Assessment of Water Quality in the Temenggor Forest Reserve Based on Physicochemical Data and Elemental Content

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The analysis of elemental concentrations as well as physiochemical parameters of water samples can determine the quality of a water system. The Temenggor area is known as one of the largest forest reserves in Peninsular Malaysia. Consequently, the Sustainability Development Goals have a significant effect on this area. This study aims to measure the basic physicochemical parameters as well as the concentrations of selected elements in water samples from this area. Measurements of basic physicochemical parameters such as pH, temperature, pressure, dissolved oxygen (DO), electrical conductivity (C), total dissolved solids (TDS), salinity, and oxidationreduction potential (ORP) of freshwater samples from rivers such as Sungai Gadong Dalam, Sungai Gadong Luar and Sungai Kelam, as well as Tasik Temenggor, were done in situ using a YSI multiparameter probe meter. The concentrations of ten elements, As, Cd, Cr, Cu, Ni, Pb, Se, Zn, U and Th were measured using an Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer. The average concentrations of all elements, except for Zn, were found to be higher than the threshold levels specified in the National Water Quality Standards for Malaysia (NWQSM). The correlation between the physicochemical data and elemental concentrations were evaluated using SPSS IBM 22 software. Seven strong correlation pairs were observed: temperature-pressure, SPC-conductivity, SPC-TDS, SPC-salinity, conductivity-TDS, conductivity-salinity, and TDS-salinity. Meanwhile, strong correlations were found between the concentrations of certain pairs of elements: As-Cr, As-Se, Cd-Cr, Cd-Zn, Cr-Pb, Cr-Zn and Pb-Zn. Cluster analysis grouped the 15 sampling locations into two clusters, Cluster 1 (low elemental concentrations) and Cluster 2 (high elemental concentrations). The heavy metal pollution index (HPI) and metal index (MI) values were also calculated to assess the contamination levels of water samples in this area. Most of the areas exhibited HPI values above 100, indicating heavy metal pollution.

Key words: Heavy metals; water Sample; Energy Dispersive X-Ray Fluorescence; metal index

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Sustainable Development Goals (SDGs) are part of a global initiative to end poverty and protect our planet, which focuses on economic, social, and environmental sustainability. In 2009, the New Economic Model was launched to strengthen the old development approach that focused on high income, inclusivity, and sustainability [1]. The sustainability of the natural forest and water ecosystems in Malaysia is one of these sustainable development goals (SDGs). Environmental pollution may be due to natural or anthropogenic input from various human activities [2]. Atmospheric processes transfer metals into soil, water and sediment wherein their biogeochemical cycles and atmospheric precipitation may create an exotoxin effect in the receiving water and soil environment [3]. Furthermore, tiny particles of heavy metal pollutants are transported in the

atmosphere and can be carried over long distances, possibly resulting in trans-border contamination. The effect of weathering will facilitate the transport of elements vertically into the soil, or into the river where it settles as sediment which is taken up by plants and aquatic animals. The Temenggor reserve forest in Perak state has the potential to become a commercialized tourism spot in the future. Located in the Hulu Perak District, it borders Thailand in the north, and the East-West Highway and the state of Kelantan in the east. Ecotourism is the main attraction of the Royal Belum Rainforest. Therefore, it is crucial to monitor this area to ensuring the sustainability of the protected areas. In addition, its location near the border with Thailand might contribute to the accumulation of metal contamination in the Temenggor forest reserve area through atmospheric transfer.

