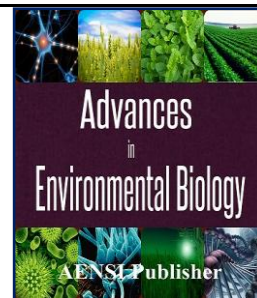




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Approximation of Polycyclic Aromatic Hydrocarbons (PAHs) presence in Kinta River and its Tributaries

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ABSTRACT

Background: The expansion of human activities around Kinta River in Ipoh city in Malaysia has increased the input of organic matters to the river. The water quality of Kinta River is deteriorated significantly as result of industrial discharges, animal husbandry and agricultural activities. In this study, twenty-six sampling points were identified from the upper stream of Kinta River to the downstream including some tributaries. The physical and chemical variables including dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), pH and ammoniacal nitrogen (AN) were measured. Then, based on that, the water quality index (WQI) were calculated and classified in accordance to Department of the Environment Water Quality Index (DOE-WQI). **Objective:** To approximate the existence of polycyclic aromatic hydrocarbons (PAHs), the specific UV absorbance (SUVA) method was conducted. The PAHs type was estimated using number of cycles in each sample resulted from SUVA values. **Results:** Results show, the range of WQI was from 71.74 to 22.81 in Kinta River and its tributaries. **Conclusion:** The highest value of SUVA (19.81 L/mg-m) was observed at Serokai River, one of Kinta tributaries river, which indicates high probability of PAHs presence.

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INTRODUCTION

The surface water resources are getting deteriorated and it becomes continuous concerning problems for many decades since increased wastewater discharges into river [1, 2]. The knowledge of surface water quality monitoring facilitates the understanding and identifying the effects of environmental stressors in rivers [3]. Assessment of water quality is a term, which is used to compare the physical, chemical and biological characteristics of water according to its suitability for a particular purpose according to standards [4]. The water quality assessment is a significant process as water pollution not only affects water quality but also threatens human health, animals, aquatic organisms and plants [5].

Kinta River is the largest river passing through Ipoh city in Malaysia from Gunung Korbu in Ulu Kinta at an altitude of around 2000 m above sea level. Kinta River is the most important water resource in Ipoh city and the second most important water resource in Perak state (after Perak River) used for drinking and irrigation purposes [6]. Water quality can be seen as an indicator of the environmental quality of an area, since deterioration in water quality can be a direct outcome of non-sustainable development. In the last 10 years, the Kinta River has turned polluted and the environmental problems became prevalent. Kinta River flows through the center of the city and has deteriorated significantly as result of industrial and residential discharges, animal husbandry farms, agriculture and sand-mining [4][7]. Not much attention has been given to industrial area, located at the upstream part of the river. The industrial discharges (not treated thoroughly or in places not at all) entering the river system; causing severe water pollution and also affect the quality of water reaches to agriculture area (downstream part). Therefore, there is high possibility for certain pollutants to penetrate into the food chain[8] and finally, reach to humans' body [9, 10]. The impact of land use changes on water quality of river is one of the main concern in water supply for various consumptions [11]. Pollution in river basins is extremely vulnerable due to transportation of domestic, industrial, and agricultural wastewater in it [12].

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Monitoring and reporting of water quality will reveal the types and severity of discharges [13] and therefore, water quality monitoring is an essential step before any other steps to control water pollution [14].

In addition to some common water pollutants such as turbidity, color, nutrients and coliform, presence of some trace pollutants like polycyclic aromatic hydrocarbons (PAHs) in water cause significant problems due to their mutagenic and carcinogenic characteristics [15, 16]. Reactive metabolites of PAHs have potential to bind with DNA and cellular proteins with toxic effects [17, 18]. The actual significant emissions of PAHs derive from industrial and other human activity such as agricultural, open burning, municipal and industrial waste incineration and disposal of hazardous waste materials [19]. In this study, the current status of water quality in Kinta River and its tributaries were measured and the water quality index (WQI) were calculated. In addition, the presence of PAHs in different points of the river was investigated.

