

Characterization of Spatial Patterns in River Water Quality Using Chemometric Techniques

(Pengenalpastian Corak Reruang Kualiti Air Sungai Menggunakan Teknik Kimometrik)

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ABSTRACT

Water pollution has become a growing threat to human society and natural ecosystem in recent decades, increasing the need to better understand the variabilities of pollutants within aquatic systems. This study presents the application of two chemometric techniques, namely, cluster analysis (CA) and principal component analysis (PCA). This is to classify and identify the water quality variables into groups of similarities or dissimilarities and to determine their significance. Six stations along Kinta River, Perak, were monitored for 30 physical and chemical parameters during the period of 1997–2006. Using CA, the 30 physical and chemical parameters were classified into 4 clusters; PCA was applied to the datasets and resulted in 10 varifactors with a total variance of 78.06%. The varifactors obtained indicated the significance of each of the variables to the pollution of Kinta River.

Keywords: Chemometrics; cluster analysis; ecosystems; principal component analysis

ABSTRAK

Pencemaran air telah menjadi satu ancaman yang semakin meningkat kepada masyarakat dan ekosistem sejak kebelakangan ini dan ini memerlukan kajian berkaitan dengan punca pencemaran dalam sistem akuatik. Kajian ini menggunakan dua teknik kimometriks di dalam penganalisan data, iaitu, analisis pengelasan (CA) dan analisis prinsipal komponen (PCA). Teknik ini adalah untuk mengenal pasti dan mengelaskan pembolehubah kualiti air ke dalam kumpulan persamaan atau ketidaksamaan dan untuk menentukan kepentingannya terhadap kualiti air Sungai Kinta. Enam stesen di sepanjang Sungai Kinta telah dipantau untuk 30 parameter fizikal dan kimia dalam tempoh 1997-2006. Menggunakan kaedah CA, 30 parameter fizikal dan kimia telah dikelaskan kepada 4 kelompok; PCA telah digunakan untuk dataset dan menghasilkan 10 varifaktor dengan varians 78.06%. Varifaktor yang diperoleh menunjukkan kepentingan setiap pembolehubah terhadap pencemaran di Sungai Kinta.

Kata kunci: Analisis kluster; analisis komponen utama; ekosistem; kimometriks

INTRODUCTION

Rivers provide the main source of drinking water and will remain so for a long time. Coastal areas and seas provide valuable resources for the economic development of a nation. It is generally accepted that goods and services delivered by the coastal and marine ecosystems are worth trillions of dollars (UNEP/GPA 2006). According to a report on pollution of Malaysian rivers, the main contributors of pollution are from land-based sources (Rosnani 2006). Major land-based pollution activities identified are urban settlements, agricultural runoffs, illegal coastal settlements, industrial discharges and sewerage/animal husbandry. In an effort to restore the Kinta River, the Department of Irrigation and Drainage (DID) (DID 2008) has taken various measures, such as waste in the landfill, proper placement of silt traps, improved water storage and identifying the effects of pollution. Kinta River has been adopted under the 'one state one river' program with the aim of using the river as a place for recreational activities for the public (Kalithasan 2008). In addition, a study of water

quality restoration of the Kinta River is required for it to continuously remain the main water source aside from serving as an attraction in Ipoh City.

The assessment of water quality contamination requires monitoring of a wide range of physical, chemical and biological parameters. Water quality analysis is difficult because of the large number of available data. Therefore, the use of specific statistical method is fundamental in obtaining meaningful results. There are two most common methods used, namely, cluster analysis (CA) and principal component analysis (PCA).

Chemometrics methods are increasingly in use, which provide several avenues for exploratory assessment of water quality datasets. The application of the statistical techniques, such as CA and PCA, helps in the interpretation of complex data matrices to better understand the identification of possible sources that influence the water systems (Helena et al. 2000).

In the present study, a datasets of water quality variables obtained from the Department of Environment

(DOE), Malaysia, for duration of 9 years (1997-2006) were subjected to CA and PCA techniques to extract information on the similarities and dissimilarities between the variables, and the outcome of the analysis may reveal possible sources of pollution in the Kinta River.