Energy Dispersive X-ray Fluorescence (EDXRF) is an XRF spectroscopy technique that has been used as an analytical tool for a very long time [4]. XRF is normally used to determine the concentrations of different elements in a sample, and has advantages such as good sensitivity and non-destructiveness [5,6]. EDXRF is a versatile method in environmental research, and is used to determine multi-element concentrations in dust, soils, sediments and plants [7, 8, 9]. Oyedotun reported that EDXRF has great accuracy and which makes this precision technique a geochemical method of choice in mineralogy and the investigation of the chemical composition of earth materials [9]. Since water is necessary for all life, the occurrence of pollutants in water due to physical or chemical contamination must be considered. systematic environmental Thus. monitoring should include not only water quality parameters but also the concentrations of other elements including radionuclides to ensure the sustainability of protected areas. Radionuclides (U and Th) are naturally present in environments and can also be produced by human activities. However, their contribution is less if there are no major sources of radionuclides, such as factories and heavy industries, nearby. This study aimed to compile data on the selected elemental concentrations as well as the basic parameters of surface water in Temenggor lake. A thorough analysis using chemometric techniques will provide a clear picture of the quality of the lake water. To the best of our knowledge, currently, no data on radionuclides (uranium and thorium) has been reported in this study area. The results of this study could be used as initial data for the monitoring and sustainability of the Temenggor area.

MATERIALS AND METHODS

Sampling Location

Belum-Temenggor Forest Reserve is located in Hulu Perak, in the state of Perak, and crosses into Southern Thailand. It is the last and largest contiguous block of natural forest in Peninsular Malaysia, covering an area of over 300,000 hectares [10]. Bird watching, Rafflessia tracking and fishing are some of the activities in the Temenggor forest reserve that attracts local and overseas tourists and researchers. Temenggor lake is the second largest lake in Peninsular Malaysia, and is made up of several rivers such as Sugai Perak, Sungai Gadong Dalam, Sungai Gadong Luar and Sungai Kelam. Temenggor Dam, a hydroelectric dam operated by Tenaga Nasional Berhad (TNB) was completed in 1978.

Sample Collection

Water samples were collected from the rivers and Temenggor lake based on their accessibility. The surface water samples were collected from 15 locations using a GO-Flo vertical water sampler. The exact locations of the sampling points were marked using Global Positioning System (GPS) coordinates as shown in Table 1 and Figure 1. About 10 mL of water were collected at each location and stored in labelled plastic bottles. In-situ basic parameters including pH, temperature, pressure, dissolved oxygen (DO), electrical conductivity (C), total dissolved solids (TDS), salinity, and oxidation-reduction potential (ORP) were measured at the sampling sites, using the YSI multi-parameter probe meter. The samples were acidified to pH 2 with 6 M nitric acid and filtered using 0.45 µm cellulose membrane nitrate filters.



Figure 1. Sampling locations surrounding Temenggor Lake (Source: Google Map, 2022)

Chemical Analysis

The concentrations of As, Cd, Cr, Cu, Ni, Pb, Se, Zn, Ca, K, U, and Th were measured using the Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer. Approximately 5 mL of a filtered water sample was placed in an EDXRF sample cup and covered with mylar film. All samples were measured in triplicate using EPSILON 3XL EDXRF machines. A range of standard solutions (Perkin Elmer Pure Plus Multi-Element Calibration Standard 3) was also measured. Similar standards were analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICPMS) in the Agensi Nuklear Malaysia laboratory to compare the accuracy and precision of the EDXRF method with the established ICPMS method.

Chemometric Analysis

In this study, cluster analysis (CA) was used to group the locations based on their elemental concentrations. Cluster analysis is a set of multivariate techniques which primarily classifies variables or cases into clusters with high homogeneity levels within a class and high heterogeneity levels between classes [11,12]. CA was used to link sampling points in the configuration of a tree with different branches (dendrogram) which provides a visual summary of the clustering process, presenting a picture of the groups and their proximity. Branches that have linkages close to each other indicate a stronger relationship between the variables, i.e., the sampling points. In this study, CA was applied to 15 sampling points for each element using Pearson's linkage method.

