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Research paper

Spatial Variation and Possible Sources Assessment at Federal Territory of Kuala Lumpur Water Treatment Plan Using Chemometric Technique

H. M. Zolkipli[2], H. Juahir[2*], G. Adiana[2], N. Zainuddin[3], A.B.H.M. Maliki[1], S. Z. Mohamed[1,] W.N.W. A. Halim[1,] N. F. Sa'adon[1], N. S. Mohamed[1], N.A.A. Hashim[1]

[1]Faculty of Applied Social Sciences, Universiti Sultan Zainal Abidin, Terengganu, Malaysia
[2]East Coast Environmental Research Institute, Universiti Sultan Zainal Abidin, Terengganu, Malaysia
[3]Ministry of Health, Engineering Services Division Department, Putrajaya, Malaysia
**Corresponding author E-mail: hafizanj@gmail.com*

Abstract

This study aims to identify the possible sources in drinking water parameters heavy metal and organic parameters (HMOPs) and spatial variation between untreated water and treated water at Federal Territory of Kuala Lumpur water treatment plant. The indicator HMOPs in drinking water in Kuala Lumpur were selected as parameters to discriminate the possible source of water treatment plants (WTPs) pollutant. Chemometric technique such as principal component analysis (PCA) and discriminant analysis (DA) was identified based on the five years' availability data starting from 2012 to 2016. PCA were used to identify the most significant parameters which are high-lighted eleven strong factors loading of parameter respectively out of sixteen for PCs and classified as possible sources in WTPs. Contin-ue with DA analysis that is successful distinguish two categories region in WTP using the forward stepwise and backward stepwise with significant amount is 98.46%. From this study, we can conclude that this chemometric is the best technique of analysis to get a lot of information such as identify possible sources of pollutant and discriminant of two station sampling categories that will give novelty to Malaysian Ministry of Health (MOH) and collaboration agency in National Drinking Water Quality Surveillances Program (NDWQSP).

Keywords: *Drinking water quality; Water treatment plants; Heavy metals and organic parameter; Principle component analysis; Discriminant analysis*.

1. Introduction

Water quality has shown that quality parameters are best suited for drinking water. Everyone on this earth needs a clean drinking water to survive. The water process needs to be processed from raw water to clean to be used as drinking water. Drinking water should be clean and free from harmful microorganisms no aesthetic problems [1]. Drinking water quality that contains lots of hazardous elements needs to be treated beforehand so that it can be used as drinking water. The existing standards may vary tenfold from others. The quality of the water quality is based on the needs of humans. Each country has various treatment methods or methods for obtaining clean water [2]. In Malaysia, clean water is derived from rainwater. Downstream rain will flow into rivers, marshes, lakes, or dam created by humans. In addition, this water can also be extracted when wells are dug and there are springs in the hillside. Clean water quality is very important because clean water is able to avoid infection or illness to the human body [3].

Most developed countries, they will decide on how their standards are to be used in their own country [4]. In Korea found uranium chemistry and radiological risk analysis in drinking water obtained from the ground have found that uranium chemistry may not cause a risk of being taken if taken. The standards should be met according to guidelines made by the World Health Organization. While in China they have their own drinking, water drafted by the Ministry of Environmental Protection in 2002. Drinking water from various sources needs to be treated first to produce clean drinking water quality and is ideal for use for certain purposes. Water treatment is made to kill the organisms that can lead to illness as well as to dispose of the unpleasant taste, color and also the unpleasant smell.

Heavy metal is defined as pollutants and will affect the environment is by participation in biogeochemical cycles, bioaccumulation, high toxicity and biomagnification. The chemical elements naturally occurring in the environment are very small, so a variety of anthropogenic sources such as the oil industry, herbicides, combustion of fossil fuels, pesticides, chemical industry, industry plastic, fertilizer minerals and other bringing significant improvement in their focus [5-6].

