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RESEARCH ARTICLE

Seasonal variations of water quality and heavy metals in two ex-mining lake using chemometric assessment approach

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Abstract

Industries involving chemical and biological substances have become major economic growth in Malaysia. Mining contribute a lot of benefits such as employment and monetary profit but there are many associated environmental hazards as well. The purpose of this study is to conduct a preliminary assessment on water quality and heavy metals contents at Puteri Lake and Puchong Lake in Malaysia for better perspective of the emerging issues. Principal Component Analysis (PCA) was conducted to analyze the seasonal variation of water quality and heavy metal contents. Based on the PCA results, most of the significant values of variation Varimax Factor (VF) are evidence that several parameters were affected by the temporal variation especially Ammonia Nitrogen (AN) and Total Phosphorus (TP). Dissolved Oxygen (0.8385, 0.9674) and Conductivity (0.9583, 0.8894) also showed significant variation in both lakes, Puteri and Puchong. Heavy metals content analysis at Puteri and Puchong Lake indicates that both lakes had different significant metal elements such as Fe, Zn, Na, Ni and Cu for Puteri Lake with percentage variation of 55.6 percent and As, Pb and Cd for Puchong Lake at 36.1 percent due to the different land use characteristic and history of mining. Water quality and heavy metal variations are due to anthropogenic (mining, construction and domestic waste) and natural processes (erosion, runoff and geological area) of the study areas. This environmental tool provided a more objective interpretation of water pollution status and sources. Therefore a lot of research needs to be carried out to assess the pollution impact of the area on the environment and for rehabilitation and tourism development of the study areas.

Keywords: Physico-chemical, lake, mining, water quality, principal component analysis, heavy metal.

INTRODUCTION

Historically, mining is one of the oldest industries that have been documented in the world. Since a century ago, mankind have been benefited from the riches of the earth (Dubiński, 2013). Natural resources have been mined and used by man especially during the industrial revolution; manufacturing has increase the demand for natural resources such as tin, iron and coal (Hudson, 2014).

Malaysia is one of the countries rich in natural resources (Haber and Menaldo, 2011). Tin mining was the leading mining industry in Malaysia especially in the 19th century. Mining has contributed a lot of socio-economic development to the communities in Malaysia (McMahon and Moreira, 2014). Iron ore mining also contributed to the mining industry as it is still operational in many mines all across Peninsular Malaysia and West Malaysia. Selangor, Perak, Kedah and Pahang have undergone mining industry development in decades that profit the government and private sectors (Iqbal, 2015). After the discovery of natural ore such as tin and iron in Perak, Selangor and Terengganu, many methods have been used. Panning and open cast method is being applied at the early stages of the mining industry in Malaysia. Other methods include lampanning and dredging (Balamurugan, 1991). It is estimated that there are about 210,000 hectares ex-mining land in the country and most of ot has been converted into useful land (Ashraf, 2010). According to JMG (2008), there are 4909.6 hectares ex-mining land in Selangor and the area under study still need rehabilitation into other purpose. Ex-mining ponds contributed significant freshwater resources amounting an area of more than 113,700 ha (Ahmad & Jones, 2013). Some ex-mining ponds such as Bestari Jaya in Selangor have been identified as alternative water resources pond during drought events (JPBD Selangor, 2015). Other ex-mining ponds such as the Mines in Sg Besi Selangor, Titiwangsa Lake in Kuala Lumpur and Taiping Lake Garden in Perak have become important tourist and recreational destinations in the country.

Mining provide a lot of benefits such as employment and monetary profit but there are many associated environmental hazards as well. These may include threats to natural reserves due to landscape changes, damage to natural drainage, pollution and destruction and loss of natural habitats, arable lands and forest (Sun *et al.*, 2010, Ndace and Danladi, 2012). Iron ore mining in Liberia has resulted in surface and ground water pollution resulting from mine tailings and litters (Gleekia, 2016).