Heavy Metal Pollution Index (HPI) and Metal Index (MI)

Two indices namely the heavy metal pollution index (HPI) and the metal index (MI) were calculated to evaluate the potential of water samples for agricultural and drinking use [13,14,15]. These two indices show the overall quality of the water sample in terms of its metal content [14]. The evaluation is based on a comparison between the measured values and reference values from the National Water Quality Standards for Malaysia (NWQSM for drinking water. Both indices were calculated using the following equations:

$$HPI = \frac{\sum_{i=1}^{n} Wi \cdot Qi}{\sum_{i=1}^{n} Wi}$$
Eq. 1
$$Qi = \sum_{i=1}^{n} \frac{|Mi - Ii|}{Si - Ii} \times 100$$

where Wi is the unit weightage defined as the reciprocal value of *Si*, *Si* is the highest permitted value for drinking water as given by the NWQSM standard, and n is the number of parameters considered [13,15].

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where Ci is the mean concentration of *ith* element and $(MAC)_i$ is the maximum permissible level derived from the NWQSM [14].

RESULTS AND DISCUSSION

Validation and Verification of EDXRF Method

Validation of the EDXRF method for the determination of elements was done using a series of multi-element standards. The standards were prepared at different concentrations (0.10 - 1.00 ppm) using Perkin Elmer Pure Plus Multi-Element Calibration Standard 3. Analysis of the standard using EDXRF gave good recoveries in the range of 83-191 %. For a comparison of accuracy and precision, the same standards were also analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICPMS) in the Agensi Nuklear Malaysia laboratory. This analysis gave comparable recovery values in the range of 70-136 %, showing the reliability of the EDXRF method for elemental analysis.

In-situ Measurement of Basic Physicochemical Parameters

Table 1 lists the GPS coordinates of the 15 sampling points and their descriptions. Basic physicochemical parameters including temperature (°C), pressure (mm Hg), dissolved oxygen, DO (mg/L), specific conductivity (µs/cm), conductivity (µs/cm), total dissolved solids (mg/L), salinity (ppt), pH and oxidation-reduction potential (mV) were determined. The readings were taken using the YSI probe at the sampling sites and their results are shown in Figure 2(a)-(h). The pressure and oxidation-reduction potential (ORP) readings of water samples were in the range of 737.30 - 740.30 mm Hg and -55.90 -61.10 mV, respectively, as shown in Figure 2(a) and 2(b). The negative values of ORP for W6 and W7 (Figure 2(b)) indicates a higher reducing agent was present in these water samples. Oxidizing agents help in decomposing and breaking down contaminants. Therefore, the higher the ORP value, the better the quality of the water body in general. However, good quality water should have ORP values in the range of 300-50 mV [16,17]. The temperature of the lake water samples was between 23 and 29°C (Figure 2(c)), which satisfied the requirements for the Class II category under NWQSM [18]. Additionally, the temperature of these areas was comparable to that reported in the study of Tasik Kapal Tujuh, Kg. Gajah, Perak, which was in the range of 29.9 to 31.7 °C [19]. The temperature varies depending on the weather at a particular time. Figure 2(d) shows the DO reading obtained from all sampling locations. The minimum DO level of the water samples was 4.78 mg/L and the maximum was 7.82 mg/L, which falls into Class I and IIA of NWQSM. This result was lower compared to the reported result by Ahmad Saat et al., (2014), in the range of 6.96 – 11.15 mg/L [19] which allowed aquatic organisms and plants to live

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in the lake. The electrical conductivity (C) values of samples were in the range of 34.40 to 64.40 μ s/cm (Figure 2(e)) and much lower than the threshold level of Class I in NWQSM (1000 μ s/cm). Figure 2(f) shows the pH values were between 6.58 and 7.27 for all 15 samples at different locations. This result was comparable with the study by Ahmad Saat et al., which reported a pH range of 6.98 – 7.81 [19]. In addition, the pH was within the threshold level of Class I in NWQSM (pH 6.5-8.5). Total dissolved solids (TDS) values for the water samples are shown in Figure 2(g). All sampling locations had very low TDS values compared to the threshold level of 500

mg/L in NWQSM for Class 1. The TDS values of water samples were in the range of 21.45 to 40.30 mg/L and much higher than the reported TDS values (0.09 to 0.13 mg/L) in Tasik Kapal Tujuh [19]. Likewise, salinity values of water samples in this study were much lower than the NWQSM of Class 1 value of 0.5 %. The salinity values of the water samples in this study area were in the range of 0.01 - 0.03 % (Figure 2(h)). According to Sabarina et al., the salinity levels were higher near the mouth of a river where the ocean water enters [20]. This explained the low salinity as this study analysed freshwater samples.