MATERIALS AND METHODS

STUDY AREA

Kinta River is one of the main tributaries of Sungai Perak, flows from Gunung Korbu at Ulu Kinta, Tanjung Rambutan to Sungai Perak. It's main function is for water supply. Hence, there is a need to protect the river's water quality. The Kinta River dam is at the last phase of the Greater Ipoh Water Supply II Scheme under implementation by *Lembaga Air Perak (LAP)*. Able to provide 639 million liters of water per day, it is expected to meet the water demand in the Kinta Valley until 2020. The major causes of pollution in the Kinta River Basin are industrial discharge,

improper sewage treatment, residential discharge, sand mining, land development and soil erosion (Kalithasan 2008). The sampling sites for this study are at Tanjung Rambutan, Tanjung Tualang, Jambatan Pengkalan, Batu Gajah, Kampung Gajah, and Kampung Baru Timah as shown in Figure 1. Table 1 shows the sampling sites coordinates.

MONITORED PARAMETERS

Thirty water quality variables studied were dissolved oxygen (DO), 5-day biochemical oxygen demand (BOD), electrical conductivity (EC), chemical oxygen demand (COD), ammoniacal nitrogen (AN), pH, suspended solid (SS), temperature (T), salinity (Sal), turbidity (Tur), dissolved solid (DS), total solid (TS), nitrate (NO_3^-), chloride (Cl), phosphate (PO_4^-), arsenic (As), mercury (Hg), cadmium (Cd), chromium (Cr), lead (Pb), zinc (Zn), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), oil and grease (O&G), methylene blue active substances (MBAS), *E. coli* and coliform. The basic

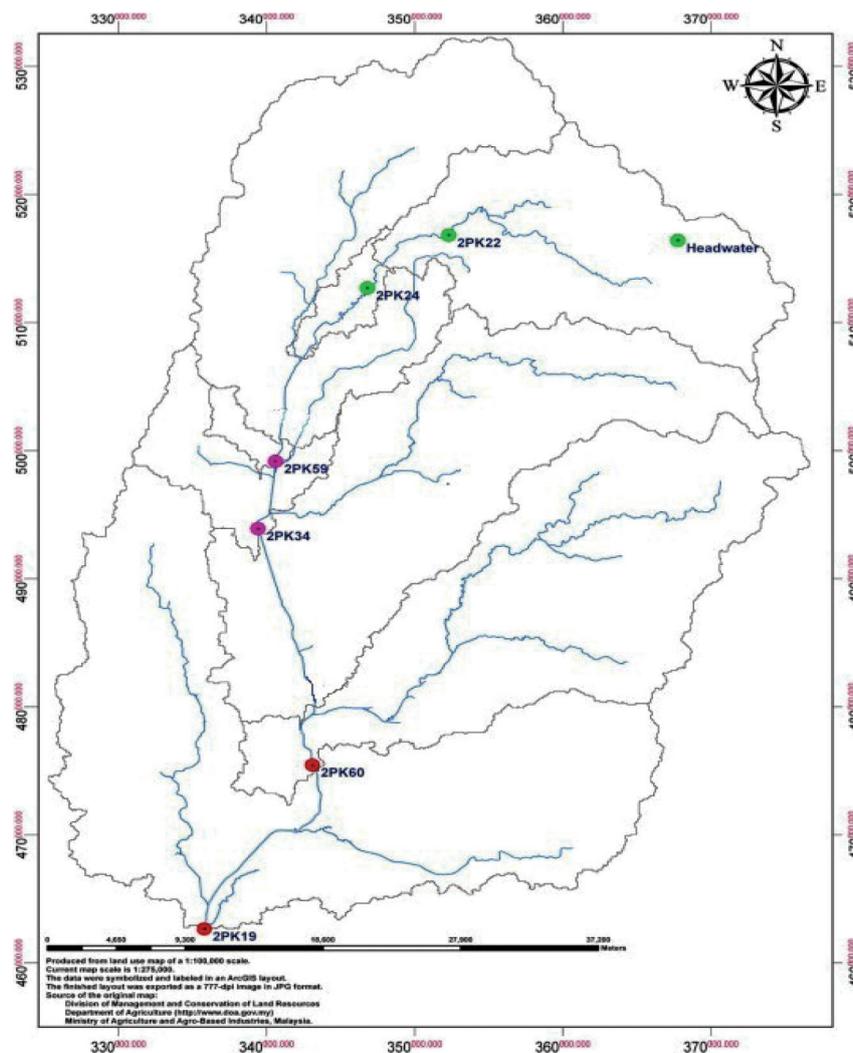


FIGURE 1. Sampling sites on the Kinta River, Perak Darul Ridzuan (Source: Alam Sekitar Malaysia)