Methodology:

A. Sampling locations:

As shown in Fig.1, twenty-six water sampling stations (A to Z) were selected. The rationale for selection of each point has been detailed in Table 1. After collection of river water samples, the parameters dissolved oxygen (DO), pH, salinity, conductivity, turbidity and temperature were measured using the SONDE equipment. Other parameters which comprised of BOD (biochemical oxygen demand), COD (chemical oxygen demand), SS (suspended solid) and AN (ammoniacal nitrogen) were determined according to standard methods for the examination of water and wastewater [20]

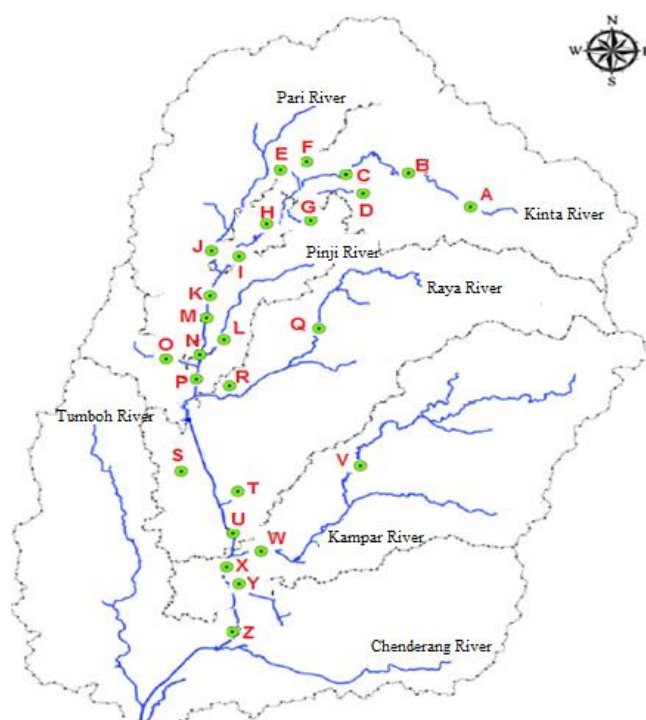


Fig. 1: Kinta River and its basin and sub-basins.

B. The Water Quality Index (WQI) Calculation:

Water quality index (WQI) was used as a basis for assessment of watercourse in relation to pollution and was derived using DO, BOD, COD, AN, SS and pH [21]. WQI has been measured with the mean of all six parameters which then converted to sub-indices (SI_s) using the best-fit equation (Eq. 1) [22].

$$WQI = 0.22SI_{DO} + 0.19SI_{BOD} + 0.16SI_{COD} + 0.15SI_{AN} + 0.16SI_{SS} + 0.12SI_{pH} \quad (\text{Eq. 1})$$

C. Specific UV Absorbance (SUVA):

The SUVA (L/mg-M) formula was calculated by dividing UV absorbance at 254 nm by the total organic carbon (TOC) and then, it was multiplied by 100 cm/M (Eq. 2) in accordance to EPA Method 415.3[23]. $SUVA_{254}$ correlates well with the aromaticity and the hydrophobicity of the organic carbon; hence, it has potential to identify the presence of polycyclic aromatic hydrocarbons (PAHs) [24]. The standard value for $SUVA_{254}$ in raw water or treated water is less than $2.0 \text{ L mg}^{-1}\text{m}^{-1}$ [25]. The assumption is that $SUVA_{254}$ is a good indicator for the humic fraction of the PAHs. A high $SUVA_{254}$ value indicates that a large portion of the organics present in the water is in aromatic compound group such as PAHs [23].

$$\text{SUVA} = [\text{UV}_{254} / \text{TOC}] \times 100 \quad (\text{Eq. 2})$$

RESULTS AND DISCUSSION

It is important to realize the relationship between human induced disturbances and their effects on aquatic resources. River-ecology disturbances from urban and industrial areas as well as agriculture development contribute to overall decrease in the (biological) integrity of the Kinta River. It is apparent that assessment of water quality cannot focus only on biological indicators, but has to focus on indicators too, which integrate the effect of both physical and chemical stressors [26]. The physical and chemical characteristics of Kinta River water and its tributaries were presented in Tables 1 and 2, respectively.

