levels are assigned to different sources of pollution, and targeted mitigation strategies are implemented. In the TMDL approach, the head of the pollutant came from a point and non-point source. Therefore, TMDL can be expressed as the sum of wasteload and load allocation along with the margin of safety (Camacho et al., 2018).The formula for TMDL is shown in Equation 2.6.

$$TMDL = \Sigma WLA + \Sigma LA + MOS \qquad\qquad (2.6)$$

WLA = the sum of wasteload allocations from point sources (kg/day)

LA   = the sum of load allocations non-point sources (kg/day)

MOS = margin of safety (%)

2.4.1 Wasteload Allocation, WLA

Waste load allocation (WLA) is the contributions of pollution from point sources. Point sources are pollution from a discharge point or direct outlet to the stream from a premise such as a factory or a wastewater treatment plan. Current or potential point sources are classified under WLA to measure TMDL (USEPA, 2001). Point sources are identified first to set the limits of effluent for point source discharge to achieved the targeted water quality.

2.4.2 Load Allocation, LA

Load allocation (LA) is the contribution of pollutants from non-point sources. Non-point sources are generated from many diffuse sources with no particular point of origin. For example, heavy rainfall events and a high water flow that seeped into the ground and deposited into water bodies are some of the causes for non-point sources to occur (USEPA, 2001).

2.4.3 The Application of TMDL in Malaysia

2.4.3(a) Lake Chini, Pahang

Dom et al. (2016) conducted a study on the sediment load analysis of Lake Chini, Pahang, to investigate the effect of mining activities on the riverbed of Jemberau River and its consequence to sediment loading in both Jemberau and Chini River. TMDL approach is implemented in the study to evaluate the concentration of sediment loading caused by sand mining activities. The estimation of TMDL in this study was divided into three different events: before 2011 to 2011, 2011 to 2012 and 2012 to present. Equation 2.7 are used in the calculation of TMDL in the study. In addition, the margin of safety (MOS) of 25% are assumed based on the satellite image of 2011 to 2014 on the expansion area of mining sites along the river. The TMDL values obtained from the analysis of the study are shown in Table 2.8.

$$TMDL = Load\ Allocations + Margin\ of\ Safety + Future\ Growth \qquad (2.7)$$

Table 2.5   The estimated value of TMDL for the concentration of suspended sediment of Jemberau River (Dom et al., 2016)

Mining sites	Mining area (ha)	% Increase	TMDL (kg/day)
Before 2011	34.15	-	-
2011	90.46	62.25	27
2012	202.97	55.43	57.50
2014	202.97	0	Active mining sites

The TMDL for the suspended sediment concentration obtained from upstream of the Jemberau River was 57.50 kg/day. From the obtained TMDL, further estimation of cumulative TMDL is made in this study for another 5, 10, 15 and 20 years based on

the assumption that there will be 111 days of rainfall per year. Therefore, it is estimated that the TMDL for suspended sediment concentration increases 35 tons for every five years. The constant loading of sediment was due to land use at upstream of Jemberau River, blockage by weirs at downstream of Jemberau River, backflow of water from Pahang River during heavy rainfall events and riverbank erosion.

2.4.3(b)   Malacca River

Osmi et al. (2016) conducted a study on implementing the TMDL plan to Malacca River. The implementation of TMDL is simulated with a water quality model, which is the Environmental Fluid Dynamic Codes (EFDC). The main water quality parameter focused on in this study is COD. This study aims to achieve a Class II COD concentration of the water quality index (WQI). The simulation of the water quality using EFDC is divided into four different scenarios of COD-load reduction. The analysis result from each simulation and scenarios will determine the best strategies that will be used to implement the TMDL program in the Malacca River. The simulations and scenarios used for COD-load reductions are given in Table 2.9, and the results obtained from each simulation is shown in Table 2.10.