The purpose of this study is to assess the water quality and heavy metal contents of two ex-mining ponds namely Puteri Lake, Terengganu and Puchong Lake, Selangor. Additionally the aim is to

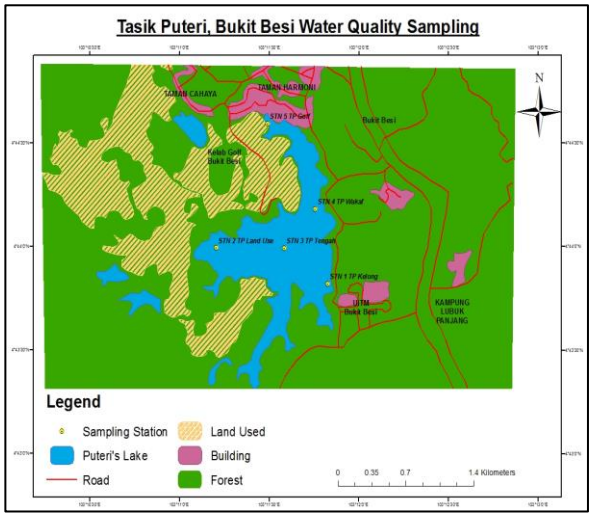
compare the water quality and heavy metal contents to the National Lake Water Quality Criteria and Standards, NLWQS (NAHRIM, 2015). This investigation of water physico- chemical parameters and heavy metals of the proposed sites will provide the baseline information of environmental conditions/degradation and pollution.

EXPERIMENTAL

Study area and sampling methods

Puteri Lake is situated about 3 km from Bandar Bukit Besi, which located at Dungun District within the range of 4° 44′ 30.0″N 4° 43′ 0″N lattitude to 103° 10′ 30″E 103° 13′ 0″E longitude (Fig 1). Puchong Lake is located at Sepang District within the range of 4° 44′ 30.0″N 4° 43′ 0″N latitude to 103° 10′ 30″E 103° 13′ 0″E longitude (figure 2). The surface areas of Puteri Lake and Puchong Lake are 1.31 and 5.88 km^2 respectively while their maximum depth are about 15 m and 45 m respectively.

a)



b)

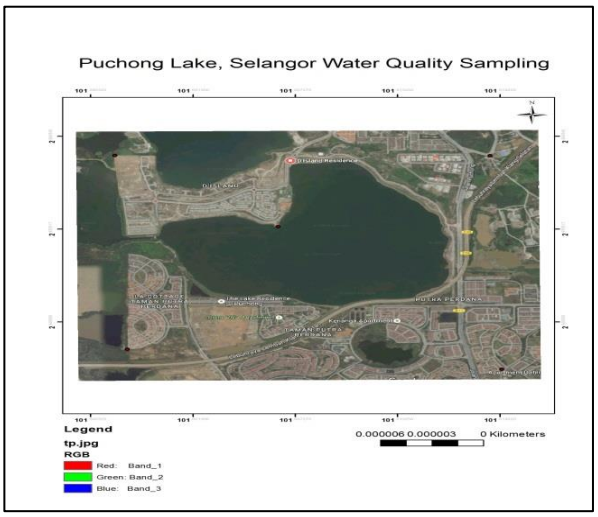


Fig. 1 (a) Puteri Lake (b) Puchong Lake.

For water quality study, there are five sampling stations for each Puteri Lake and Puchong Lake as indicated in figure 1 and 2. The water samples of both lakes were collected at 0.5m below water surface in both lakes. The water samples were preserved by two ml of nitric acid (70%) and stored in an icebox and transported to laboratory for analysis. The water samples were refrigerated at temperature below 4°C. Laboratory analysis was carried out for determination of chemical oxygen demand (COD), total phosphorus (TP), total suspended solids (TSS), turbidity and heavy metals using standard methods (APHA 1995) while in-situ measurements were performed for records of pH, dissolved oxygen (DO) and ammoniacal nitrogen (AN)(YSI Multiparameter). Biochemical oxygen demand (BOD) was analysed at field using BOD Check instrument.

Principal Component Analysis (PCA)

In this research, PCA is to extract a set of independent linear combination of the parameters of the study such as water quality parameters and heavy metals so as to capture the maximum amount of variability of a given dataset (Panigrahi *et al.* 2007). This analysis is based on eigenvalue criteria where value >1 is considered as significant and a new group of variables built based on the resemblance of the entire data set (Mitrea *et al.* 2013). The PCs generated by PCA are sometimes not readily interpreted. It is advisable to rotate the PCs by varimax rotation to obtain new groups of variables called varimax factors (VFs). The correlation between the VFs and the original variables is given by the factor loading; while the individual transformed observations are called factor scores (Vega *et al*., 1998). The VF coefficients having a correlation > 0.75 are considered 'strong', 0.74 – 0.50 are considered 'moderate' and 0.49 – 0.30 are considered 'weak' significant factor loadings (Liu *et al*., 2003). For this study, factor loading >0.75 both positive and negative will be considered (Juahir *et al*., 2011). Data were statistically calculated and analyzed using the Xlstat version 2014.