Water pollution is a main problem in the global environment. This will require continued evaluation and review of water resources policies at all levels. Water pollution occurs due to the disposal of industrial waste and food waste into the river. The cause people get chronic and adverse effect towards human health. Among the chronic diseases associated with water pollution is a disease of the heart and kidneys that can be affected badly if always use contaminated water. This disease getting worse if people ignoring on water quality usage that the clean. In addition, other disease associated with water pollution is unhealthy blood circulation, lesions on the skin, vomiting, gastroenteritis and cholera, damage to the nervous system and so on [7]. As a result, effect of water pollution causes the death rate increasing if the problem is not addressed. Human should be emphasizing water quality used every day so that able can stay away from the dangerous disease. Therefore, all

mankind need water quality that is clean to get a clean bill of health and can doing daily routine smoothly [7].
Nowadays, water pollution is due to the alternation in physical, chemical and biological characteristics which is lead to harmful effect on human and aquatic biota. It is important for us to ensure the quality of the water [43]. Our drinking water are depending on the surface and ground water sources. We also need water to produce energy, to plant crops, to harvest fish, to run machinery, to carry out wastes, to improve landscape and many more. Many human activities and their products have potential in water pollution [8]. Present study uses DA and PCA analysis also known as multivariate statistical analysis or chemometric analysis [48, 50]. The uses of DA analysis are to know the difference between treated and untreated water. The PCA analysis is to know the possible sources of pollutant.

2. Methodology

2.1. Study area

The Federal Territory of Kuala Lumpur is the nation capital of Malaysia and forms the core of the nation's most populous urban region [9]. Kuala Lumpur is the largest city in Malaysia with population 1, 588, 750 and the longitude is 101o 41ˈ 15.04" E [10]. The geographical coordinates of this area are 30o, Wind NE at 3km/h, 70% Humidity [49]. The sampling was carried out at the Water Treatment Plant and intake for Raw in Kuala Lumpur. There are five treated point Water Treatment Plant and Raw Intake in Kuala Lumpur had been taken at the point raw untreated water and treated water at water treatment plant. Raw sampling station are Klang Gate or Gombak and intake Loji Bukit Nanas WTP and treated sampling area are Wangsa Maju, Kolam Air Bukit Weld, Kolam Air Utara and TPO Loji Bukit Nanas [11]. The location of WTPs in Kuala Lumpur are shown in Fig. 1.

Fig. 1: The location of water treatment plant and raw intake in Federal Territory of Kuala Lumpur

2.2. Data collection

Drinking water quality data was obtained from Malaysian Ministry of Health at the selected sampling stations for this study which are raw (R) and treatment plant outlet (TPO). All drinking water quality was identified based on the availability data starting from 2012 to 2016. Five years data was recorded based on group parameters with each group sampling frequency (every three months). A total of 16 samples were taken to study water quality in Kuala Lumpur Federal Territory area. The 16 water quality variables used in this study were categorized as heavy metal and organic parameters (HMOP). There are 16 heavy metal parameters, namely, mercury (Hg) (mg/l), cadmium (Cd) (mg/l), arsenic (As)(mg/l), chromium (Cr) (mg/l), copper (Cu) (mg/l), zinc (Zn) (mg/l), sodium (Na) (mg/l), sulphate (SO4) (mg/l), selenium (Se) (mg/l), argenturn (Ag) (mg/l), magnesium (Mg) (mg/l), bromoform (CHBr3) (mg/l), dibromochloromethane (CHBr2CI) (mg/l), plumbum (Pb) (mg/l), bromodichloromethane (CHBr2Cl) (mg/l) and chloroform (CHCI3 (mg/l).

2.3. Pre-treatment data

Using chemometric techniques in carrying out analysis data needs to clean up first to be perform data observations. If the data show in error and data containing the alphabet and it is a data symbol that needs to be lost replaced is empty data. It is obligatory because the analysis of chemometric techniques have been performed after pre-treatment data. HMOPs group with 53.03% of missing data from the overall observation data (1,056). The nearest neighbour approach discussed the analysis of spatial point patterns and field experiment analysis. To test whether the location is to observed or not, can be determined by the awareness of specific space distance from point to nearest neighbour, or may use relevant quantities. By using the nearest neighbour method, the researchers can identify lost data due to the large number of data, this method will provide information about missing data by using certain symbols [34]. The equation applied in this method is shown in (1):

$$Y = Y1 \text{ if } x \leq x1 + (x2 - x1)/2 \quad (1)$$

where y is the important, x is time point of the interpolant, y1 and x1 are the coordinates of the starting [35].