Table 2.6   COD-load reduction simulations and scenarios (Osmi et al., 2016)

Simulation	Scenario	Description
A	1	50% reduction at two major point sources
	2	70% reduction at two major point sources
	3	80% reduction at two major point sources
B	4	30% reduction at three different tributaries
	5	50% reduction at three different tributaries
C	6	50% reduction at several major point sources

	7	70% reduction at several major point sources
	8	80% reduction at several major point sources
D	9	50% reduction at point sources and 30% at tributaries
	10	70% reduction at point sources and 30% at tributaries
	11	80% reduction at point sources and 30% at tributaries

Table 2.7   The results of COD-load reduction analysis (Osmi et al., 2016)

Simulation	Scenario	Does it improve water quality?	Does it achieve the targeted COD concentration?
A	1	No	No
	2	Yes	No
	3	Yes	Yes
B	4	No	No
	5	No	No
C	6	Yes	No
	7	Yes	Yes
	8	Yes	Yes
D	9	Yes	Yes
	10	Yes	Yes
	11	Yes	Yes

Scenario 10, comprising the reduction of pollutants in both point sources and tributaries, was chosen as a part of the TMDL plan in Malacca River for this study. The COD loading obtained from point source is 733.7 kg/day while the COD loading estimated for tributaries is 1546.6 kg/day (Osmi et al., 2016).