RESULTS AND DISCUSSION

Water quality analysis

Puteri Lake and Puchong Lake water quality and heavy metals contents were observed for seven months starting from May 2016 until November 2016. The mean values of the water quality are shown in Table 1. In Puteri Lake, the pH levels at the various sampling sites were below the NLWQS threshold limit of 6.5-8.5 while the mean concentration of TP was above the NLWQS threshold limit of 0.01 mg/L for primary contact recreation. In Puchong Lake, BOD, COD and TP concentrations exceeded the threshold limits of the NLWQS indicating pollution by domestic waste from the nearby urbanised areas. High BOD and COD concentrations have been reported in other ex-mining lake located in urban areas such as Aman Lake (Sharip *et al*., 2014).

Table 1 Mean values of water quality in Puteri and Puchong Lake.

Parameter	Unit	Puteri Lake	Puchong Lake
		mean±SD	mean±SD
temperature	°C	30.77±1.79	30.55±0.66
pH		3.0±0.17*	7.24±1.79
conductivity	mS/cm	798.67±94.92	203.26±22.86
DO percent	%	83.15±8.76	123.26±28.46*
DO conc	mg/l	6.44±0.65	9.22±2.08*
salinity	%	0.34±0.03	0.08±0.01
s. solid	mg/l	0.06±0.06	6.01±1.75
turbidity	NTU	0.29±0.63	12.46±13.84
COD	mg/l	1.26±5.15	12.27±2.58*
BOD	mg/l	0.86±0.23	7.68±1.20*
AN	mg/l	0.04±0.11	0.04±0.06
T. Phosphorus	mg/l	2.22±6.72*	0.33±0.52*

* Non compliance to the NWQS 2015.

Principal Components Analysis (PCA) is used to explore the relationship between physico-chemical and water pollution..

Table 2 Bartlett's Sphericity Test.

Bartlett's sphericity test:	Puteri Lake WQI	Puchong Lake WQI	Puteri Lake Heavy Metals	Puchong Lake Heavy Metals
Chi-square (Observed value)	427.1731	433.104	353.7033	342.8471
Chi-square (Critical value)	85.9649	85.96491	41.3371	41.3371
DF	66	66	28	28
p-value	< 0.0001	< 0.0001	< 0.0001	< 0.0001
alpha	0.05	0.05	0.05	0.05

Bartlett's Sphericity Test (Table 2) and Kaiser-Meyer-Olkin (KMO) test were conducted using PCA to identify and ensure the observed data of water quality and heavy metals used in the study at Puteri Lake and Puchong Lake do not conflict with assumptions produced by PCA factor analysis (Azid *et al*., 2014). In this test, KMO measure of sampling adequacy or observed data and Bartlett's Sphericity also investigate the relationship between the variables used in this study (Hinton and Brownlow, 2004). KMO results obtained from both lake data and the Bartlett's Sphericity test (0.001, p <0.05) were significant and clear. PCA is carried out to provide reliable information of relationship between the variables of the observed parameter (Platon *et al*., 2015). Varimax rotation method was employed to maximize the coefficient of variance to the factor that would better explain the source of contamination in Puteri Lake and Puchong Lake.

Table 3 Puteri Lake's Water Quality PCA.

variables	VF1	VF2	VF3	VF4
Temperature	-0.6306	0.1572	0.3318	-0.0033
pH	0.2541	-0.9177	-0.1277	-0.0124
Conductivity	-0.0636	**0.9583**	-0.0817	-0.0227
DO percent	-0.3146	-0.1352	**0.8385**	-0.1008
DO conc	-0.2384	0.0372	**0.9194**	0.06
Salinity	**0.6381**	0.5955	-0.2422	0.113
S.solid	-0.122	0.527	0.5675	0.2611
Turbidity	**0.8475**	-0.0083	-0.4512	-0.0411
COD	-0.0578	0.0364	0.0236	**0.9622**
BOD	-0.7767	-0.0261	0.0798	0.2103
AN	**0.8652**	-0.3613	-0.0446	0.0618
T.Phosphorus	**0.9226**	-0.0866	-0.2412	0.0192
Eigenvalue	5.0926	2.5123	1.3215	1.0236
Variance	33.0728	21.4782	19.4389	8.9274
CV (%)	33.0728	54.551	73.9899	82.9173

According to the Kaiser one criterion rules, there are four Varimax factors (VF) extracted that represent the total variation of 82.9 percent at Puteri Lake according to Table 3. VF1 discussed the 33.1 percent of the total variance and was represented by salinity, turbidity, AN and TP. PCA was carried out to identify the temporal variation parameter variation time basis from May 2016 to November 2016, i.e. seven months.

