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Heavy Metals and Water Quality Assessment Using Multivariate Statistical Techniques and Water Quality Index of the Semenyih River, Peninsular Malaysia

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Abstract: The present study was carried out to investigate and determine the water quality and the pollution sources affected on Semenyih River using multivariate statistical techniques and water quality index (WQI). Temperature, pH, dissolved oxygen (DO), conductivity, total dissolved solids (TDS), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2), phosphate (PO_4^{3-}), turbidity, ammonia-nitrogen (NH_3-N), total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total hardness (TH), oil and grease (O&G), *Escherichia coli* and total *Colifor* (TC) as water quality variables and Cd, Cu, Ni, Zn, Fe, Pb, Mn, Cr and Hg as heavy metals variables have been analyzed in the collected water samples during the year 2012 from 8 sampling stations along Semenyih River. Cluster analysis (CA) categorized 8 stations into three clusters based on the similarity of water quality characteristics and categorized 27 variables analyzed to four clusters to determine the relationship among the variables and their possible sources. Principal component analysis (PCA) determined that 96.63% of the total variance was accounted for five factors which pointed to the variables responsible for deterioration of water quality attributed to anthropogenic activities associated with urbanization, industrialization, agriculture, livestock husbandry and mining activities. In addition, WQI classified the river as clean (Class I) at station 1, slightly polluted (Class II) at stations 2 and 3 and as moderately polluted (Class III) at stations 4-8; in general; however, the river falls into class III and thus is required extensive treatment before using for domestic purposes. Therefore, this study verified that the multivariate statistical techniques and water quality index are mainly required for interpreting complex data sets for the purpose of analysis of water quality variations.

Key words: Heavy metals · Water quality · Cluster analysis · Principal component analysis · Water quality index (WQI)

INTRODUCTION

The concentrations of water quality variables are known to play a main role in determining the status of aquatic systems [1, 2]. The excessive concentrations of these variables may result in diverse problems in aquatic ecosystem such as loss of oxygen, fish deaths, an increase in the extent of algal blooms and general loss of biodiversity. Pollutants enhancementc ritically deteriorates aquaticecosystems, reducing the use of water for domestic water supply, agriculture, industry, recreation and other purposes [3]. In addition, different human activities have influenced aquatic ecosystems as a result of discharge of toxic chemicals, modification in hydrology, alternations of physicochemical water characteristic as well as increase nutrient inputs [4, 5]. Activities related to urbanization and agriculture basically are main contributors to alterations in the chemical composition of

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aquatic habitats [6, 7]. Comprehension the impacts of anthropogenic activities on aquatic ecosystems hadincreased importance because of association with contamination of essential water resources such as lakes, streams and rivers.

Recently, there has been an increasing awareness of river system contamination with different contaminants inparticular heavymetal. Essentially, rivers play more important roles in the community particularly as a source of water supply and the fishing industry, in order that rivers pollution either directly or indirectly can mostly influence humansas final consumers. Nevertheless, some of the heavy metals are essential micronutrients in their low concentrations but toxicwhen exceed the minimum requirements [8].

In Malaysia, river systems are a fundamental part of the water supply. More than 150 river systems present in Malaysia, 100 of themlocated in Peninsular Malaysia while the other 50 found in Sabah and Sarawak. These rivers are evaluated to contribute about 97% of the water supply sources [9]. However, the river's water quality is degraded by reason of the leaching of pollutants and undiscriminating disposal of anthropogenic wastes from developed area which resultsin from urbanization, increase of population and industrialization [10]. Thus, it is important to perform river quality assessment so as to detect the alterations of the water quality and the evaluation of pollution sources [11]. The state of Selangor, Malaysia, has a long history of rivers contamination problems related to urbanization and land use alterations. Semenyih River is one of the mainrivers draining a residential area and densely inhabited of Selangor. Over the past 20 years, it has supplied about one million of Selangor population and is a source of management of overflow discharges [12]. According to literature [13], Semenyih River has been classified as slightly polluted. Additionally, Semenyih River is one of the important rivers in Malaysia which from a source of domestic water supply. Therefore, study of water pollution of the river is of particular importance because of the river receives huge effluents from livestock farms, industrial and agricultural activities as well as urban runoff which cause deterioration of the river water quality [14]. In general, human activities related to land use around Semenyih River basin pose a threat to aquatic ecosystem and the provinces where the river water usually uses as domestic supply [15]. Consequently, to protect the water resources, the land use activities must be planned and controlled. A study was conducted to determine the concentration of selected water quality parameters and heavy metals in Semenyih River, and to evaluate the contamination levelusing Water Quality Index (WQI) of Malaysian rivers and the multivariate statistical methods namely cluster analysis and factor analysis in order to assess the effect of unregulated waste discharge on the quality of the river.

MATERIALS AND METHODS

Study Area and Samples Collection: The Semenyih River has area ranged from 1.37 to 35.57 km^2 and consists of 25 water catchment valleys and 36 sub-basins (Fig. 1). The river lies between longitude 101° 48'32.9 "E to 101° 52'30.5 "E and latitude 02° 54'14.9 "N to 03 ° 03'23.1 "N. The river originates from the forested areas and hilly in the western slope of BanjaranTitiwangsa, northeast of Hulu Langat [13, 15]. In addition, it flows southwards toward Hulu Langat and Sepang. The riveris negatively affected by industrialization and urbanization since the early 1990. Overall, the river is a resource of domestic water supply after the treatment for Bandar Tasek Kesuma Semenyih town and Bandar Rinching [12, 15]. Eventually, the climate of the study area is characterized by high rainfall, high average and homogeneous annual temperatures and high humidity. This climate has influenced the geomorphology and hydrology of the study area.

Sampling stations were selected along the river based on the characteristic of the water condition and anthropogenic activities along the river. Stations 1 and 2 were located in the upstream and represent clear water. Furthermore, station 3 was located in the area where mining activity and deforestation took place where the water was turbid. Station 4 was more turbid due to runoff from human activities including random settlements. Station 5 was situated in the Semenyih City in which pollution was contributed by the urban activity as well as domestic and industrial effluents. In addition, station 6 was located after livestock farms and agricultural activities that adversely impact on the water quality in this station. Station 7 was affected by deforestation and discharge from rural areas. Thelast station was located after Bangi City in JenderamHilir and characterized by turbid and contaminated water as a result of accumulated pollutants from previous stations and water treatment plant as well as erosion and human activities (Fig. 1). Water sampling has been carried out in March, July and November 2012. Water samples were collected from each station in triplicate in specific bottles based ondescription reported in literature [16].