TABLE 1. Kinta River basin sampling sites and their coordinates

Site	Coordinates (RSO) ^a		Distance (Km)		Altitude ^d (m)
	Latitude ^b (N)	Longitude ^c (E)	From source	Between stations	
Mount Korbu ^c	518256.14	367777.98	-	-	1599
2PK22 ^f	516816.52	352365.48	15.5	15.5	264
2PK24	512701.07	346869.20	22.4	6.9	50
2PK59	499164.57	340907.99	37.5	15.1	28
2PK34	492824.41	338308.55	43.9	6.4	23
2PK60	472475.77	342025.07	64.8	20.9	9
2PK19	462757.07	336011.65	77.1	12.3	7

^a RSO: Rectified Skew Orthomorphic (the map projection system used for mapping in Peninsular Malaysia)

^b N: north, ^c E: east, ^d Height above sea level, ^e The headwater of the Kinta River, ^f Water quality monitoring station

statistics of the datasets and the water quality parameters are summarized in Table 2.

and XLStat 2012. Prior to analysis, the raw data was standardised and the non-detected values were replaced with half the detection limit (Reimann & Filzmoser 2000).

CHEMOMETRICS ANALYSIS

The statistical program used to compute chemometric analysis; cluster analysis (CA) and principal component analysis (PCA) were Microsoft Office Excel 2007

CLUSTER ANALYSIS (CA)

CA is an exploratory data analysis tool for solving classification problems and is an unsupervised classification

TABLE 2. Mean of water quality variables at different locations of the Kinta River during 1997-2006

Parameters	Tanjung Rambutan (2PK22) Average	Jambatan Pengkalan (2PK59) Average	Tanjung Tualang (2PK24) Average	Batu Gajah (2PK34) Average	Kampung Gajah (2PK19) Average	Kg. Baru Timah (2PK60) Average
DO	7.5	5.72	2.3	3.5	2.7	4.3
BOD	3.0	11.26	7.7	4.9	2.6	3.9
COD	45	49.36	43.7	35.7	23.5	29.5
SS	998	381	505	245.2	91.4	209
pH	6.9	7.01	6.9	29.7	6.7	7.0
NH ₃ -NL	0.3	0.63	1.1	1.6	0.2	0.4
Temp.	26.4	27.15	27.5	27.9	28.3	27.8
EC	454	131.11	197.4	715.8	141.6	562
Salinity	0.3	0.03	0.1	0.3	0.04	0.3
Turbidity	554	379	345	312.4	121.5	259
DS	218	61.66	93.3	210.5	77.7	231
TS	1216	443	599	479	169	440
NO ₃	0.5	0.75	1.0	1.5	1.0	1.3
Cl ₃	124	5.99	8.4	81.5	7.3	105
PO ₄	0.2	0.16	0.2	0.3	0.3	0.3
As	0.003	0.003	0.01	0.01	0.007	0.01
Hg	0.004	0.003	0.0003	0.0002	0.0002	0.0002
Cd	0.002	0.001	0.002	0.002	0.002	0.002
Cr	0.002	0.002	0.003	0.004	0.003	0.003
Pb	0.015	0.01	0.01	0.01	0.01	0.01
Zn	0.027	0.04	0.05	0.03	0.03	0.03
Ca	5.1	8.59	17.5	19.1	11.9	14.7
Fe	0.4	0.46	0.4	0.3	0.4	0.3
K	3.9	4.56	4.5	5.3	7.2	5.0
Mg	6.9	1.24	2.4	5.5	2.7	5.9
Na	59.8	7.18	9.3	41.3	6.3	45.8
O&G	0.5	0.66	0.6	0.7	0.6	0.6
MBAS	0.02	0.03	0.02	0.1	0.03	0.1
<i>E. coli</i>	12819	53391	46783	43856	11488	22139
Coliform	40146	326782	97914	162615	41827	61915

Note: A total of 240 samples were collected from 1997 - 2006

used to normalised data by measuring either the distance or the similarity between the objects to be clustered. In CA, the variables are grouped into classes (clusters) based on similarities within a class and dissimilarity between different classes. This analysis is applied to discover the similarities or dissimilarities of the variables.