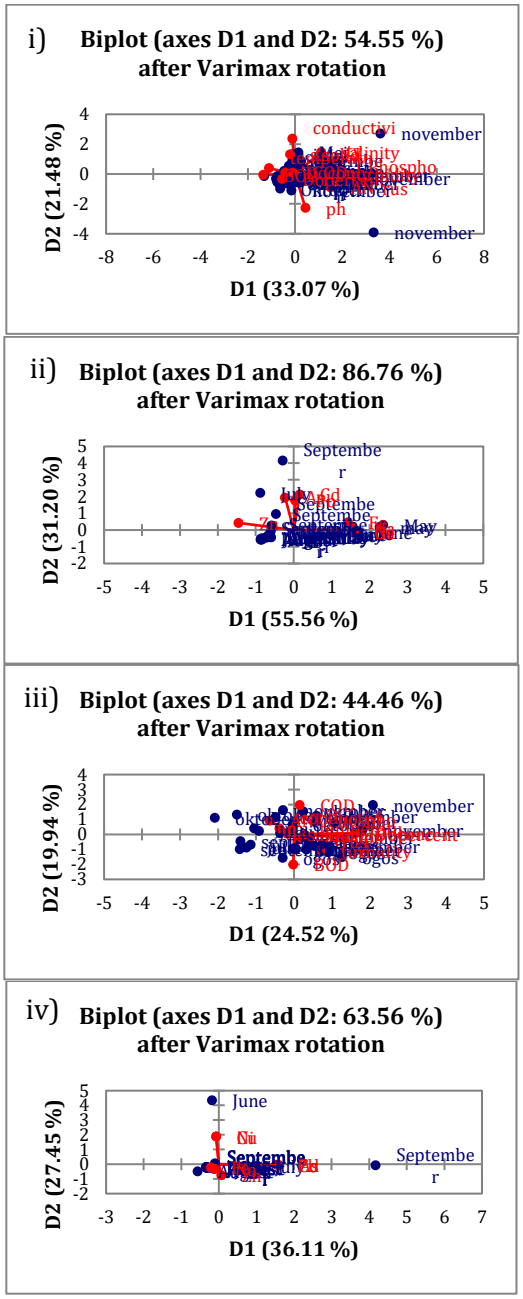


Fig. 2 Biplot of water quality and Heavy metals of Puteri Lake and Puchong Lake (i) WQ Puteri Lake (ii) Heavy metals Puteri Lake (iii) WQ Puchong Lake (iv) Heavy metals Puchong Lake.

Salinity shows the varimax factor significantly in the medium level 0.6381. Salinity levels in Puteri Lake were at significantly moderate due to changes in salinity levels in each month not showing much change except in November 2016, that exceeds the normal limits of the criteria. The area around Puteri Lake, Bukit Besi is a region rich in iron ore and minerals. The high salinity levels were consistent to conductivity levels in the water (Jeppesen *et al*., 2015; Gasim *et al*., 2015). The varimax factor of turbidity issued by PCA showed significant changes at 0.8475. Varimax factor also increased at the high level of significance during the monsoon season for example in November 2016. In addition, the AN and TP also showed a highly significant value of factor loading at 0.8652 and 0.9226. The varimax factor for both parameters discussed increased in November 2016. The surface run-off during the monsoon season causes an increase in the value of AN and TP at Puteri Lake (Huang *et al*., 2014). The average value of TP in Puteri Lake does not comply to the standard level specified in category A of the NLWQS for primary contact recreational activities. Puteri Lake is located near the UiTM Bukit Besi campus and the Bukit Besi village. There are also land use areas such as soil excavation nearby Puteri Lake area. Increasing level of surface run-off

can increase the TP level (Mayer, 2013). The swamp areas around Puteri Lake are also likely contributing to increased variance of AN and TP, respectively.