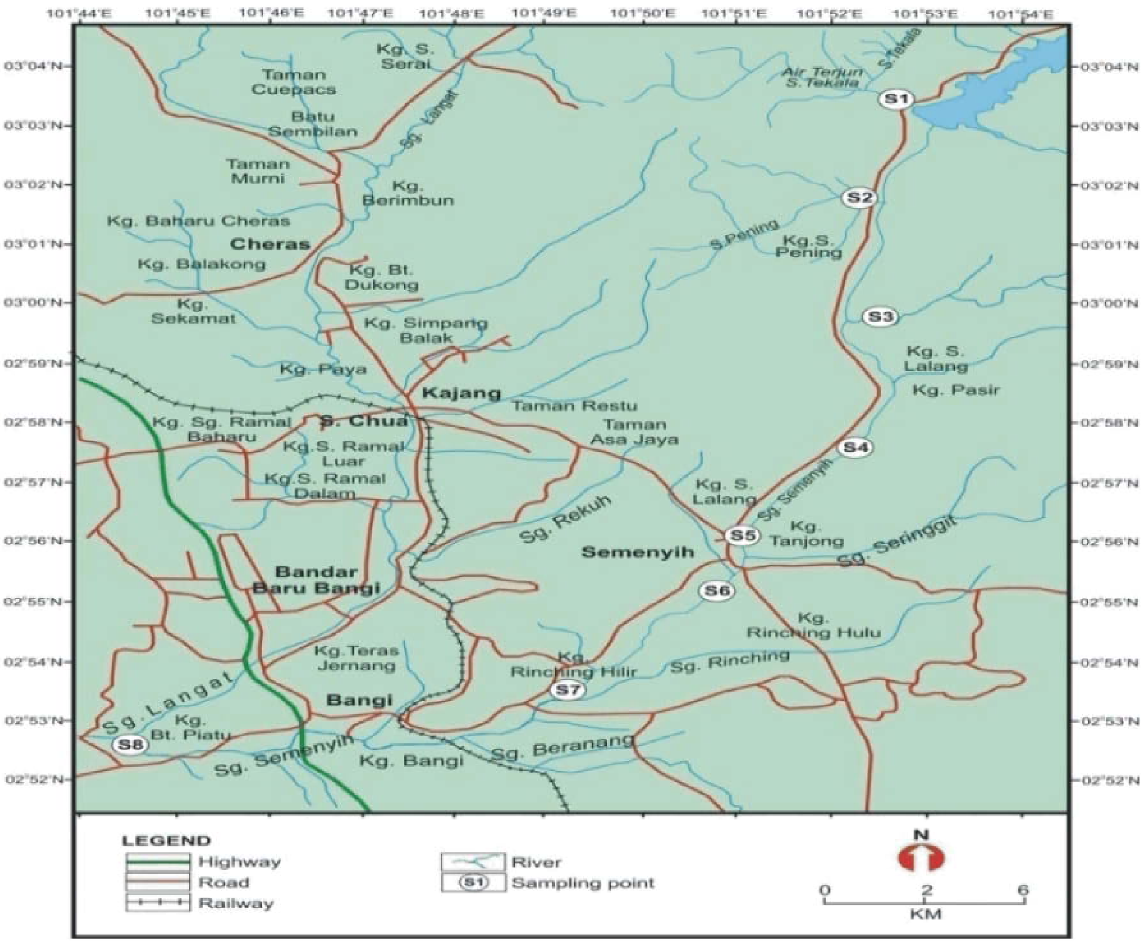

Fig. 1: Study area and sampling stations along Semenyih River

Analytical Determinations: Water quality parameters such as temperature, dissolved oxygen (DO), conductivity and pH were measured *in situ* using Multisensor probe YSI model 449D, whereas chemical oxygen demands (COD), biochemical oxygen demands (BOD_5), Total suspended solids (TSS), oil and grease (OG), turbidity, phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), nitrate (No_3^-), nitrite (NO_2), ammonia nitrogen (NH_3-N), total hardness (TH), *E. coli* and total *Colifor* (TC) were analyzed in the laboratory. COD was measured by the open reflux method and BOD_5 was analyzed by 5-day test [15]. Additionally, TSS was analyzed by total solids dried at 103–105°C and O&Gwas assayed as described by liquid-liquid, partition-gravimetric method[16]. Moreover, turbidity, (PO_4^{3-}), (SO_4^{2-}), NO_2, (NO_4^-) and NH_3-N were assayed by absorptometric, acid ascorbic, SulfaVer 4®, cadmium reduction, diazotization and Nessler methods, respectively [16, 17]. Total hardness was determined by the convenient Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). In addition, dissolved heavy metals (Fe, Zn, Cd, Mn, Cr, Ni, Pb, Cu and Hg) were measured by convenient Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). Finally, *E.coli* and TC were determined based on the membrane filter technique [16]. All the equipments used were calibrated before use based on the manufacturer's directions.

Water Quality Index: The Water Quality Index (WQI) is attributed to quality value ofasummation set of calculated variables. It generallycontains sub-index values indicated each pre-identified variables bycomparing its measurement witha parameter-specific rating curve, optionally weighted as well as to integrate into the last index. The WQI aimed ofsummarizing amounts ofwater quality data into simple for a particular river [18]. Six variables were preferred for the WQI; Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Suspended Solids (SS), Ammoniacal Nitrogen (AN) and pH. Calculations are executed on the sub-indicesof variables. The sub-indices

Table 1: The best fit equations used for the estimation of the six sub-index values to calculate WQI