A. Physical characteristics:

As it is shown in Table 1, the most stable parameter was pH with range from 6.2 to 7.7 which is stretched within National Drinking Water Standard for Malaysia (7.0 - 8.5) [27]. The DO concentration of the upper stream is less polluted compared to downstream. Similar trends can be observed when Pari River and Serokai River (tributaries of Kinta) join to the Kinta River and the DO concentration in mainstream was found to decreased from 6.20 to 5.60 mg/L when Pari River joining with the Kinta river. The DO concentration at Kinta River drop again from 5.60 to 3.30 mg/L when Serokai River joining Kinta River. Serokai River was having the highest turbidity (60.1 NTU) due to industrial discharges. Higher turbidity and low concentration of dissolved oxygen (DO) can be used as an indicator for industrial discharges to river [28]. The toxicity level of industrial discharge may influence the environmental factors such as conductivity, temperature, pH, carbon dioxide (CO₂) and oxygen. Ulu Kinta has the lowest salinity (0.001 PPT) and conductivity (0.006 ms/cm) among all the sampling points as it is located in upper stream of Kinta River. The other factor which influenced the water quality of Kinta River was leachate discharge from nearby dump site. It is stated in Table 1 that, the sampling point F near to Bercham dump site has the highest salinity and conductivity among all the sampling points (0.32 PPT and 0.674 ms/cm), respectively. Conductivity and salinity of sampling point F indicates the presence of elevated concentrations of ions and salts. Large amount of inorganic compounds from the buried wastes dissolved in the infiltrating water and attributed to the high ionic strength [29].

B. Chemical characteristics:

Leachate from landfill usually is characterized by high values of BOD and COD, acidic pH values (typically 5-6) and high ammonia (NH₃) content due to hydrolysis, and fermentation in particular of proteins [30]. Based on achieved results shown in Table 2, the river water is polluted by leachate from Bercham dump site and therefore considerable levels of COD (113.3 mg/L), BOD (52.56 mg/L), TSS (59.7 mg/L) and NH₃ (62.42 mg/L) was observed at this point. In addition to concerns on leachate discharge, Kinta River is passing by some areas, which are extremely industrialized. As indicated in Table 2, the condition get worsen in Serokai River (sampling point O) with increase trend in water quality deterioration.

Table 1: The physical water quality parameters at Kinta River

Sample point	place	Reasons of selection	DO (mg/L)	pH	Salinity (PPT)	Conductivity (ms/cms)	Turbidity (NTU)	Temperature (°C)
Ulu Kinta	A	Initial point	9.24	7.4	0.001	0.006	55.4	21.5
Before Tanjung Rambutan	B	Before wet market; after sewage inflow	9.08	7.7	0.02	0.04	16.5	26.7
After Tanjung Rambutan	C	After wet market; after sewage inflow	9.8	7.52	0.02	0.045	18.8	27
Papan River	D	Near Lahat dump site	7.93	6.27	0.01	0.027	13.8	23.57
Kedang River	E	Farming area	9.22	7.4	0.01	0.029	6.6	24.5
River water which is polluted by Bercham dump site	F	Leachate discharge	2.75	6.47	0.32	0.674	22.4	27.13
Johan River	G	Flow and urban use	6.45	7	0.04	0.087	12.1	26.9
Micheal school and hawker center	H	After commercial area; sewage inflow	6.85	7.1	0.02	0.07	26.5	24.3
Kinta River before Pari River	I	Residential area	6.2	7.3	0.02	0.06	29	27.8
Pari River	J	Industrial discharge inflow	5.2	7.3	0.03	0.05	27.9	27
Kinta River mix with Pari River	K	Residential area; industrial discharge inflow	5.6	7.42	0.02	0.05	17.8	28
Kinta River before Pinji River	L	Residential area	3.98	6.91	0.04	0.07	40.8	30

Pinji River	M	Industrial discharge inflow	7.1	7.1	0.05	0.11	36.3	27.1
Kinta River mix with pinji River	N	Residential area; industrial discharge inflow	5.55	7.4	0.08	0.17	40	28.4
Serokai River	O	Industrial area	3.04	6.2	0.25	0.349	60.1	27.8
Kinta River mix with Serokai	P	Industrial area	3.3	6.63	0.25	0.53	44	28
Sengat River	Q	Agricultural area	3.47	7.28	0.19	0.41	18.7	24.4
Raya River	R	Agricultural area and tourists attraction	7.01	7.14	0.04	0.09	32.2	21.8
River water which is polluted by Batu Gajah garbage dump	S	Leachate discharge	3.06	7.36	0.06	0.139	8.5	30.4
Teja River	T	Agricultural area	3.78	7.7	0.07	0.16	16	25.7
Tunjung Tualang Bridge	U	The waste from the slaughter of animals	10.6	7.44	0.03	0.06	24.5	25.11
Kranji River	V	Agricultural area	10.45	7.1	0.02	0.04	8.5	21.6
Kampar River	W	Agricultural area	11.3	6.4	0.01	0.04	16.5	21.5
Kinta River mix with Kampar	X	Agricultural area	9.86	7.26	0.02	0.06	22.8	25
Bangali River	Y	Agricultural area	2.2	7.34	0.08	0.19	14.1	26.5
Kinta River before Chenderang	Z	Forest	7.65	7.38	0.08	0.18	28.4	25.2