PRINCIPAL COMPONENT ANALYSIS (PCA)

The result of PCA was generated in the form of principal components (PCs) known as eigenvalues. The eigenvalues of the correlation matrix measure the amount of the variation explained by each factor and will be the largest for the first factor and become smaller for the subsequent factors. Varimax rotation was applied on the PCs with eigenvalues more than 1 (Kim & Mueller 1987) in order to obtain new groups of variables known as varimax factors (VFs). A factor with an eigenvalue more than or equal to 1 is usually considered as being of statistical significance (the Kaiser criterion). The higher the loading of a variable (either positive or negative), the more that variable contributes to the variation accounted for by the particular varifactors. Only loadings with absolute values greater than 60% are selected for the factor interpretation (Jolliffe 1986). In this study, the factor loading for each of the variable correspond to the significant impact of the variable to the river water quality and this will relate to the sources of the pollution.

RESULTS AND DISCUSSION

The application of chemometrics techniques such as cluster analysis (CA) and principal component analysis (PCA) has been applied for analyzing environmental data and drawing meaningful information (Boyacioglu & Boyacioglu 2010; Bulut et al. 2010). These techniques allow identification of the possible sources that influence the water quality and are

responsible for the variations in the water quality, which therefore offers valuable tool for developing appropriate strategies for effective management of the water resources. In this study, an evaluation of thirty water quality variables monitored by Department of Environment (DOE) during the period from March 1997 to November 2006 was subjected to cluster analysis (CA) and principal component analysis (PCA) to extract information about the similarities and dissimilarities between the water quality variables; and to transform the original variables into new, uncorrelated variables.

CLUSTER ANALYSIS (CA)

CA was applied to the water quality datasets of Kinta River in order to classify the thirty water quality variables based on similarities and dissimilarities between the variables. Performing CA on variables rather than cases is preferred in most research studies (Yalcin et al. 2008). Figure 2 shows the resulted dendrogram.

Clustering of the thirty water quality (WQ) variables produced 4 main clusters (Figure 2). Cluster 1 formed by DO, Cd, Cr and Pb corresponds to either anthropogenic activities such as wastewater discharge, natural causes or river flow (Otto 1998). Cluster 2 consisted of BOD, pH, NH₃-N, Temp., PO₄, As, *E. coli* and coliform may be caused by manure, organic matter and the leaching of fertilizer residue on agricultural land into the river system. According to a study by Azyana and Nik Norulaini (2012) on the land use activities of Kinta River, BOD and NH₃-N were the variables that were most related to agricultural activities. The presence of BOD in the river might be caused by the manure and the organic matter while the NH₃-N is caused by the non-biodegradable matter. The findings are also consistent with the study by Silva et al. (1999) who reported that BOD, total nitrogen and phosphate contamination were due to anthropogenic activities such

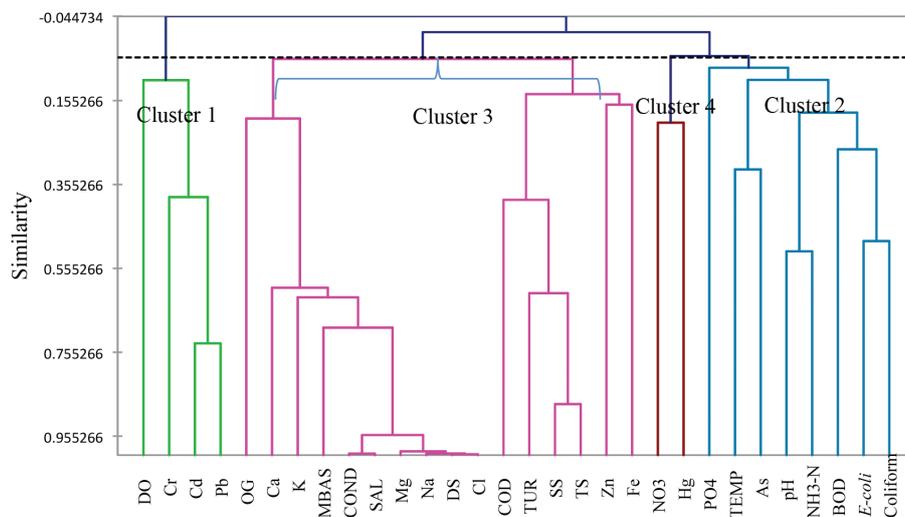


FIGURE 2. Dendrogram of clustering of the water quality variables from the Kinta River using Ward's method

as fertilizer usage, organic pollutants release and domestic sources. Cluster 3 consisted of COD, SS, Cond., Sal., Tur., DS, TS, Cl, Zn, Ca, Fe, K, Mg, Na, Oil & Grease and methylene blue active substances (MBAS). These variables may be related to the industrial activities such as pulp and paper production located along the Kinta River. Cluster 4 formed by NO_3 and Hg that could be related to organic pollution, household wastes, agricultural sources and chemical industries. Silva et al. (1999) also reported that nitrate contamination resulted from activities such as fertilizer usage.