Subindices for DO (in % saturation), BOD and COD	Subindices for NH3-N, TSS and pH
SIDO = 0 for x ≤ 8	SIAN = 100.5 - 105x for x ≤ 0.3
SIDO = 100 for x ≥ 92	SIAN = 94 * exp(-0.573x) - 5 * I x – 2 I for 0.3 < x < 4
SIDO = -0.395 + 0.030x2 - 0.00020x3 for 8 < x < 92	SIAN = 0 for x ≥ 4
SIBOD = 100.4 - 4.23x for x ≤ 5	SISS = 97.5 * exp(-0.00676x) + 0.05x for x ≤ 100
SIBOD = 108 * exp(-0.055x) - 0.1x for x > 5	SISS = 71 * exp(-0.0061x) - 0.015x for 100 < x < 1000
	SISS = 0 for x ≥ 1000
SICOD = -1.33x + 99.1 for x ≤ 20	SIpH = 17.2 - 17.2x + 5.02x2 for x < 5.5
SICOD = 103 * exp(-0.0157x) - 0.04x for x > 20	SIpH = -242 + 95.5x - 6.67x2 for 5.5 ≤ x < 7
	SipH = -181 + 82.4x - 6.05x2 for 7 ≤ x < 8.75
	SipH = 536 - 77.0x + 2.76x2 for x ≥ 8.75

Source: [18]

are named SIDO, SIBOD, SICOD, SIAN, SISS and SIPH [19]. The finestequations used for the six sub-index value evaluation are shown in Table 1. Subsequently, the particular sub indices have been computed the WQI using the following equation;

WQI = 0.22*SIDO + 0.19* SIBOD +0.16 * SICOD + 0.15 * SIAN + 0.16 * SISS +0.12 * SIPH

Statistical Analysis: Statistical analysis was executed using SPSS version 20. In the cluster analysis (CA), the Ward's method and squared Euclidean distances were performed to determine water quality indicators and the variables of sampling stations [15, 20]. In addition, factor analysis (FA) orprincipal component analysis (PCA) was carried out tocategorizethe pollution factors influenced on water quality. The Bartlett's sphericity and Kaiser–Meyer–Olkin (KMO) tests were used to examine the suitability of the data regardingfactor analysis. However,all data analyzed were standardized by scale transformation to ensure normal distributions for cluster analysis and factor analysis [15, 21].

RESULTS AND DISCUSSION

Theconcentrations of Water Quality Variables: Table 2 shows the mean values of 18 variables of water quality in Semenyih River.Generally,river affectedby urbanization, agriculture, industry, mining and other human activities such as sewages from random settlements. The temperature values of the eight stations showed less variation, ranging from 25.25°C at station 1 to 27.18°C at station 8. Principally, several factors such as weather condition as well as sampling time result in variations of temperature [22]. The pH values ranged from 6.29 to 6.91, the acceptable range for aquatic life is from 6.5 to 9. Therefore, it is very significant to preserve the aquatic ecosystem within this range due tolow or high pH can causedisturbance in nature [19, 23]. The lowest DO concentration (4.77 mg/L) was found at station 8; and the DO concentrationsat stations 4,5,6 and 7 were also significantly lower than the other three stations. This attribute to the discharge of domestic effluents and industry induced serious organic contamination in the river, because of the decrease of DO was mostlyresulted from the organic compounds disintegration [24]. Further more, extremely low DO value generally pointsto the degradation of aquatic systems [25, 26]. The highest DO values were found at station 1 (6.34 mg/L). The conductivity mean values of all stations were ranged from 26.67 to 95.55 µS/cm, station 8 showed thehighest and station 1 the lowest values. This can be attributed to the effluent of domestic sewage, industrial wastewater, water treatment plant and agricultural activities, which discharge massivel evels of anions in the river system, because conductivity of surface water mainly relieson ion concentrations [27]. In addition, TDS values were ranged from 20.22 mg/L at station 1 to 61.55 mg/L at station 8. The TDS concentration in the river is essentially influenced by extreme anthropogenic activities and runoff with high suspended matter [14].The eighth station showed the highest concentrations of NO_3^- (9.51 mg/L) and PO_4^{3-} (1.01 mg/L); while showing station 7 the highest concentrations of NH_3-N (1.09 mg/L) and NO_2 (0.09 mg/L). This suggests that measures of nutrient decrease from industrial and domestic wastewater are largelyrequired to improve the water quality of Semenyih Rivertaking into consideration; that it receives highlevels of wastewater from random settlements [13]. Stations 4,5,6 and 7 showed relatively high NO_4^- and PO_4^{3-} contents; while Stations 4, 5, 6 and 8showed high NH_3-N and NO_2 concentrations. Generally, the excessive nutrients concentrations can stimulate aquatic plant and algae growth, which can lead to *eutrophication* [28]. The high nutrients and phosphorus concentrations were found in river mainlyimpacted by urbanization, industrialization and

Table 2: Mean values of water quality measurement along Semenyih River in March, July and November, 2012