C. Water Quality Index of Kinta River and its Tributaries:

The calculation of WQI was depicted using the value of various physicochemical parameters presented in Tables 1 and 2. Based on the results, Serokai River, which is one of the tributaries of Kinta River, is having the lowest water quality among all the sampling locations due to the industrial discharges to the river. The water quality of Kinta river after joining to Serokai River was decreased from 39.43 (Class IV) to 22.81 (Class V). This makes the water improper for any application. During and after the rain, Kinta River is relatively unstable due to rapidly increasing of water rates by surface run-off of the surrounding land such as Bercham and Batu Gajah garbage dumpsites. The WQI at sampling points F and S near Bercham and Batu Gajah dumpsites were found to be 24.7 and 28.09, respectively. This makes the water quality in category of severely polluted. The water quality status at downstream of Kinta River after joining to two longest tributaries, Pari and Pinji Rivers, were classified to be slightly polluted. The BOD and COD in Kinta River before joining to Pari River cause the WQI to be fallen from class III to class IV. In other tributaries, Raya and Sengat River, the decrease in water quality to class IV happened due to increase in COD and NH₃ concentrations. Growing of ammonia contents in Raya and Sengat River is most probably due to extended use of pesticides and fertilizers at farming area [5].

Table 2: The chemical water quality parameters characteristics at Kinta River

Sampling point	TSS (mg/L)	COD (mg/L)	BOD (mg/L)	NH ₃ (mg/L)	WQI	CLASS
A	25.5±1.5	22.5±1.2	2.56±0.09	0.70±0.06	62.37	III
B	38±3.1	6.67±1.8	15.08±0.20	0.41±0.07	57.21	III
C	18±1.5	22±2.5	8.76±0.04	0.36±0.09	60.34	III
D	3.3±0.7	3.33±0.3	0.96±0.26	0.22±0.03	71.74	III
E	16.3±1.5	10±2.5	1.35±0.32	1.26±0.18	64.24	III
F	59.7±4.4	113.3±1.9	52.56±0.11	62.42±2.8	24.70	V
G	14±1.5	9±2.5	3.60±0.19	0.61±0.08	65.23	III
H	16.3±1.5	17±0.8	2.12±0.11	14.63±3.3	55.60	III
I	28±0.6	11.5±1.2	4.58±0.20	4.50±0.74	53.71	III
J	25±2.1	16.67±3.3	6.56±0.04	1.80±0.32	56.51	III
K	29.7±0.3	21.5±0.4	11.68±0.24	2.14±0.12	50.90	IV
L	39±4.5	48±0	16.36±0.07	2.27±0.05	43.36	IV
M	38.7±3.9	46±1.6	19.50±0.29	0.38±0.07	48.69	IV
N	41.7±3.0	76±3.9	28.34±0.15	0.96±0.03	39.43	IV
O	97±0	85±4.6	75.20±0.09	7.42±1.33	22.81	V
P	63±3.9	87±3.0	69.40±0.21	5.29±0.23	25.23	V
Q	27±2.5	75±4.0	12.80±0.04	1.05±0.25	46.52	IV
R	27.7±0.9	67.67±4.9	11.60±0.26	0.36±0.03	51.16	IV
S	67.0±2.5	87±1.6	63.16±0.34	2.57±0.13	28.09	V
T	21.7±1.3	59.33±4.8	10.30±0.17	0.12±0.01	55.85	III
U	29.7±2.3	58.5±1.2	8.04±0.07	0.06±0.02	58.63	III
V	26.3±1.2	36.67±4.9	4.78±0.14	0.02±0	64.76	III

W	27.3±1.5	54±4.3	8.86±0.11	0.04±0.04	59.05	III
X	33.3±1.5	66±4.9	14.26±0.06	0.16±0.02	52.16	III
Y	34.7±1.3	54.33±4.4	5.52±0.07	0.03±0	60.68	III
Z	46.0±2.3	44±1.6	5.78±0.09	0.46±0.03	56.01	III