VF2 explains 21.5% of the total variance and has strong factor loading on conductivity. Varimax factor for conductivity was extracted at 0.9583 which has significantly high correlation with water pollution. Puteri Lake is an example of a former iron ore mine, which typically also has a high salinity level (Beukes *et al*., 2013). VF3 shows the total variance at 19.44 percent and the positive factor loading has been identified to have a significantly high correlation at 0.9194 for DO. Dissolved oxygen in Puteri Lake showed a significant correlation because the oxygen dissolved in the Puteri Lake water is likely due to the absence of aquatic life in the lake. The absence of aquatic life led to the minimum usage of DO and high surface areas of Puteri Lake also contribute to high oxygen dissolved in the lake water (Khan *et al*., 2012). The level of acidity and high salinity as a result of geological factors, such as in Puteri Lake, resulted in the absence of aquatic life in the lake (Leoni *et al*., 2014).

VF4 shows 8.93% of the total variance. Chemical Oxygen Demand (COD) shows a strong factor loading value at 0.9622. While the Biochemical Oxygen Demand (BOD), which is also an indicator of organic pollution is showing weak factor loading value at 0.2103. The concentration of BOD recorded in the water can be used to determine the level of pollution caused by microorganisms through biodegradation (Kazi *et al*., 2009). High value of varimax factor for COD may be due to a significant increase in July 2016 where the COD value increased dramatically in June at the TP2 near the area of land use (development in forest area) in Puteri Lake. The total value of COD and BOD are below the limit <1 mg/L. The source of contamination needs further investigation because there is no flow from the industrial area or residential area or nearby village that indicates the increased value of COD. DO levels in the water of Puteri Lake also showed a high value corresponds to a low BOD levels (Bhutiani *et al*., 2016). The absences of aquatic life as discussed previously is also factor for lower BOD value.

There are four independent Varimax Factors (VF) that have been extracted to explain the total variation in the water quality of Puchong Lake at 79.8 per cent. Table 4, VF1 indicates the variants at 24.5 per cent. The varimax factors analyzed in VF1 shows pH and dissolved oxygen showed significant values for pH (0.7890), DO percent (0.9694) and DO concentration (0.9707). Puchong Lake pH varied from neutral to alkaline. Based on site observation, this is likely due to inflow from residential areas drainage that drain into Puchong Lake such as Putra Perdana, Rasta Villa and Kenanga residential area which are likely to result in increased alkalinity of the lake water. Puchong Lake also shows significant value varimax factor for DO. Higher DO values in Puchong Lake are likely due to higher biological productivity in the lake and wind-induced mixing.

VF2 show 19.9 percent of the total variance. Varimax factor values showed significant values for chemical oxygen demand (COD). According to PCA Biplot shown in Figure 2, the COD show an increase in November 2016. For VF3, the value of factor loading for total phosphorus is 0.6544 which is moderately significant (Liu *et al*. 2003). Phosphorus is a nutrient required by plants for growth. Based on the analysis, the amount of phosphorus in Puchong Lake show non-significant changes. VF4 explained 18.1 percent of the total variance. The factor loading value of conductivity and salinity show at highly significant at 0.8894 and 0.8847. Conductivity and salinity are interrelated with each other because the sodium content in the water will affect the flow of conduction. Puchong Lake is located in an area surrounded by urban and industrial activity. Being a former tin mine, Puchong Lake also exhibits high content of minerals such as nickel, copper and cadmium.

Table 4 Puchong Lake's water quality PCA.

variables	VF1	VF2	VF3	VF4
Temperature	0.0814	-0.1663	-0.872	-0.0712
pH	**0.789**	-0.0924	0.4088	-0.2629
Conductivity	-0.2275	0.1917	0.0344	**0.8894**
DO percent	**0.9694**	0.0231	-0.104	-0.126
DO conc	**0.9707**	0.0388	-0.0772	-0.1267
Salinity	-0.1071	0.0212	0.3654	**0.8847**
S.solid	0.1606	-0.0157	0.4579	-0.5764
Turbidity	0.4278	-0.5269	-0.1668	-0.3543
COD	0.0914	**0.9506**	0.0986	0.0742
BOD	-0.0104	-0.9602	-0.1005	-0.0312
AN	-0.3874	0.4424	-0.5448	0.1114
T.Phosphorus	-0.0324	0.1357	**0.6544**	0.1433
Eigenvalue	3.9413	2.4734	1.8415	1.3179
Variance	24.5213	19.942	17.1775	18.1427
CV (%)	24.5213	44.4634	61.6409	79.7836