Variables		Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7	Station 8
Temp °C	MEAN	25.25	25.78	25.80	26.13	26.42	26.67	26.94	27.18
	SD	0.89	0.77	0.80	0.57	0.69	0.73	0.52	0.48
pH	MEAN	6.91	6.30	6.39	6.35	6.39	6.38	6.29	6.59
	SD	1.32	1.20	0.91	0.91	0.68	0.98	0.75	0.46
DO mg/L	MEAN	6.34	6.20	6.17	5.87	5.60	5.27	5.51	4.77
	SD	0.81	0.56	0.31	0.21	0.27	0.27	0.41	0.83
DO %	MEAN	77.23	72.43	72.66	68.20	65.11	60.42	63.11	52.91
	SD	6.92	5.29	6.57	6.61	5.35	5.58	5.96	2.75
Cond µS/cm	MEAN	26.67	40.78	44.55	59.89	67.78	74.22	78.00	95.55
	SD	13.50	18.95	24.50	28.34	29.18	32.85	39.18	34.62
TDS mg/L	MEAN	20.22	26.55	28.33	39.78	45.00	47.78	50.89	61.55
	SD	5.02	12.03	14.29	19.73	21.00	21.72	26.67	22.84
SO_4 mg/L	MEAN	2.30	5.87	7.51	14.81	9.90	23.21	28.44	19.69
	SD	0.82	1.83	0.34	7.76	1.84	19.79	28.28	6.54
NO_3 mg/L	MEAN	2.49	5.14	6.15	7.94	6.74	7.33	8.09	9.51
	SD	1.63	3.27	3.45	5.71	5.11	4.96	3.89	3.80
NO_2 mg/L	MEAN	0.01	0.02	0.03	0.05	0.05	0.05	0.09	0.07
	SD	0.01	0.01	0.02	0.03	0.01	0.01	0.09	0.03
PO_4 mg/L	MEAN	0.34	0.41	0.52	0.53	0.72	0.76	0.97	1.01
	SD	0.27	0.57	0.40	0.28	0.29	0.61	0.81	0.36
TUR NTU	MEAN	5.00	37.57	40.54	50.01	56.44	65.64	129.46	119.44
	SD	2.65	21.47	24.10	44.57	51.93	54.34	84.02	68.28
NH_3-N mg/L	MEAN	0.04	0.26	0.36	0.66	0.73	0.93	1.09	1.07
	SD	0.03	0.08	0.04	0.12	0.13	0.17	0.72	0.29
TSS mg/L	MEAN	17.33	38.86	67.44	87.36	70.53	74.04	264.82	93.88
	SD	10.99	9.52	20.05	74.39	35.56	59.79	198.41	41.81
BOD mg/L	MEAN	0.46	1.18	1.94	2.66	2.72	3.47	3.48	3.78
	SD	0.16	0.52	0.62	0.76	0.92	1.07	0.93	0.82
COD mg/L	MEAN	8.26	15.53	30.89	41.68	49.05	82.64	76.22	103.49
	SD	2.33	2.29	16.76	13.97	10.26	68.32	40.81	84.38
TH mg/L	MEAN	4.25	3.27	3.55	5.15	5.88	6.57	6.29	10.07
	SD	1.03	0.83	0.39	1.27	1.99	2.09	2.65	4.59
OG mg/L	MEAN	1.20	2.77	2.91	3.54	4.40	3.74	4.00	4.46
	SD	0.26	1.21	1.10	1.24	1.73	1.12	1.04	0.88
E.coli CFU/100mL	MEAN	688.9	3000	24444.4	43222.2	68666. 7	167111.1	106555. 6	135222.3
	SD	226.90	1193.04	26738.10	28636.29	46855.57	97288.99	26077.52	68350.86
T.C *CFU/100mL*	MEAN	1666.7	7855.6	68777.8	91666.7	136222.2	256000.0	203888.9	252000
	SD	218.58	2313.33	49137.37	44035.34	74765.06	61199.13	14241.31	41929.84

agricultural activities [29]. This refers to the urgent need to control pollutionsource in the river. In contrast, station 1 represented the lowest concentrations of NO_3^- (2.49 mg/L), NO_2 (0.01 mg/L), NH_3-N (0.04 mg/L) and PO_4^{3-} (0.34 mg/L). The seventh station showed the high value of SO_4^{2-} (28.44 mg/L); while station 1 recorded the lowest value (2.30 mg/L). In general, the rock weathering and human activities such as mining, fossil fuel combustion process and waste discharge are the main sources of sulfate in rivers [30]. The high turbidity values were found 129.46 NTU and 119.44 NTU at stations 7 and 8, respectively, resulted from bridge construction at station 7 which was an indicator of a high measured of turbidity. Furthermore, relatively high turbidity values were at stations 4, 5 and 6. Generally,the overland flow, stream flow and surface runoff in natural waters increase the turbidity levels in the water [15, 31]. Conversely, station 1 showed the lowest value of turbidity (5 NTU). Relatively high BOD contents were found in the stations 6 (3.47 mg/L), 7 (3.48 mg/L) and 8 (3.78 mg/L); the COD contents also showed high concentrations at stations 6 (82.64 mg/L), 7 (76.22 mg/L) and 8 (103.49 mg/L). The BOD and COD concentrations were continually increased in particular at these stations because of livestock husbandry before station 6. The BOD and COD concentrations in surface water are impacted mainly by the natural plant decomposing process andother contributors which increase the total nutrient in water bodies such as construction effluent, fertilizer, septic system and animal farms [15, 22, 32]. The seventh station showed the highest value of TSS (264.82 mg/L). This attributed to serious erosion and drifts mud as a result of the rapidly increased flow rate along the river especially at the latest stations. Additionally, the TSS valueswere increased starting from station 3, because of deforestation, mining and palm plantation activities along the river. On the other hand, the upstream station recorded the lowest value of TSS (17.33 mg/L). TH contents were relatively low at all stations and ranged from 3.27 to 10.07 mg/L.The highest value of oil and grease (4.46 mg/L) was found in the station 8, while smaller amounts of oil and grease (1.20 mg/L) were found at station 1. Oil and grease concentratios can seriously affect the ecology of a water body [15]. These concentrations are increased along the river due to the untreated domestic and industrial wastewater from Semenyih and Bangi Cities as well as the discharges of surrounding area wastewater.All stations showed high concentrations of *E. coli* and TC. Station 6 recorded the highest concentrations of *E. coli* (167111.1 CFU/100 mL) and TC (256000 CFU/100mL). The *E. coli* and TC countswere increased drastically at station 6 that receives large amounts of effluents from livestock husbandry farms situated before station 6. Moreover, human recreational activities were also a source of *Colifor* contamination [32]. On the contrary, station 1 showed the lowest concentrations of *E. coli* (688.9 CFU/100 mL) and TC (1666.7 CFU/100mL). In general, the high counts of coliform bacteria are attributed to rapid growth of population in the basin area and the open defecation along the river banks [33, 34]. On the other hand, the mean values of temperature, pH, conductivity, TDS, SO_4 and TH werecategorized under class I, whereas DO, BOD_5 were categorized under class II based on NWQS for Malaysian rivers [20]. Consequently, these parameters were within the acceptable range. Moreover, the mean values of NO_3, NO_2, NH_3-N, TSS and COD were categorized as class III and reached the threshold limit. Likewise, the mean values ofturbidity, PO_4^{3-}, O&G, *E. coli* and TC were exceeded the allowable threshold levels of NWQS, hence, categorized as class V. Therefore, the river is slightly polluted with NO_4^{-}, NO_2, NH_3-N, TSS and COD, whereas it is extremely contaminated with turbidity, PO_4^{3-}, O&G, *E. coli* and TC.