Location	G	PS	Description			
Location	Ν	Е	Description			
W1	05°37'02.7	101º17'44.8	Sungai Gadong Dalam			
W2	05°36'58.7	101º18'00.3	Sungai Gadong Dalam			
W3	05°36'52.5	101º18'19.3	Sungai Gadong Dalam			
W4	05°36'35.4	101º18'37.4	Tasik Temenggor			
W5	05°36'41.2	101º18'44.9	Tasik Temenggor			
W6	05°35'17.0	101º18'40.5	Sungai Gadong Luar			
W7	05°33'37.7	101º18'14.7	Tasik Temenggor			
W8	05°33'29.8	101º19'01.3	Tasik Temenggor			
W9	05°33'02.1	101º19'44.6	Tasik Temenggor			
W10	05°32'38.7	101º20'03.7	Tasik Temenggor			
W11	05°31'48.4	101º19'29.3	Teluk Nyor			
W12	05º31'58.8	101º20'10.6	Tasik Temenggor			
W13	05º24'56.1	101º18'00.2	Tasik Temenggor			
W14	05º27'47.1	101º17'34.3	Sungai Kelam			
W15	05°29'40.3	101º18'51.1	Sungai Rokan			

Table 1. GPS of 15 sampling locations





(e)

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> W14 W15

> > W15

W14

(**f**)





Figure 2. Basic physicochemical parameters determined at sampling sites: (a) pressure (mmHg), (b) oxidationreduction potential, ORP (mV), (c) temperature (°C), (d) dissolved oxygen, DO (mg/L), (e) conductivity, C (μs/cm), (f) pH, (g) total dissolved solids, TDS (mg/L) and (h) salinity (%)

Correlation Matrix ^a										
		Temperature	Pressure	DO	SPC	Conductivity	TDS	Salinity	pН	ORP
Correlation	Temperature	1.000	502	360373		189	362	436	.475	097
	Pressure	502	1.000	128	.298	.223	.336	.137	.126	.035
	DO	360	128	1.000	288	384	352	314	230	088
	SPC	373	.298	288	1.000	.981	.961	.942	130	416
	Conductivity	189	.223	384	.981	1.000	.943	.904	025	469
	TDS	362	.336	352	.961	.943	1.000	.899	117	334
	Salinity	436	.137	314	.942	.904	.899	1.000	271	262
	pН	.475	.126	230	130	025	117	271	1.000	351
	ORP	097	.035	088	416	469	334	262	351	1.000
a. Determinant = $1.629E-8$										

Pearson Correlation of Physicochemical Parameters

Pearson's correlation is a test statistic that measures the statistical relationship, or association, between two continuous variables. It is known to measure the association between variables of interest because it is based on the method of covariance Thus. correlations between [21]. the physicochemical parameters support and explain the relationships between them. In this study, the correlation matrix between physicochemical parameters was calculated using IBM SPSS Statistics 22, and the results are given in Table 2. An R value that is greater than ± 0.5 to near ± 1 indicates a strong correlation, while one that is below ± 0.5 is considered a weak correlation. Seven strong correlation pairs were observed from the data, which included temperature-pressure, SPCconductivity, SPC-TDS, SPC-salinity, conductivity-TDS, conductivity-salinity, and TDSsalinity. Other pairs showed weak correlations to each other.