2.4. Principle component analysis (PCA)

Reducing the dimensionality of the data sets with used the PCA analysis allowed the identification of an association between variables [12]. PCA are involving three major steps firstly to produce new variables, the adjustment of dimensions need has equal weights in the analysis by auto scaling the data. In other words, the mean is equal to zero and the standard deviation is equal to the unit. Secondly is to identifying the eigenvalues and their corresponding eigenvectors by calculation of the covariance matrix and thirdly for a small proportion of the variation in data sets, the elimination of components that account only [13, 22].
The PCA techniques extract the eigenvalues and eigenvectors of the covariance matrix of original variables and provides a clear view about the relationship of a big number of variables with sufficient details [14, 25, 51]. Principle components provide facts on the significant parameters that describe the total data set affording data reduction without losing the original sources [15]. The principle components can be expressed in (2):

$$z_{ij} = a_{i1}x_{ij} + a_{i2}x_{2j} + \ldots + a_{im}x_{mj} \quad (2)$$

where z is the component score, a is the component loading, x is the measured value of the variable, i is the component number, j is the sample number, and m is the total number of variables.
They will be rotated by varimax rotation if the principle components generated by PCA cannot be analysed. Varimax rotations are considered significant if applied to the principle components with eigenvalues more than one. Varimax rotation generates a new group of variables called varimax factors (VFs). The varimax rotations achieve the same numbers of varimax factors as the variables in in line with general features and may consist unobservable, hypothetical, and latent variables [16].
Present study, only varimax factors with values more than 0.70 will be interpreted. Variables with loadings greater than 0.7 are considered strong, less than 0.7 to 0.5 are moderate and lower than 0.5 are considered a weak variable [17- 19].

3.5. Discriminant Analysis (DA)

On the basic application, DA is extensively used to discriminate of a set of clustered data or observation into several pre-defined classes. This method enables the grouping or clustering of the observations based on input variables or the variables known as predictors. This technique construct set of a linear function of the predictors, known as the discriminant functions (DF) and the equation is as follow:

$$L = b_1X_1 + b_2X_2 + \ldots\ldots\ldots\ldots + b_nX_n + C \quad (3)$$

where, b is the discriminant coefficient, x is the input variables or predictors and C is a constant. Further, Discriminant analysis (DA) functionality aids in determining the best cluster. The applied DA on the original dataset offers similar discriminant ability towards the original dataset with or without standardization in constructing the discriminant factor (DF) based on in (4) [20]:

$$f(G_i) = k_{i+} \sum_{j=1}^{n} wij.pij \quad (4)$$

where i denotes the number of groups (G), ki is the constant coherent to each group, n is the number of parameter used to classify a set of data into given group and wij is the weight coefficient assigned by discriminant factor (DF) to a given parameter (pij) [21- 25]. In this study, DA was used to study the spatial variation between two station categories (R and TPO) for heavy metal and organic parameters in drinking water. The purpose of PCA and DA using XLSTAT in this study is to investigate heavy metals and organic parameters (HMOPs) in drinking water in KL. These multivariate methods predict the origin of pollutants from water sources in order to curb problems originating from WTPs.

3. Results and discussion

3.1. Possible sources pollutant

PCA were used for forming new variable which are linier composite of the original variables and used in normal data to compare pattern of composition between the analyzed water samples and to identify the pollutant sources that influenced in drinking water quality. Rotation exist in the PCA will produce a new set of factors, involving primarily a subset of the original variable divide into to group. Eigenvalue highest is most important. Fig. 2 in the scree plot show the eigenvalue greater than 1.