Heavy Metals Concentrations: The heavy metals concentrations in the sampling stations of Semenyih River are shown in Table 3. For Cd, it ranged from 0.12 to 0.68 µg/L, compared to 0.06-0.98 µg/L as reported in literature [35] of the same basin. All the sampling stations recorded levels less than 10 µg/L recommended other researcher [19], to be categorized as Class II. The Cu values ranged from 0.84 to 7.33 µg/L, compared to Cu ranged from 5.96 to 21.2 µg/L reported for Semenyih River [35]. All the sampling stations recorded level less than the recommended limit(10 µg/L) by DOE in 2011. The Ni concentrations were ranging from 0.29-0.88 µg/L, compared to 0.80 to 24.72 µg/L reported [36] of the Langat river basin. All the sampling stations showed levels less than 50 µg/L recommended bythe other researcher [19]. Generally, the Ni sources are representing chemical and mining industries [37]. The values of Zn ranged from 33.10-49.19 µg/L, compared to 40-60 µg/L as reported in literature [32] of the Langat river basin. The highest Zn value was recorded at station 7, whereas the lowest at station 6. Adequate Zn is essential to neutralize the toxic influences of Cd [38]. Principally, Zn content had been shown as an example of the evolution of toxic metals related to mining pollution [39]. The Fe concentrations of water samples ranged between minimum 280.76 mg/ L at station 7 to maximum 488.60 µg/ L at station 5 and all stations had values less than 500 µg/L, compared to 340 to 1980 µg/L reported for Langat River [32]. When compared to NWQS [19], the normal criterion is 1000 µg/L for Fe. Therefore, all stations were within this range. Stations 5 and 6 received urban runoff and wastewater from Semenyih city and livestock farms that contributed to the high Fe concentration. In addition, the Pb values ranged from 0.70 to 3.08 µg/L. This study recorded lower content of Pb compared to the findings reported in literature [36], which ranged between 0.5-6.99 µg/L. Generally, Pb deposits in water partitions rapidly between the sediments and an aqueous phase, depending on pH, salt content and the presence of organic chelating agents [40]. For Mn, it ranged between minimum 30.11 µg/L at station 4 and maximum 59.79 µg/L at station 7, compared to Mn between 8.93-492 µg/L as reported in literature [30] of the same basin. Moreover, the Cr concentrations of water samples ranged between minimum 1.64 at station 2 to maximum 5.46 µg/ L at station 8. Eventually, Hg values ranged from 0.0 -0.96 µg/ L. The order of heavy metal concentrations in water samples was Fe> Zn>Mn>Cr> Cu>Pb> Ni> Cd>Hg.

Comparison with various water quality standards showed that the mean Cu, Ni, Pb, Hg and Cr were low and within the range of natural background concentrations (Table 4). Although, the mean value of Fe in the water was higher than the Canadian Standard (CCME), it was found to be lower than that of the United States Environmental Agency (USEPA (CCC)) and the Malaysian standard (NWQS). Furthermore, the mean value of Cd was also lower than the USEPA (CMC) and Malaysian standard (NWQS), while was higher than CCME and USEPA (CCC).

Table 3: Mean concentrations of heavy metals in the water samples at each station inSemenyih River during March, July and November, 2012

Heavy metal µg/L	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8
Cd	0.64	0.35	0.26	0.68	0.61	0.12	0.15	0.29
Cu	1.99	0.84	1.70	1.78	2.03	7.33	1.81	1.95
Ni	0.86	0.29	0.33	0.37	0.88	0.53	0.38	0.72
Zn	34.80	40.13	37.79	35.16	47.55	33.10	49.19	47.41
Fe	310.17	317.67	283.98	385.06	488.60	486.79	280.76	396.98
Pb	1.20	0.76	0.70	1.50	2.18	3.08	2.10	2.49
Mn	48.73	32.35	33.72	30.11	32.16	39.38	44.40	59.79
Cr	2.90	1.64	3.97	2.62	1.99	2.57	2.34	5.46
Hg	0	0	0.01	0.14	0.96	0.12	0.17	0.15

Table 4: Criteria of heavy metals concentrations in freshwater ecosystem

Metal	*Present study µg/L*	*CCME µg/L*	*USEPA-(CMC) µg/L*	*USEPA-(CCC) µg/L*	*NWQS, Class II (µg/L)*
Cd	0.39	0.017	2.0	0.25	10
Cu	2.43	2-4	13	9.0	10
Ni	0.54	52-150	470	52	50
Zn	40.64	30	120	120	5000
Fe	368.75	300	-	1000	1000
Pb	1.75	1-7	65	2.5	50
Mn	40.8	-	-	-	100
Cr	2.94	8.9	570	87	50
Hg	0.19	-	1.4	0.77	1

Source: [19, 41, 42]

The mean value of Zn exceeded CCME, while was below USEPA (CMC and CCC) drinking water quality guidelines and Malaysian standard (NWQS). Lastly, the mean concentration of Mn was above CCME guidelines, USEPA (CMC and CCC) drinking water quality guidelines, whereas was found to be within the Malaysian standard (NWQS). It was determined that the concentrations of heavy metals in the Semenyih River were lower than the maximum permitted concentrations for protection of aquatic life, except Cd, Zn, Fe and Mn which were slightly elevated. The accumulation of heavy metals along the Semenyih River may depend largely on common sources of pollution, which are identified as industrial discharges, domestic sewage and livestock farms [12].

Cluster Analysis: Cluster analysis (CA) was used to test water quality data and determine the similarity of sampling stations as well as to classify specific areas of pollution [2, 43, 44]. H CA was executed on the standardized data set using Ward's method with Euclidean distances to the determination of similarity. CA yielded a dendrogram (Fig. 2), where all eight sampling stations were grouped into three significant different clusters at $(D_{link}/D_{max}) \times 100<40$. Cluster 1 comprised stations 1, 2 and 3. Cluster 2 encompassed stations 4 and 5, whereas Cluster 3 consisted of stations 6, 7 and 8. The classification of clusters varied with significance level due to the stations in these clusters had anthropogenic backgrounds and similar features and that influenced by parallel sources. Cluster 1 pointed out relatively low polluted stations. In cluster 1, stations were situated in the upstream thatwas surrounded by extended forest covering. The upstream area of rivers commonly is covered with intense forest covering [20, 44]. In these stations, human activitieswere limited except some recreational activities at upstream waterfall [15]. Cluster 2 corresponded to moderate polluted stations, which wereinfluenced by anthropogenic activities and land use. Station 4 receives pollutants from agricultural activities, domestic effluents and mining as well as discharge of unsewered areas, whereas station 5 was affected by surface runoff, industrial activities and wastewater from Semenyihtown [15]. Cluster 3 indicateddownstream stations which wereimpacted by palm plantation, deforestation, livestock farms particularly at station 6, runoff from agricultural fields and discharges from vehicles washing and workshops as well as water treatment plant at station 8. Additionally, the anthropogenic activities in this area included settlements and industries, which covered Rinching, Bangi, Broga and Beranang [12]. Therefore, the high deterioration of water quality was recorded at these stations that received contamination from point and non-pointsources such represented above.