D. Specific UV Absorbance (SUVA):

The SUVA determination consists of paired analyses composed of total organic carbon (TOC) and UVA analyses. SUVA was used as an indicator for estimation of PAHs in Kinta River and its tributaries. The SUVA analysis of Kinta River and its tributaries is presented in Table 3. In principle, SUVA values less than 2 indicates a high fraction of hydrophilic non-humic matter with low UV absorbance and low probability of the presence of PAHs formation [25, 31]. SUVA values more than four, shows the presence of humic highly aromatic hydrophobic matter associated with high UV absorbance and high probability of the presence of PAHs formation. Results indicate that majority of sampling points at Kinta River and its tributaries have the SUVA value below permissible limits (2 L/mg-m). This indicates low probability of the presence of polycyclic aromatic hydrocarbons (PAHs). However, SUVA values more than four were observed in Serokai, Teja, Pari and Bangali River as well as sampling point S near to Batu Gajah dump site. This indicates high probability of PAHs presence in water.

Conclusion:

Kinta River is the main source of water for drinking and irrigation in Ipoh, and is the major tributary of Perak River. The water quality of Kinta River passing through the center of the city has deteriorated significantly due to industrial discharges, leachate from dump sites, animal husbandry, agriculture activities and release of domestic sewage to the river. Serokai River as one of Kinta River tributaries is having the lowest water quality among all the sampling locations due to receiving of industrial discharges from the surrounding area. Huge decline in water quality of Kinta River was observed after joined to Serokai River. Specific ultra violet absorbance (SUVA) in Kinta River after joining Serokai River has shown the highest level (19.81 L/mg-m), which indicates high possibilities of PAHs existence at this sampling point. Further investigation using precise analytical tools such as Gas Chromatography-Mass Spectroscopy (GC-MS) and High Performance Liquid Chromatography (HPLC) is required for confirmation of approximations made in this study.

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Table 3: Determining specific UV absorbance

Sampling point	UV ₂₅₄ (cm ⁻¹)	TOC (mg/L)	SUVA	Aromaticity and PAHs	Predict types of PAHs
A	0.302±0.008	0	-	-	-
B	0.131±0.017	0	-	-	-
C	0.130±0.012	0	-	-	-
D	0.147±0.01	0	-	-	-
E	0.101±0.020	0	-	-	-
F	0.828±0.002	30.9±0.9	2.68±0.07	Less than four rings	B[a]a ¹ , Ch ²
G	0.142±0.008	0	-	-	-
H	0.129±0.011	0	-	-	-
I	0.119±0.001	0	-	-	-
J	0.111±0.020	0	-	-	-
K	0.123±0.010	1.07±0.18	12.53±3.12	More than four rings	B[a]p ³ , B[b]f ⁴ , B[k]f ⁵ , B[ghi] ⁶ , D[a,h] ⁷
L	0.130±0.008	0	-	-	-
M	0.129±0.004	0	-	-	-
N	0.116±0.006	0	-	-	-
O	0.177±0.011	2.43±0.02	7.28±0.51	More than four rings	B[a]p ³ , B[b]f ⁴ , B[k]f ⁵ , B[ghi] ⁶ , D[a,h] ⁷
P	0.182±0.014	0.92±0.03	19.81±1.24	More than four rings	B[a]p ³ , B[b]f ⁴ , B[k]f ⁵ , B[ghi] ⁶ , D[a,h] ⁷
Q	0.137±0.006	2.94±0.13	4.69±0.40	Less than four rings	B[a]a ¹ , Ch ²
R	0.126±0.002	0	-	-	-
S	0.167±0.001	1.17±0.04	14.26±0.43	More than four rings	B[a]a ¹ , Ch ²
T	0.164±0.011	0.93±0.10	17.85±0.85	More than four rings	B[a]p ³ , B[b]f ⁴ , B[k]f ⁵ , B[ghi] ⁶ , D[a,h] ⁷
U	0.117±0.004	0	-	-	-
V	0.119±0.008	0	-	-	-
W	0.105±0.008	0	-	-	-
X	0.104±0.006	0	-	-	-
Y	0.171±0.013	2.49±0.09	6.91±0.71	Less than four rings	B[a]a ¹ , Ch ²
Z	0.126±0.004	0	-	-	-

B[a]a¹ = Benz[a]anthracene, Ch² = Chrysene, B[a]p³ = Benzo[a]pyrene, B[b]f⁴ = Benzo[b]fluoranthene, B[k]f⁵ = Benzo[k]fluoranthene, B[ghi]p⁶ = Benzo[ghi]perylene, and D[a,h]p⁷ = Dibenzo[a,h]anthracene.

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