CHAPTER 3

METHODOLOGY

3.1   Research Flow Chart

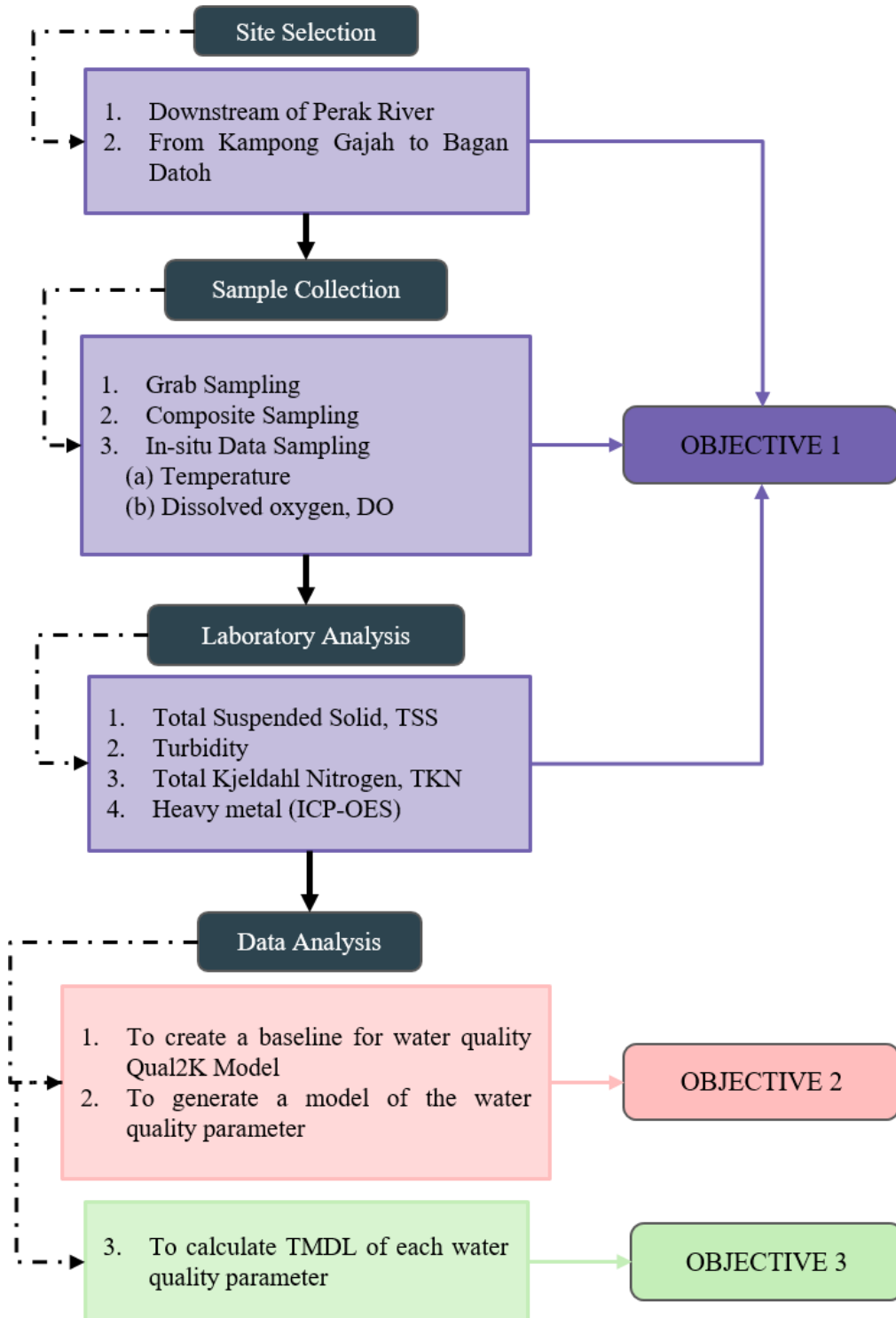

Figure 3.1   Research flow chart

3.2 Background Study Area

Perak is located on the west of Malaysian Peninsular with a total land area of 20,976 square kilometers. The state has 11 major river basins with an area of more than 80 km. Perak River is the second largest river behind the Pahang River, covering 70% of the total state area (Snu et al., 2018). The boundaries of the Perak River Basin catchment area are shown in Figure 3.2. The length of the river is approximately 400 km with an area of 14900 km^2. The river travels from the border of Perak-Kelantan-Thailand of the Belum Forest Reserve to the Straits of Malacca. Perak River became an essential asset to the state and the people of Perak, as the river functioned as the main irrigation system, water supply, hydropower generation, fisheries and tourism.

The focused study area for this research is downstream of the Perak River, which covers from Kampong Gajah to Bagan Datoh, with 36 sampling locations. The sampling points and their coordinates is shown in Figure 3.3 and Table 3.1. At the lower catchment of Perak River, there are two main tributaries: the Kinta River and Bidor River, each comprising many other small branches (Noh et al., 2020). The river channel pattern for the downstream section of the Perak River is straight and meandering with moderate to low distribution of sand bars. The river width at the downstream section ranges from 500 m up to 2 km.
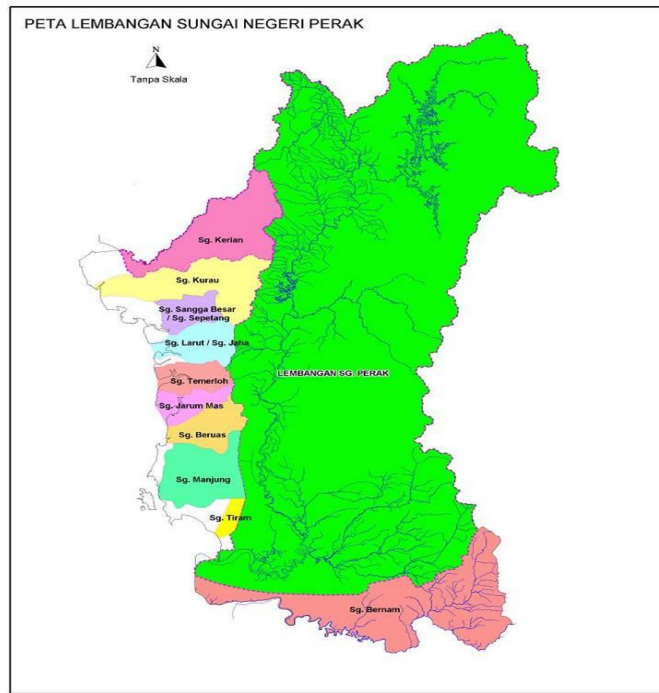
Figure 3.2   Perak River Basin catchment area (Source: Perak State Department of Irrigation and Drainage 2018)
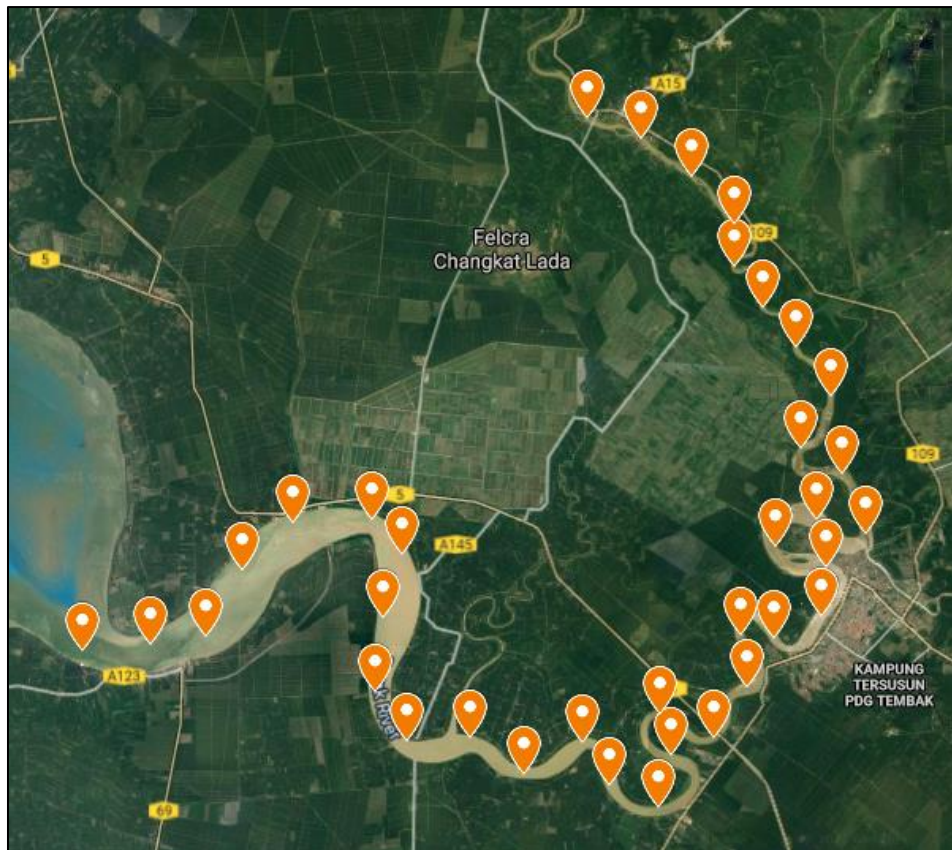