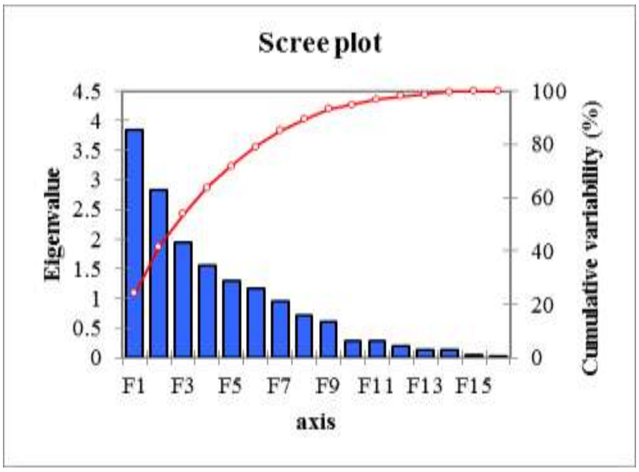

Fig. 2: Scree plot of eigenvalue greater than one (> 1) assign by PCA

PCA for the entire data set allowed forming six PCs with six eigenvalues greater than 1. After get this eigenvalue, run the data again to get a varimax rotation which is applied on the PCs with eigenvalue more than 1 are consider significant in order to obtain new groups of variables called varimax factors (VFs). Table 1 explained that 79% of the total cumulative in the water quality data set. Only six of significant parameter respectively out of sixteen. The original variable in the bottom of the PCs are called loading. The principle component analysis showed that the eigenvalue of the two-main principle up to 33.78% of the total variance (D1 19.61; D2 14.17) for total observation. PCA was performed on the raw data set comprising all the 16 water quality parameters with 1056 observation to identify drinking water quality standard source in water treatment plant and raw intake in Federal Territory of Kuala Lumpur.

Table 1: Eigenvalue from Principle Component Analysis shows variability and cumulative

Principle Component Analysis	Eigenvalues					
	D1	D2	D3	D4	D5	D6
Eigenvalue	3.8516	2.8347	1.9452	1.5542	1.2955	1.1619
Variability (%)	19.6078	14.1681	13.9978	10.6247	11.8436	8.7777
Cumulative %	19.6078	33.7759	47.7737	58.3984	70.2420	79.0197

The table 2 show Factors loading for D1 have four strong parameters (three strong positive and one strong negative) and one moderate strong factor loadings. First is arsenic (As) -0.732 which is strong negative factor loading. Arsenic may be found in water which has flowed through arsenic rich rocks. Arsenic is naturally occurring element present in the environment in both organic and inorganic forms. Arsenic is widely distributed throughout the earth's crust. Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks [26-27]. Secondly is sulphate (So4) 0.877 which is strong positive factor loading.

Sulphate are combination of Sulphur and oxygen and they are a part of naturally occurring minerals in some soil and rock formations that contain groundwater. The mineral dissolves over time and is released into groundwater [28, 44]. Another factor is Magnesium (Mg) 0.800 which is strong positive factor loading. Magnesium as a mineral in drinking water expose during treatment process which is nutrient (Mg) that insert into the water next to fluoride [29]. Next is Bromoform (CHBr3) 0.731 which is strong positive factor loading. Locally, significant amounts of bromoform enter the environment formed as disinfection by-products known as trihalomethanes when chlorine is added to drinking water to kill bacteria [30].

Factors loading for D2 have 2 strong parameters and both are 2 strong positive factors loading. First is Mercury (Hg) 0.868 which is strong positive. Mercury which is common form in drinking water is inorganic mercury. It is natural and anthropogenic sources. Natural sources from soil with rich of mercury, volcanic explosion and plantation fires and anthropogenic sources are fossil fuels, battery industries, gold mining and more [31, 46]. Next is Chromium (Cr) 0.964 which is strong positive factor loading. Chromium is the 22nd most abundant element in Earth's crust with an average concentration of 100 ppm. [32]. Chromium compounds are found in the environment from the erosion of chromium-containing rocks and can be reconstructed by volcanic eruptions [33, 52].

That variable drinking water met the factor 0.70 loading is strong. The variable in D3 Se and CHBrCl2. This contaminant is then classified as a major pollutant contribution at the selected monitoring stations at the Federal Territory of Kuala Lumpur WTPs. The D3 principle components are Selenium (Se, 0.9294) and Bromodichloromethane (CHBrCl2, 0.9218) are very strong positive factors that load more than the maximum of 0.70. Se is a naturally occurring metal element of plant food in soil or taken from groundwater [36, 45]. While, by-product of the chlorination of drinking water was exposure CHBrCl2 [37, 42, 47].

Factor loadings of selected heavy metal and organic parameters in your water shows D5 has two positive strong value which is Pb

0.869 whilst Cu is 0. 946. Lead can be found in water, soil, and plants. The most convenient source of lead found was from the lead that spread in the ground and water [38]. While, Cu is a natural concentration in drinking water and become high concentration through the cooper pipes. It also depending on such assets as hardness, the technical environments of the plumbing system, pH, anion concentrations, temperature and oxygen concentration [39-40].