The CA technique applied to the water quality data was able to relate the water quality variables with the sources of contamination. Thus, this approach can be used in offering reliable technique in classifying the water quality variables based on similarity or dissimilarity of each variables. However, in cluster analysis, the clustering and the number of existing clusters are only a qualitative statement. Therefore, as suggested by Astel et al. (2006), cluster analysis should be confirmed in an additional step such as applying the principal component analysis (PCA) technique.

PRINCIPAL COMPONENT ANALYSIS (PCA)

PCA is the most powerful pattern recognition technique that provides information on the most significant variables, which describes the whole dataset by excluding the less significant variables with minimum loss of original information (Helena et al. 2000). PCA was applied to the normalized dataset to compare the compositional patterns between the water quality variables and to identify the components that influence each one. PCA of the entire dataset evolved ten principal components (PCs) with eigenvalues greater than 1 explaining about 78.06% of the total variance in the water quality dataset.

A rotation of principal components can achieve a simpler and more meaningful representation of the underlying factors by decreasing the contribution to PCs of variables with minor significance and increasing the more significant ones by means of varimax rotation (Helena et al. 2000). Varimax rotations applied on the PCs with eigenvalues greater than 1 are considered significant (Reghunath et al. 2002) in obtaining new groups of variables called Varifactors (VFs). VF coefficients having a correlation greater than 0.75, between 0.75 and 0.50 and between 0.50 and 0.30 are considered to have 'strong', 'moderate' and 'weak' significant factor loading, respectively (Reghunath et al. 2002). Although rotation does not affect the goodness of fitting of the principal component solution, the variance explained by each factor is modified.

A varimax rotation of the principal components led to 10 rotated PCs (called henceforth varifactors). Eigenvalues and loadings of these varifactors are displayed in Table 3. The first factor accounts for 25.1% of the total variance (Table 3) and highly participated by Cond. (0.968), Sal. (0.981), DS (0.993), Cl (0.990), Mg (0.980), Na (0.986), Ca

(0.692), K (0.701) and MBAS (0.717) of which the factor loadings between moderate to strong loadings. This factor may be interpreted as a measure of dissolved solids. This could also likely resulted from dissolution of limestone and gypsum soils which can be simplified as soil erosion (Vega et al. 1998).

The second factor explains 9.2% of the variance in the WQ data (Table 3). It consisted of high loadings from three variables: SS (0.933), TUR (0.818) and TS (0.850); and moderate loading from COD (0.562). These variables are related to surface runoff sources which may originated from agricultural fields, domestic areas and waste disposal sources.

The third factor describes 6.2% of the variance in the dataset obtained a high loadings from BOD (0.852) and coliform (0.675) (Table 3). These variables are indicators of microbial pollution of which the sources of these bacteria include failing septic systems, wastewater treatment plants and the application of manure to agricultural lands (Singh et al. 2005).

The fourth factor accounts for 7.6% of the variance in the dataset (Table 3). It exhibits high loadings from Cd (0.860) and Pb (0.837) and moderate loadings from Cr (0.670). This relates to the toxic metals that may be due to the discharges from several industries along the river such as metal fabrication, metal furnishing and electroplating and electrical/electronic industries (Singh et al. 2005).