Figure 3.3   Location of sampling sites along downstream of Perak River

Table 3.1   Coordinates of Sampling Locations

Points	Coordinates		Points	Coordinates	
	Latitude (N)	Longitude (E)		Latitude (N)	Longitude (E)
1B	3.9966	100.7520	**19B**	3.9835	100.9838
2B	3.9984	100.7754	**20B**	4.0020	100.9816
3B	4.0011	100.7950	**21B**	4.0006	100.9934
4B	4.0246	100.8076	**22B**	4.0081	101.0100
5B	4.0408	100.8253	**23B**	4.0255	101.0115
6B	4.0423	100.8529	**24B**	4.0324	100.9938
7B	4.0297	100.8633	**25B**	4.0422	101.0085
8B	4.0080	100.8568	**26B**	4.0372	101.0254
9B	3.9818	100.8538	**27B**	4.0579	101.0172
10B	3.9649	100.8650	**28B**	4.0669	101.0029
11B	3.9661	100.8871	**29B**	4.08486	101.0133
12B	3.9534	100.9058	**30B**	4.1019	101.0012
13B	3.9646	100.9262	**31B**	4.1162	100.9894
14B	3.9497	100.9360	**32B**	4.1303	100.9796
15B	3.9418	100.9532	**33B**	4.1454	100.9797
16B	3.9601	100.9574	**34B**	4.16152	100.9647
17B	3.9744	100.9534	**35B**	4.1750	100.9469
18B	3.9662	100.9723	**36B**	4.1821	100.9282

3.3   Sample Collection

Sample collection for selected water quality parameters includes 36 sampling locations along the downstream of the Perak River. The samples were collected from September to December 2020. All samples collected were stored in plastic bottles that had been rinsed with distilled water to avoid any contamination that may disturb the test results. An adequate volume of water sample was collected for the test to be conducted in triplicate and reducing waste disposal. The samples were then analyzed immediately after collection and kept in the cold room at 4˚C for storage to avoid the breaking down

of contaminants. Samples that are required to be used for analysis are taken out of the cold room and left at room temperature (Daoudi, 2000). Samples are also preserved by adding acids with pH less than two into the water sample. The acidification of sample functioned to prevent any flocculation or precipitation that can alter the sample components (Sliwka-Kaszyńska et al., 2003). The changes in the sample components may affect the rate of reaction of the water sample during laboratory analysis.