In addition, the value of parameter D6 Cd shows strong values which this indicates 0.889. strong. The metal cadmium is a metal found in the earth's crust that is 0, 13 µg/g and colored white, silver and software but this does not go on the metals found in the form of the range. In addition, this Cd was contaminated from pollution in the water heaters, taps, water coolers and zinc of galvanized pipes [41].

Table 2: Factor loadings of selected heavy metal and organic parameters in drinking water

	D1	D2	D3	D4	D5	D6
Hg	-0.077	0.868	0.140	-0.075	0.140	0.153
Cd	0.034	0.078	-0.066	-0.099	0.024	0.889
As	-0.732	0.175	-0.148	0.485	0.139	-0.018
Lead	-0.059	0.356	-0.008	-0.048	0.869	-0.020
Cr	0.130	0.963	0.071	-0.006	0.120	0.017
Cu	-0.058	-0.025	0.025	0.048	0.946	0.032
Zn	-0.022	0.032	0.399	0.676	0.254	0.187
Na	0.275	-0.126	-0.328	0.535	-0.024	-0.263
SO4	0.877	-0.082	0.171	0.161	0.033	0.073
Se	-0.016	0.204	0.929	-0.034	0.044	-0.044
Ag	-0.007	0.279	-0.017	-0.655	0.273	0.316
Mg	0.800	0.196	-0.146	-0.031	-0.144	-0.084
$CHCl_3$	0.480	0.153	0.268	0.446	-0.070	0.537
$CHBr_3$	0.713	0.217	0.292	0.130	0.029	0.248
$CHBr_2Cl$	0.528	0.411	0.021	0.124	-0.145	-0.139
$CHBrCl_2$	0.262	-0.018	0.922	0.115	-0.033	0.0302

3.2 Spatial variation of UTW and TW

Table 3 shows the confusion matrix summarizes the reclassification of the observations, which is the ratio of the number of observations that have been well classified over the total number of observations. It is here equal to 96.92%. The accuracy of spatial classification using standard DA mode were 96.92% is a very convincing value. So, further analysis of DA using forward stepwise and backward stepwise mode will be carried out in order to identify the most significant drinking water quality parameters which plays an important role in discriminating the variation of HMOPs in Kuala Lumpur.

Using forward stepwise discriminant analysis, Bromoform, and SO4 were found to be the significant variables with the accuracy of spatial classification were 98.46% and using backward stepwise discriminant analysis As, Zn, Mg, Chloroform were found to be the significant variables with the accuracy of spatial classification were 98.46%. They have 5 parameters which is < 0.05 and this result shows that 5 drinking water quality parameters which gave high variations (the most significant) by forward stepwise and backward stepwise mode were then used for further analysis. In the spatial pattern recognition analysis, the result showed that the DA successful in discriminating drinking water quality samples according DA for spatial variation of HMOPs in Federal Territory of Kuala Lumpur and water treatment plant.

Table 3: Classification matrix by DA for spatial variation of heavy metal and organic parameters in Kuala Lumpur

Sampling Category	Categories Assigned by DA		
	R	TPO	% Correct
Standard DA mode (8 variables)			
R	28	2	93.33%
TPO	0	35	100.00%
Total	28	37	96.92%
Forward stepwise mode (2 variables)			
R	28	2	93.33%
TPO	0	35	100.00%
Total	28	37	96.92%
Backward stepwise mode (5 variables)			
R	29	1	96.67%
TPO	0	35	100.00%
Total	29	36	98.46%

4. Conclusion

The significant of possible source of pollutant contributes to changes in the quality of drinking water in water treatment plant was assigned by PCA are including Hg, As, Pb, Cu, SO4, Se, Mg, CHBr3, and CHBrCl2. PCA technique was successful proved that on half of HMOPs on drinking water was reduced (sixteen to nine). Together with another chemometric technique that is also effective to differentiate pollutant from two categories of sampling station that is UTW and TW in HMOPs parameters. DA has identified seven parameters which is <0.05 gives high variation (the most significant) using the forward stepwise and backward stepwise with the percent of variation is 98.46%. Therefore, both of them give the innovation and idea to the MMOH for improve the future sampling task in term of reduce the cost, time and management tasking also one of the suggestion approach of chemometric analysis to get a lot of information that was generates from a million of data set and solve the problem faced.

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