Concentration of Elements in Water Samples

Table 3 shows the concentrations obtained for As, Cd, Cr, Cu, Ni, Pb, Se, Zn, U and Th. Comparing the results in this study with that of the NWQSM requirements for Class IIA/IIB, all elements except for Zn were found in concentrations higher than allowed by the standard [18]. The concentrations of Ni and Pb in the water samples were below the limits of the USEPA Surface Water Quality Standard (SWQS). However, Cd and Cr had higher concentrations compared to the USEPA limits.

Studies on water samples have long been conducted worldwide. A study of heavy metal concentrations in Tasik Chini by Mohammad Ebrahimpour & Idris Mushrifah showed that the mean concentrations of Cd, Cu, and Pb were in the range of 0.06-0.32, 1.50-8.36 and 2.85-18.7 µg/L, respectively These heavy [22]. metal concentrations were very low compared to this study. The Cd, Cu and Pb concentrations in Tasik Chini were measured using sequential extraction procedures based on defined fractions: exchangeable, acid reduction, oxidation, and residual [22]. In another research paper, Akinbile et al. highlighted a surface water study of six heavy metals, Cd, Cr, Cu, Ni, Zn, and Fe, in Bukit Merah Reservoir, Malaysia [23]. Inductively Coupled Plasma Mass Spectrometry (ICPMS) was used to determine the concentrations. The concentration ranges of the elements were -0.001 -0.077, -0.001 - 0.11, -0.005 - 0.019, -0.007 -0.189, -0.0006 - 0.072, and 3.916 - 8.485 mg/L, respectively, for Cd, Cr, Cu, Ni, Zn, and Fe [23]. These values were also lower than the concentrations measured in this study.

Another study by Dautović et al. reported the sources and distribution of certain major and trace elements in Plitvice Lakes, a pristine cascade hydrological system of sixteen karst lakes situated in a sparsely populated area of central Croatia [24]. From 17 locations including springs, tributaries, lakes and rivers, 22 elements were analyzed using high-resolution Inductively Coupled Mass Spectrometry. Compared to this study, concentrations of all elements except for Ca in Plitvice Lakes were much lower than in Temenggor Lake [24]. Meanwhile, a study on the distribution of heavy metals in the Selangor River basin by Faridah Othman et al., showed lower concentrations of As, Cd, Cr, Cu, Ni, and Zn compared to Temenggor lake. The study used Inductively Coupled Plasma Optical Emission (ICP-OES) Spectroscopy [15].

Elements (mg/L)		As	Cd	Cr	Cu	Ni	Pb	Se	Zn	U	Th
Temenggor, 2021	Min	0.06	0.14	0.67	0.95	0.58	2.08	0.10	0.56	0.05	0.29
	Max	0.15	0.49	2.06	2.20	2.63	2.74	0.20	5.23	0.61	0.86
National Water Quality Standards for Malaysia [*]		0.05	0.01	-	0.02	0.05	0.05	0.01	5	-	-
USEPA (SWQS**)		-	0.009	0.08	-	8.3	8.5	-	-	-	-

Table 3. Comparison of As, Cd, Cr, Cu, Ni, Pb, Se, Zn, U and Th concentrations

*Class IIA/IIB

**Surface Water Quality Standard (SWQS)



Figure 3. Distribution of Cr, Cu, Ni, Pb, Th, Zn, As, Cd, U and Se in surface water

Figure 3 shows the distribution of 10 elements samples including Cr, Cu, Ni, Pb, Th, Zn, As, Cd, U and Se in surface water. Most elements displayed an even distribution in terms of concentrations based on their mean and median. For example, Th, As, Cd and Se had similar mean and median values for all samples, showing that their concentrations were evenly distributed at all 15 locations. On the other hand, the other six elements had different mean and median values, indicating that their concentrations were not evenly distributed over the 15 locations. As can be observed from the box plot, outliers were present at some locations for Ni, Pb, Th, Zn and Se. In

addition, Zn had the biggest distribution range, while As and Se had the smallest.