3.4   Methods of Sampling

3.4.1   Grab Sampling

Grab sampling, is a techniques used in measuring in a single point of depth and location, and the equipment that is used for this method is a grab sampler (Federation & Works, 2005). Grab samplers which consist of two steel clamshells, are one of the most common methods of retrieving soil samples from the surface of the soil in a water body. The grab sampler will be connected with a rope, opened like a scissors, locked in this position, and lowered into the water. The grab sampler was then held above the water's surface and was lowered slowly into the water until it reached the bottom of the river. When it reached the river's base, the grab sampler will open and unlock, and sediment will be ready to be collected. The collected deposits are then kept in plastic bags or airlock zip bags and stored at a cool temperature for further laboratory analysis.

3.4.2   Composite Sampling

Composite sampling is a method of sampling that requires multiple grab samples to be taken over an area or a period, usually 24 hours (Lancaster & Keller-mcnulty, 2012). The collection of the samples can either by continuous sampling or by

mixing. The analysis of samples through this sampling method will represent the average performance of the specimen during the collection period. There are two methods of composite sampling, which are time and flow proportioning. A time composite sample consists of an equal volume of discrete samples collected at a constant time interval into one container. The sample can be collected either by manual or automatic sampling. Flow proportional composite sampling, on the other hand, can be managed using two methods. The first method is by collecting the sample at a constant volume at a different time interval, proportional to water flow. The second method contains the sample at different volumes with a continuous-time gap between collections, proportional to the water flow. Flow proportional composite samples can be collected using an automatic sampler connected with a flow-measuring device.

3.5   In-situ Sampling

3.5.1   pH

pH analysis for water sample functioned to measure the acidity or the alkalinity of water. The range of pH value goes from 0 to 14, with seven being neutral. pH lower than 7 indicates that the water sample is acidity, while pH greater than 7 shows that the water sample is alkaline. The determination of pH in the water sample can be conducted in three methods: pH indicator paper/pH strips, colorimetric method, and electronic meters. The use of pH indicator paper/pH strips is the simplest and inexpensive method for determining the pH level in a water sample. On the other hand, the colorimetric method used a liquid colorimetric indicator that changed colour according to the pH when mixed with the water sample. The accuracy of the method is up to 0.2 pH units. Another method in pH analysis is portable electric meters with an accuracy of up to

0.05 pH units. This method is suitable for field use, where the determination of the pH of water is conducted immediately after the sample is obtained.

For this research purpose, portable electrodes probes are used to measure the water sample's pH, temperature and dissolved oxygen. After the value of pH of the water samples was obtained, the electrodes were removed out of the water sample, rinsed with distilled water, and dried using tissue paper for another analysis.

3.5.2   Dissolved oxygen (DO)

For in-situ data sampling, the method applied for the determination of dissolved oxygen is the electrometric method, where the DO meter is used. This method is preferred for field use as it is simple to perform, and the device is portable, making it easier to be taken everywhere. First, the calibrating of the DO meter was done by taking a reading of oxygen against air or any sample of known dissolved oxygen content. Next, the electrode of the DO meter was rinsed with a portion of the water sample that will be analyzed for dissolved oxygen. When the electrode was immersed into the water sample, the water flow was ensured to be continuous to obtain a steady response on the meter.

3.6   Laboratory Analysis

3.6.1   Total Suspended Solid (TSS)

Total suspended solids (TSS) can be referred to as particles in the water that are larger than 2 microns and do not pass through the filter used to separate them during testing. The suspended solids are made up of organic and inorganic materials and can settle as sediment at the bottom of a water body over some time. The settlement of

suspended solids can prevent the transfer of oxygen to the bottom of the water body, thus affecting the ecosystem of aquatic habitat at the bottom of the water body. The high concentration of suspended solids also can increase the temperature of the water and decreasing the concentration of dissolved oxygen.