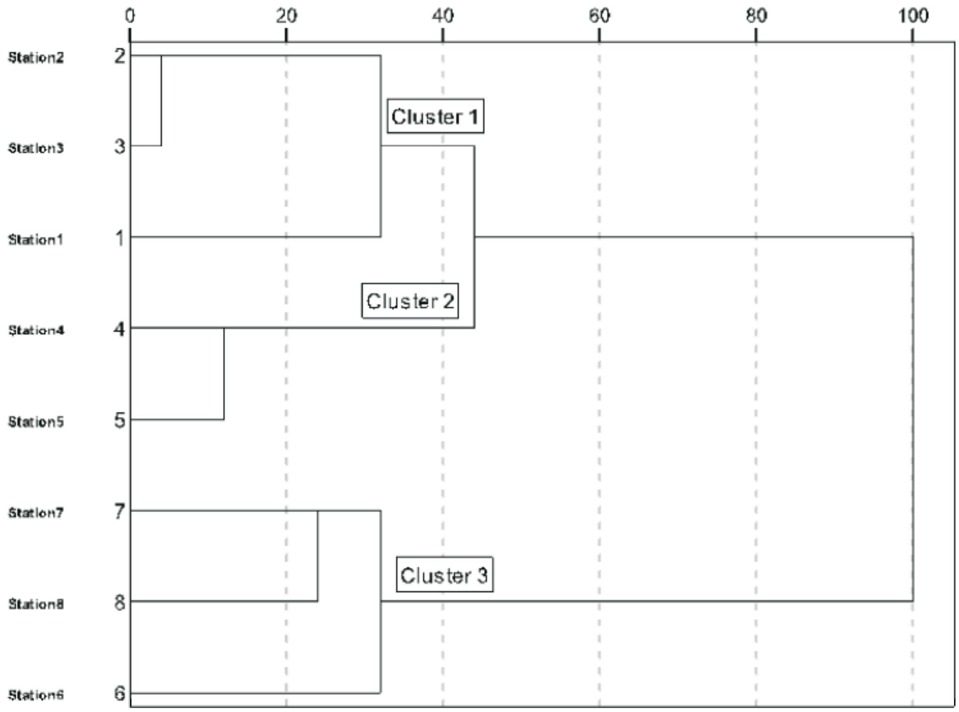

Fig. 2: Dendrogram showing clustering of sampling stations on Semenyih River

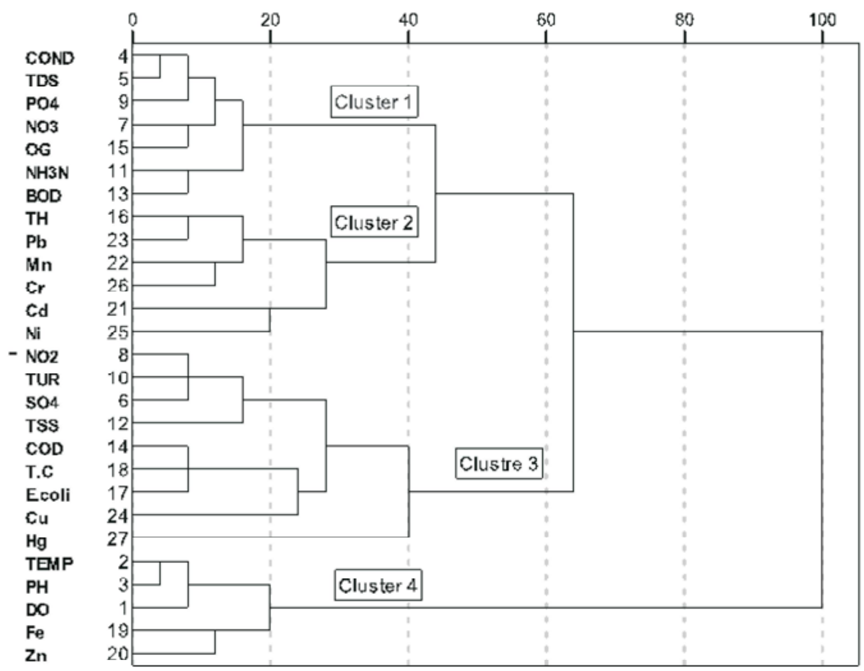

Fig. 3: Dendrogram showing clustering of the analyzed variables in water samples

Correspondingly, to confirm the associations among the variables in the total dataset, CA was carried out to classify the relationships among the analyzed variables and their possible sources [36]. CA yielded a dendrogram (Fig. 3) where all 27 variables were grouped into four statistically significant clusters at $(D_{link}/D_{max}) \times 100<40$. Cluster 1 comprised conductivity, TDS, PO_4^{3-}, NO_3^{-}, O&G, NH_3N and BOD which recognized as pollutants derived from anthropogenic sources like agricultural runoff and domestic wastewater. Cluster 2 consisted of TH, Pb, Mn, Cr, Cd and Ni. Principally, Cd and Ni are derived from anthropogenic sources such as discharges of mining activities, while total hardness mostly derived from lithogenic sources as well as Cr and Mn is derived from lithogenic and anthropogenic sources (hardness is not associate with pollutant, normally cause by natural rock/sediment in the area, its significant effect is on metal toxicity). Cluster 3 contained NO_2, turbidity, SO_4^{2-}, TSS, COD, TC, *E. coli*,Cu and Hg. This cluster is primarily affected by anthropogenic sources like discharges of livestock farms and random settlements. In addition, it is greatly impacted by lithogenic sources such as erosion and surface runoff. Cluster 4 encompassed temperature, pH, DO, Fe and Zn, they are influenced by anthropogenic and lithogenic sources such as discharges of mining, agricultural activity discharges as well as surface runoff due to Fe is found in the Earth's crust. Moreover, most of these parameters reflected positive loadings of the first factor in PCA. Eventually, CA represent a useful classification of the Semenyih River basin that could be used by authorities and decision makers to design a comprehensive future monitoring network with low cost [43, 44]. According to CA results, the number of monitoring stations might be reduced and selected only from Clusters 1, 2 and 3.