Pearson Correlation of Elemental Concentrations

Table 4 lists the correlation coefficients between As, Ca, Cd, Cr, Cu, K, Ni, Pb, Se, Th, U, and Zn. Most of these elements had weak correlations to each other based on their R-values ($< \pm 0.5$). However, certain elements showed a strong correlations to each other, with R-values of more than ± 0.5 . Strong correlations were observed between As-Cr, As-Se, Cd-Cr, Cd-Zn, Cr-Pb, Cr-Zn and Pb-Zn.

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		As	Cd	Cr	Cu	Ni	Pb	Se	Th	U	Zn
Correlation	As	1.000	082	630	004	.077	.179	.516	.025	120	.179
	Cd	082	1.000	.518	231	.074	410	.347	.469	036	735
	Cr	630	.518	1.000	078	.133	566	140	.268	.041	666
	Cu	004	231	078	1.000	046	387	.425	.305	.140	.077
	Ni	.077	.074	.133	046	1.000	078	.078	.134	140	086
	Pb	.179	410	566	387	078	1.000	293	386	181	.757
	Se	.516	.347	140	.425	.078	293	1.000	.299	.282	269
	Th	.025	.469	.268	.305	.134	386	.299	1.000	457	380
	U	120	036	.041	.140	140	181	.282	457	1.000	.012
	Zn	.179	735	666	.077	086	.757	269	380	.012	1.000

Table 4. Pearson correlation of the elemental concentrations

Chemometric Analysis

Cluster analysis (CA) was carried out using the data set of elemental concentrations to evaluate the spatial variability among the sampling points. This analysis resulted in the sampling points being separated into two groups for each element based on their concentration levels as shown in Figure 4. Cluster 1 represents the sampling locations with low concentration levels and Cluster 2 the locations with high concentration levels of selected elements. Based on the CA, the distribution of each element varied at each sampling point. However, most of the elements gave approximately the same linkage distance between the sampling locations, indicating a small range of concentrations between the locations for each element. This was supported by the box plot constructed in Figure 3. In general, the locations from rivers are grouped in C2, which had higher concentrations. This might be due to the accumulation of contaminants as the rivers were shallow compared to the lake.



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Figure 4. Cluster analysis of elemental distributions

Heavy Metal Pollution Index (HPI) and Metal Index (MI)

In order to assess the risk of metal contamination in the study area, the heavy metal pollution index (HPI) and metal index (MI) were calculated based on the concentrations of selected metals and their permissible limits under NWQSM. The higher the ratio, the lower the quality of the water sample. The critical value for HPI is 100. All sampling locations in Temenggor reported HPI values greater than 100, indicating that these areas were most likely to have high pollution from heavy metals. Meanwhile, the threshold level for MI is 1 and MI > 1 signifies a potential threat. The MI values for all 15 locations tested were > 1 except for W01 with 0.98. The highest MI value (3.03) was at W07, whereas other locations reported MI values in the range of 1.19 - 2.26. The high HPI and MI values might be due to elemental concentrations that exceeded the threshold limit of NWQSM for drinking water. Weathering and landslides could also be sources of contamination in the water bodies of the Temenggor area [25,26].

CONCLUSION

This study revealed that the physicochemical parameters of waters from all the sampling points satisfied the NWQSM Class I requirements with values either lower or within the threshold range. Observation of the relationships between parameters using IBM SPSS showed strong correlations between temperature-pressure, SPC-conductivity, SPC-TDS, SPC-salinity, conductivity-TDS, conductivity-TDS-salinity. salinity, and All elemental concentrations, except for Zn, were higher than the threshold values of NWQSM. Besides, strong correlations were observed between As-Cr, As-Se, Cd-Cr, Cd-Zn, Cr-Pb, Cr-Zn and Pb-Zn. Cluster analysis separated the sampling locations into two groups: Cluster 1 contained low concentration levels while Cluster 2 had high concentration levels for each element. All locations reported HPI values > 100, which indicates they were likely to be highly polluted in terms of heavy metals. Additionally, all 15 sampling locations had MI values > 1 except for W01, indicating a possible health risk in terms of metals for drinking water.

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