Heavy metal analysis

Two Varimax Factors (VF) which can be presented independently for variation of heavy metals in Puteri Lake at 86.975 percent as shown in Table 5. VF1 discuss about the percentage of the variance of the 55.55 per cent. Strong factor loading can be seen in some types of metal element such as Iron (Fe) (0.8794), Sodium (Na) (0.9635), Nickel (Ni) (0.9769) and copper (Cu) (0.9819). Varimax factor is significant for Fe because Puteri Lake is a former iron ore mine and, according to the Ketengah (2012) the reserves of iron ore in Tasik Puteri are still at a high level. In addition, sodium also showed a high value factor loading likely due to the mineral content of the local area. In addition, water salinity of Puteri Lake also showed high levels of sodium. VF2 shows the total value of the variance at 31.2 percent. Factor loading value indicates lead (Pb), cadmium (Cd) and arsenic (As) were significant especially in May 2016. The content of lead and arsenic are high in the dry season in Dungun districts. The analysis also showed the levels of lead and arsenic were still under control and below the standard limits of NLWQS (NAHRIM, 2015) and human heath risks (Elom, 2012). Lead content were observed consistently in the water of Puteri Lake from May until September.

Table 5 Puchong Lake's water quality PCA.

Variables	VF1	VF2
Fe	**0.8794**	0.2157
Zn	-0.8918	0.1976
Na	**0.9635**	0.0607
Ni	**0.9769**	-0.0486
Cu	**0.9819**	-0.0487
Pb	0.0265	**0.8089**
Cd	0.0965	**0.9748**
As	-0.1372	**0.8931**
Eigenvalue	4.4449	2.4956
Variance	55.5554	31.2008
CV (%)	55.5554	86.7563

There are three Varimax factors (VF) which can be presented independently of the variation of heavy metals in Puchong Lake at 86.1 percent. In Table 6, VF1 indicates the percentage of the variance at 36.1 percent. The factor loading of Lead (Pb), Cadmium (Cd) and arsenic (As) show very high significant effects of heavy metal that exists in Puchong Lake water. The most significant factor varimax is for arsenic (As). The presence of arsenic in Puchong Lake likely resulted from the industrial area around Puchong Lake such as metal alloy industries and pesticides from residential area. VF2 also shows the percentage variance of 27.4 percent. Elements of heavy metals Ni and Cu indicate the varimax significant factor. The presence of copper in the water of Puchong Lake is most probably originated from the tin mining as the clay mineral waste from the mining contain high copper level (Pickering, 1986).

VF3 explains 22.5% of the total variance. Zinc shows the high significant value at 0.9071. Zinc element probably originated from lake sediment (Dhanakumar *et al*., 2013). It should be taken into account that sediment is a reservoir of heavy metals. As is known, the mining will generate sediment waste apart from the mineral ores such as clay minerals, which are waste products of mining (Pickup *et al*., 1983). Even so, the level of heavy metals in Puchong Lake is still below the level set by the Interim National Water Quality Standards (INWQS) as well as National Lake Water Quality Standards (NLWQS, NAHRIM 2015).

Table 6 Puchong Lake's Heavy metals PCA.

Variables	VF1	VF2	VF3
Fe	-0.1349	-0.1229	0.0799
Zn	0.0402	-0.4043	**0.9071**
Na	-0.0679	-0.1708	-0.9778
Ni	-0.0439	**0.996**	-0.0405
Cu	-0.0437	**0.9964**	-0.0349
Pb	**0.9578**	-0.0205	0.0487
Cd	**0.9801**	-0.0326	0.1036
As	**0.9914**	-0.0436	0.0268
Eigenvalue	3.0214	2.2391	1.6264
Variance	36.1115	27.4501	22.525
CV (%)	36.1115	63.5617	86.0867

CONCLUSION

In conclusion, the preliminary result obtained from this study suggested that the water quality and heavy metals variations are due to anthropogenic (mining, construction and domestic waste) and natural processes (erosion, runoff and geological area) of the study areas. The water quality of Puteri Lake at Bukit Besi shows that natural process affect environmental variables such as pH where the level is acidic and too low for recreational purpose. Treatment of pH levels in Puteri Lake water is needed to minimize and prevent health issues to the public. PCA rendered an important factors of significant parameters such as DO, COD, turbidity, AN and TP. All these significant parameters are linked to absences of aquatic life in the lake due to high acidity of water. Treatment of heavy metals is also recommended to ensure safe environment especially for recreational purpose. Control of domestic effluent into Puchong Lake is needed to prevent further deterioration of lake water quality. Parameter such as DO, COD and TP show significant effects. High reading of As and Pb also needed to be remedied to prevent health issues to the public as the lake also supply fresh water fish to the local market.

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