Principal Component Analysis/ Factor Analysis: Factor Analysis (FA) or Principal Component Analysis (PCA) was performed on the normalized datasets for the eight sampling stations to determine the factors influenced on each water sample and to assess the composition structure among them. Five factors were obtained for the study area with total variance 96.63%, whenEigenvalues >1. The factor loadingswere classified based on the loading values to strong (>0.75), moderate (75-0.50) and weak (0.50-0.30)[45]. In this study, the data set of 28 water quality variables encompasses five factors (Table 5).

Factor 1 represents 58.19% of the total variance, showing strong positive loadings on temperature, EC, TDS, SO_4^{2-}, No_3^-), NO_2, PO_4^{3-}, turbidity, NH_3N, BOD, COD, O&G, TH, *E. coli* and TC, moderate positive loading on TSS, Zn and Pb. In addition, it has strong negative loadings on DO. Temperature is most possibly associated with seasonal influences. Furthermore, conductivity, TDS, TSS and turbidity can be identified to originate from both nonpoint pollution sources and water treatment plants at station 8 [13, 32]. TSS, TDS and turbidity are commonly associated with discharge from urban areas involving the erosion of road edges due to surface runoff, clearing of lands and agricultural runoff [13, 46, 47]. In addition, the conversion of forest or agricultural land to urban areas has indeed caused large negative impacts on the ecosystem of Semenyih basin in the form of mud flood, landslide and river floods [13]. The presence of NO_3^-, NO_2, SO_4^{2-}) and PO_4^{3-} are due to agricultural runoff such as livestock waste and fertilizers [16], as well as PO_4^{3-} is an important constituent of detergentsthat discharge into the river by municipal sewage, industrial effluents and existing water treatment plants [48]. In addition, these contaminants may also derive from nitrogen decomposition and degradation processes [27]. Positive loadings on NH_3-N, BOD, COD and O&G attributed to the anthropogenicsources, particularly the organic pollutants from point sources such as the discharge of domestic wastewater, water treatment plants, livestock farms and untreated sewage of random settlement areas as well as industrial effluents [12]. Furthermore, the positive loadings of TH is ascribed to the lithologic sources (rocks and sediments) as well as the presence of *E. coli* and TC are due to discharge into the river via surface runoff of domestic wastewater and fertilizer (animal waste) used in agricultural activities. According to [49], the transport of *Colifor* is primarily through the soil or direct input by a warm blooded animal (e.g., livestock). Moreover, strong positive loadings on *E. coli* and TC are related to municipal wastes, animal husbandry and recreation activities. The moderate positive loadings on Zn and Pb were allegedly attributed to industrial and municipal activities [13]. Furthermore, the automobile exhausts are another source of Pb, where surface runoff carries the Pb deposits into the river [32].

Factor 2, represents 11.5% of the total variance and has strong positive loadings on Cu, moderate positive loadings on *E.coli*, Fe and Pb. The presence of Cu indicates pollution from anthropogenic sources due to the discharge of domestic sewage and industrial effluents that cause Cu pollution in receiving water. On the other hand, the moderate positive loadings of *E.coli* is strongly related to municipal sewage and wastewater treatment plants [50], whereas the presence of Fe and Pb basically represents the metal group originating from industrial effluents.

Factor 3, elucidates 11.14% of the total variance, showing strong positive loadings on pH and Mn, while having moderate positive loadings on Ni and Cr. The positive loading of pH attributed to dissolved minerals, domestic wastewater and acid rain, which can affect on the pH values of the river to change any which way.

Table 5: Factor loadings of the 27 variables on varimax rotation in Semenyih River

	Rotated Component matrix				
Variables	F 1	F 2	F 3	F 4	F 5
DO	-0.921	-0.251	-0.252	-0.097	0.079
DO	0.980	0.141	0.024	0.031	0.105
pH	-0.425	0.032	0.883	0.086	0.111
COND	0.984	0.130	0.073	0.091	0.005
TDS	0.974	0.131	0.107	0.132	0.022
SO_4	0.824	0.307	-0.080	-0.181	0.377
NO_3	0.961	-0.023	-0.182	-0.070	-0.143
NO_2	0.908	-0.034	-0.046	0.021	0.350
PO_4	0.893	-0.035	0.015	-0.031	0.266
TUR	0.930	-0.100	0.075	-0.122	0.322
NH_3-N	0.958	0.194	-0.040	0.057	0.170
TSS	0.614	-0.159	-0.148	-0.157	0.691
BOD	0.959	0.229	-0.090	0.025	0.027
COD	0.941	0.278	0.184	-0.046	0.031
OG	0.920	0.007	-0.267	0.267	-0.062
TH	0.846	0.135	0.479	0.114	-0.107
E. coli	0.814	0.560	0.122	-0.003	0.085
T.C	0.890	0.421	0.123	0.006	0.082
Fe	0.347	0.582	-0.084	0.625	-0.365
Zn	0.622	-0.536	0.108	0.323	0.371
Cd	-0.457	-0.416	-0.005	0.538	-0.313
Mn	0.365	0.000	0.898	-0.187	0.110
Pb	0.693	0.622	0.189	0.286	0.102
Cu	0.187	0.977	-0.006	-0.046	-0.029
Ni	-0.085	0.098	0.667	0.730	-0.032
Cr	0.423	-0.152	0.605	-0.355	-0.471
Hg	0.232	-0.057	-0.176	0.918	0.079
Variance (%)	58.198	11.497	11.143	9.694	6.104
Cumulative (%)	58.198	69.695	80.838	90.532	96.637