The fifth factor explains 6.6% of the variance in the dataset (Table 3). It exhibits high loadings from DO (-0.807) and Temp. (0.723) and moderate loading from As (0.561). Loadings of these variables can be indicative of mineral oxidation processes. Specifically, association of As with DO can be related to the redox-sensitive nature of iron oxides and sulphide minerals since exchange of substantial amounts of As between solid phases and the surrounding water can results from redox-enhanced dissolution reactions. Similar relationship was suggested by Hinkle (1997) who analysed 47 samples of filtered ground water from Willamette Basin (USA) and reported that the median As concentration in the low DO samples (DO concentrations < 1.0 mg L^{-1}) was significantly higher than that in the well-oxygenated ones (DO concentrations > 1.0 mg L^{-1}). Besides, Kurosawa et al. (2005) hypothesized that co-association of As with low levels of DO in water may be explained by the associated high $\text{NH}_3\text{-N}$ levels. Microbial decomposition of organic matter results in consumption of high amounts of DO and production of $\text{NH}_3\text{-N}$, thus leading to a low oxidation-reduction potential which in consequence accelerates release of As in anoxic environments from sediments to the surrounding water. As in nature can be found at low level, the anthropogenic activities might have triggered the concentration of this metal in this river water. Since As is not volatile and soluble in water it can be found from the used of insecticides to kill off weeds surrounding the agricultural area.

The sixth factor explains 4.8% of the variance (Table 3). It demonstrates high loading of NO_3 (0.709) and

TABLE 3. Loadings of 30 variables on components rotated according to the Varimax method

	VF1	VF2	VF3	VF4	VF5	VF6	VF7	VF8	VF9	VF10
DO					-0.807					
BOD			0.852							
COD		0.562								
SS		0.933								
pH									0.918	
NH ₃ -N									0.718	
TEMP					0.723					
COND	0.968									
SAL	0.981									
TUR		0.818								
DS	0.993									
TS		0.850								
NO ₃						0.709				
Cl	0.990									
PO ₄										0.799
As					0.561					
Hg						0.643				
Cd				0.860						
Cr				0.670						
Pb				0.837						
Zn										
Ca	0.692									
Fe							0.784			
K	0.701									
Mg	0.980									
Na	0.986									
O&G								0.895		
MBAS	0.717									
E-coli										0.578
Coliform			0.675							
Eigenvalue	7.633	3.329	2.935	2.064	1.533	1.311	1.283	1.162	1.128	1.042
Variance (%)	25.128	9.239	6.182	7.607	6.600	4.762	4.937	4.017	5.002	4.590
Cumulative (%)	25.128	34.368	40.550	48.156	54.756	59.518	64.455	68.472	73.474	78.064

moderate loading of Hg (0.643). The presence of NO₃ reflect organic pollution and relate to anthropogenic point sources like domestic sewage and additionally derive from agricultural areas where inorganic nitrogen fertilizers are in common use. The contributors of Hg could be from the bleaching process of the textile industries, disposal of household items such as compact fluorescent light bulb and waste from chemical industries.

The seventh and eighth factors account for around 5 and 4% of the variance, respectively. The seventh factor has a high loading of Fe (0.784), while the eighth factor high loading of O&G (0.895). The high loading of Fe

could relate to the industrial coatings that are applied to metals so as to give their surfaces rust-resistant properties, also related to activities like paints, metal-finishing and electroplating industries. The O&G could relate to surface runoff from road drainage that contain fossil fuel from vehicles as a result of leakage.

The ninth factor demonstrates 5.0% of the variance of the data (Table 3). It is characterized by high, exclusive loadings from pH (0.918) and NH₃-N (0.718). The strong loading of pH could be due to seasonal changes and human activities. On the other side, ammonia is present naturally in ground and surface water. It is one of the products of the

microbiological activity and is indicator of septic pollution especially when associated with NO_3^- .

Finally, the tenth factor demonstrates 4.6% of total variance (Table 3). It is distinguished with high loading from PO_4 (0.799) which indicate the waste from fertilizer used in agricultural activities, moreover a wide range of fertilizer might also come from urban landscaping and moderate loading from *E.coli* (0.578) associated with wastewater treatment plants or animal husbandry.

CONCLUSION

In this study, the CA helped to group the datasets into four clusters of similar characteristics pertaining to water quality characteristics and pollution (natural and anthropogenic) sources. PCA of the datasets evolved ten principal components (PCs) with eigenvalues greater than 1 explaining about 78.06% of the total variance in the water quality datasets. The results of the PCA suggested the pollution sources responsible for water quality variations in Kinta River was mainly related to anthropogenic activities generated from wastewater discharge, agricultural activities, inorganic and organic pollution generated from the industrial activities along the river. Thus, the chemometric statistical techniques served as an excellent exploratory tool in analysis and interpretation of complex dataset on water quality in understanding the sources of pollution of Kinta River.

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