The first step in determining the TSS in a water sample was to place the dry glass fiber filter in the oven for 15 minutes. After 15 minutes, the initial weight of the dry glass fiber filters along with the crucible was measured on the analytical balance and labelled as X. The water sample was ensured to be well mixed before transferring the water sample for testing due to the settlement of the soil and sediment particles that may be disrupting the results of the test. Secondly, 50 ml of water sample was measured and filtered by vacuum suction on the dry glass fiber filter. Both measuring cylinder and funnel used were rinsed with distilled water for three times to remove any excess suspended solid on the surface of the apparatus. The glass fiber filter was then placed into the crucible and dried in the oven at temperature 130 – 150˚C for at least 1 hour. After 1 hour, the glass fiber filter with the crucible was left in the desiccator to reduce the temperature of the filter to room temperature. Both glass fiber filter and crucible were weighted again using the same analytical balance and labelled as Y. The steps were then repeated twice until a constant weight were obtained for all crucibles. The calculation of TSS was then determined using Equation 3.1.

$$TSS \left(\frac{mg}{L}\right) = \frac{(Y - X) \; x \; 1000 \; mg/L}{Volume \; of \; sample, mL} \tag{3.1}$$

X = the initial weight of glass fiber filter + crucible

Y = the final weight of glass fiber + crucible after drying

3.6.2 Turbidity

Turbidity is a measurement of the dispersion of light in the water due to the presence of organic matter content, dissolved inorganic matter and suspended particles. Turbidity increases as the amount of light dispersed increases (Kitchener et al., 2017).

The method that is applied to measure the turbidity of the water sample from the downstream of Perak River Basin was by using the portable turbidity meter, TB400. The meter can measure the turbidity of water from any source (domestic and industrial waste, drinking water, groundwater, surface and saline water) up to 1000 NTU (nephelometric turbidity unit). Therefore, the first step in determining the turbidity of water sample was to prepare a blank solution that consists of distilled water in a standard solution test bottle to calibrate the meter. Next, the sample was thoroughly mixed, scattering the solids inside, and a standard solution test bottle containing water sample was prepared. Both blank and sample test bottle were then placed into the turbidity meter, and readings were taken directly from the meter (O'Dell, 1996).

3.6.3 Total Kjeldahl Nitrogen (TKN)

Total Kjeldahl nitrogen (TKN) is a method of chemical analysis to determine the amount of nitrogen in organic and inorganic substances. The method also can be used as a parameter to assess water quality by evaluating the amount of nitrogen in a water sample. The determination of TKN in water samples can be divided into several processes: reagent preparation, distillation, and digestion.

For reagent preparation, six different reagents are needed to prepared for TKN analysis. The first reagent is the sulphuric acid solution, where 7 ml of 36N H_2SO_4 was diluted with distilled water until 250 ml of total solution volume is achieved. Next, 20

ml of the solution were then diluted once again with distilled water until the volume of the solution reached to one litre. The second reagent is the sodium hydroxide solution, where 0.8 g of sodium hydroxide pallets, NaOH, was dissolved with distilled water and diluted to 1 L. Next, the thiosulphate solution was then prepared by mixing 5 g of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, with distilled water until the volume of the solution reached to 200 ml. The forth reagent is the boric acid solution, where 4 g of boric acid, H_3BO_4 was mixed with 2 ml of mixed indicator solution and dissolved to 200 ml with distilled water. The mixed indicator solution was prepared by adding 0.2 g of methyl red indicator with 100 ml of 95% ethanol, C_2H_6O, to 0.1 g of methylene blue with 50 ml of 95% ethanol, C_2H_6O. The preparation of the fifth reagent is done by dissolving 0.05 g of phenolphthalein indicator into 100 ml of methanol, CH_3OH. Lastly, the preparation of digestion reagent can be divided into two parts. The first part was to mix 67 g of potassium sulphate, K_2SO_4, with 325 ml of distilled water. 100 ml of concentrated sulphuric acid, H_2SO_4, was then added slowly into the solution. The second part of digestion reagent involved the dilution of 16.7 ml of concentrated sulphuric acid, H_2SO_4, with distilled water until the volume of solution reached 100 ml. Then, 1 g of red mercury oxide, HgO, was mixed with 12.5 ml of the previous solution.

After the entire required reagent is prepared, the analysis of TKN began with the distillation of the tested water sample. Either through the addition of dilute H2SO4 or NaOH, the pH of the water sample is adjusted to pH 7. 62.5 ml of water sample was then placed into the Kjedahl reactor tube and added with 12.5 ml of digestion reagent. The reactor tube was then placed in the distillation apparatus for one hour and rest at room temperature for 45 minutes. After distillation process completed, all of the reactors were placed into the heater of Buchi Apparatus and let to be heated for a few minutes.