Table 6: Water Quality Index (WQI) at eight stations of Semenyih River

Station	DO SI	BOD SI	COD SI	AN SI	SS SI	pH SI	WQI	CLASS
1	86	98	88	96	88	99	92	I
2	81	95	78	73	77	95	83	II
3	81	92	62	68	65	96	78	II
4	76	89	52	58	58	96	71	III
5	72	89	46	56	64	96	70	III
6	65	86	25	50	63	96	64	III
7	69	86	28	46	43	95	61	III
8	54	84	16	46	56	98	58	III
Average	73	90	44	58	58	96	70	III

Mn is associated withanthropogenic sources byeffluents from mining and mineral activities andsewage sludge as well as Mn can be released to water by discharge from industrial facilities or as leachate from landfills and soil [42]. The presence of Ni attributed to anthropogenic activities such as mining, while Cr ascribed to anthropogenic sources such as industrial effluents derived from the production of corrosion inhibitors and pigments [15], which then becomes a pollutant of aquatic ecosystems and thus harmful to aquatic organisms [32].

Factor 4, accounts for 9.69% of the total variance and has a strong positive loading on Hg, moderate positive loadings on Fe, Ni and Cd. The positive loading of Hg is related to rocks, sediments, water and soils which naturally contain small but varying amounts of mercury. The moderate positive loading of Fe is associated with iron in rocks and clay soils and argillaceous limestone as well as industrial wastes and mine drainage. Both Ni and Cd are associated with high fluxes from industrial and urban wastes including the immense urban runoff. Ni and Cd also affected by using rechargeable batteries in the region [51].

Factor 5 stands for 6.1% of the total variance and has a moderate positive loading on TSS. The TSS with moderate positive loading can be resulted from soil erosion, surface runoff and mining activities in the river [27].

Water Quality Index (WQI): The water quality index (WQI) has been considered to give criteria for surface water classification based on the use of standard variables for water characterization and mathematical instrument to transform them into a single number which represents the water quality status [52]. In this study, the values of WQI of the eight stations in the Semenyih River were fluctuated from 58 to 92; the highest value of WQI was recorded at station 1 which was the lowest pollution, while the lowest value was recorded at station 8 which showed high levels of contamination (Table 6). The WQI of the Semenyih River was classified as Class I at station 1 which was situated in the upstream, while stations 2 and 3 categorized as Class II due to receive low contaminants compared to the other stations. Moreover, stations 4, 5, 6, 7 and 8 were classified under class III, because these stations receive several pollutants from cleaning and industrial effluents, road runoff, animal and human wastewater, discharge of water treatment plant and septic system as well as agricultural activities particularly covered agriculture that affects negatively on the water quality of the river from station 4 to 8, therefore they recorded higher levels of pollution. Overall, the WQI of the Semenyih River was 70; hence it was classified as class III, which represents that the river is slightly polluted [19]. However, the river water may be required extensive treatment before using for domestic purposes.

CONCLUSION

In this study, multivariate statistical techniques and water quality index were used to investigate the water quality of the Semenyih River. Cluster analysis categorized the eight sampling stations into three clusters based on the similarity of water quality characteristics and grouped 27 variables analyzed to three clusters to identify the relationship among the variables and their possible sources. Based on obtained information, optimal sampling strategy can be designed, which could reduce the number of sampling stations and related costs. Furthermore, this analysis permitted the classification of three various regions in the river, with various water quality. Principle component analysis identifies the sources responsible for variations in river water quality. Five factors generated from the factor analysis point to that the variables responsible for deterioration of water quality are largely attributed to anthropogenic activities associated with urbanization, industrialization, agriculture and mining activities. Therefore, this study demonstrates that the multivariate statistical techniques are valuable for analysis and interpretation of data sets to evaluate water quality and identify contamination sources as well as understanding the variations in water quality for efficient river water quality management. Eventually, WQI was classified the Semenyih River as clean (Class I) at station 1, slightly polluted (Class II) at stations 2 and 3 and as moderately polluted (Class III) at stations 4-8; in general, however, the river falls into class III and thus is required extensive treatment before using for domestic purposes.

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Persian Abstract

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چکیده

در این تحقیق، بررسی و تعیین کیفیت آب و منبع آلودگی رودخانه سمنیه با استفاده از روش‌های آماری و شاخص کیفیت آب (WQI) صورت گرفته است دما، pH، اکسیژن محلول (DO)، هدایت، کل مواد جامد محلول (TDS)، سولفات (SO_4^{-2})، نیترات (NO_3)، نیتریت (NO_2)، فسفر (PO_4^{-3})، کدورت، نیتروژن آمونیاک (NH_3-N)، کل مواد جامد معلق (TSS)، اکسیژن مورد نیاز شیمیایی (COD)، اکسیژن مورد نیاز بیولوژیکی (BOD)، سختی کل (TH)، روغن و گریس (G & O)، اشریشیا کلی و کلی فرم کل (TC) به عنوان متغیر کیفیت آب؛ کادمیم، مس، نیکل، روی، آهن، سرب، منگنز، کروم و جیوه به عنوان متغیرهای فلزات سنگین در آب، در طی سال ۲۰۱۲ از ۸ ایستگاه در امتداد رودخانه سمنیه، نمونه برداری و تجزیه و تحلیل شده است. تجزیه و تحلیل خوشه ای ۸ ایستگاه بر اساس شباهت در مشخصه های کیفیت آب به سه گروه تقسیم شده و به منظور تعیین ارتباط بین متغیرها و منابع احتمالی آنها ۲۷ متغیر در چهار گروه مورد تجزیه و تحلیل قرار گرفته است. به علاوه شاخص کیفیت آب رودخانه را به تمیز (دسته ۱) در ایستگاه ۱، کاملا آلوده (دسته ۲) در ایستگاه‌های ۲ و ۳، و آلودگی متوسط (دسته ۳) در ایستگاه‌های ۴ تا ۸ تقسیم گردید. البته رودخانه در انتها به گروه ۳ منتهی می‌شود که نیاز به تصفیه کامل برای استفاده‌های شهری را دارد. این مطالعات لزوم استفاده از روش‌های آماری چند متغیره و شاخص‌های کیفیت آب برای تفسیر بهتر از داده‌های پیچیده جهت آنالیز متغیرهای کیفیت آب را مشخص می نماید.