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Pollutants distribution using environmetric technique in surface water sited at Gebeng, Kuantan, Pahang, Malaysia.

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Abstract. The quick response of contaminants from various sources and the extensive deterioration of rivers' water quality may harm our biodiversity, aquatic creatures, and environment. The depletion of this river water quality can be caused by both natural and manmade factors and this condition will jeopardize its use for many human uses and may harm the residents' health. Our concerning phenomenon prompted this investigation to study the primary pollutant source in two rivers near Gebeng. A total of ten sampling stations from both Balok and Tunggak Rivers were selected and physicochemical parameters reading were measured monthly afore and in COVID-19 Pandemic spread in Malaysia from March 2019 to October 2020. Later, the Cluster and Principal Component Analysis (CA and PCA) were applied. CA grouped the ten sampling stations into three clusters which are upstream areas that were considered as most polluted. PCA yields only four significant components that represented 90.68% of the total variability. The findings of this study can provide useful information regarding the current state of river water quality in the Gebeng area, and the proposed method can be used as a strategy for sustaining the use of water resources in support of long-term development goals.
Keywords: Sources of pollution, Rivers, Covid-19 Pandemic, Environmetric Technique

1. Introduction

The Movement Control Order (MCO) in Malaysia, which has been in effect since March 18, 2020, to combat the COVID-19 pandemic, has turned out to be a blessing in disguise for the milieu. Many rivers were said to be substantially cleaner and clearer than they had been previously. [1] point out that the lockdown period has significantly reduced industrial waste creation, pollution, and the input of heavy metals and plastic to the hydrosphere from many sources.

Both point and nonpoint sources could contribute to the pollution in the river water [2] because the point source pollution is categorized as discharges from a single source directly towards the water such as an industrial effluent whereas nonpoint source pollution is defined as multiple sources that diffuse together causing more significant pollution [3]. Anthropogenic activities are acknowledged to be one of the leading sources of pollution in a variety of environmental spheres. The rivers in Malaysia have been exploited by massive land reclamations, developments for livestock productions, uncontrolled discharge of industrial, domestic wastes, and energy development projects. Besides, agricultural activities tend to increase pesticide load and nutrient deposition in the river due to land runoff [4, 5]. Inadequate treatment of sewage or effluent from manufacturing industries attributes to high biochemical oxygen demand (BOD) and low dissolved oxygen (DO) in rivers [6,7]. Other pollutants such as heavy metals, wastewater, crude oil, and plastic also may affect the ecosystem [1]. Since toxic pollutants such as heavy metals, radioactive elements, and rare earth elements tend to dilute in the rivers, their approved average safety levels in surface water are frequently high [8].

As described by [9] water pollution arises when unwanted substances flow into the water, the water's physicochemical properties change, and eventually, the condition of water poses negative effects to humans' health and the environment. Exposure to infectious pathogens secreted in feces can lead to the spread of water-related disorders [10], and exposure to heavy metals and radioactive elements can lead to cancer and harm public health [11, 12]. Moreover, aquatic ecosystems cover more than two-thirds of our planet and play an important role in climate stabilization as well as providing a variety of services to a fast-growing human population. Anthropogenic activities, on the other hand, are gradually wreaking havoc on aquatic ecosystems, particularly before the pandemic.

In this case, endless water quality and pollution monitoring of Balok and Tunggak River are dire in ensuring the sustainability of aquatic organisms living in its water bodies. To do so, a picture of continuous monitoring on surface water quality, heavy metals, and radioactive elements, should be recognized, as this will offer keywords or primary data for simpler detection of major pollutant sources in rivers. Recently, environmetric techniques have been utilized to estimate and characterize environmental quality information such as water, land, and air because spatial changes produced by natural or environmental causes are vital to note [13, 14].

Several studies on water quality and heavy metals have been conducted [15, 16] but no research on radioactive elements in surface water has been performed to trace contamination sources using environmetric techniques. In these circumstances, this study looked at the current state of rivers within an industrial area by employing the environmental forensic concept to pinpoint the major source of pollutants in Balok and Tunggak Rivers, Pahang by using environmetric technique including cluster analysis (CA) and principal component analysis (PCA).

2. Materials and Methods

2.1. Sampling Area of Balok and Tunggak Rivers

There were ten sampling stations in total, namely SB1, SB2, SB3, SB4, SB5, SB6, ST1, ST2, ST3, and C. Six of them were located at Balok River and three were at Tunggak River as shown in Figure 1, while C was for Control. Due to the length of Balok River is longer than Tunggak River (Balok River = 10.5km and Tunggak River = 2.4km), thus the sampling points chosen for Balok River is more than the other. The sampling points for both rivers were chosen on a location basis, classified into three parts, which are the upstream, middle stream, and downstream area to distinguish which part is the main polluted area of both rivers [17]. The most interesting aspect of this study is the selection of control area (C), where no control site could be chosen from the upstream area of both rivers because the upstream is already densely populated with factories and industries, and this area is physically polluted and unsuitable for use as a control area. As a result, the estuary area is the greatest place to be a control since both rivers will converge at this point, and all pollutants will have been washed away by the sea water. Sampling activities for this study were carried out once a month, from March 2019 to October 2020.

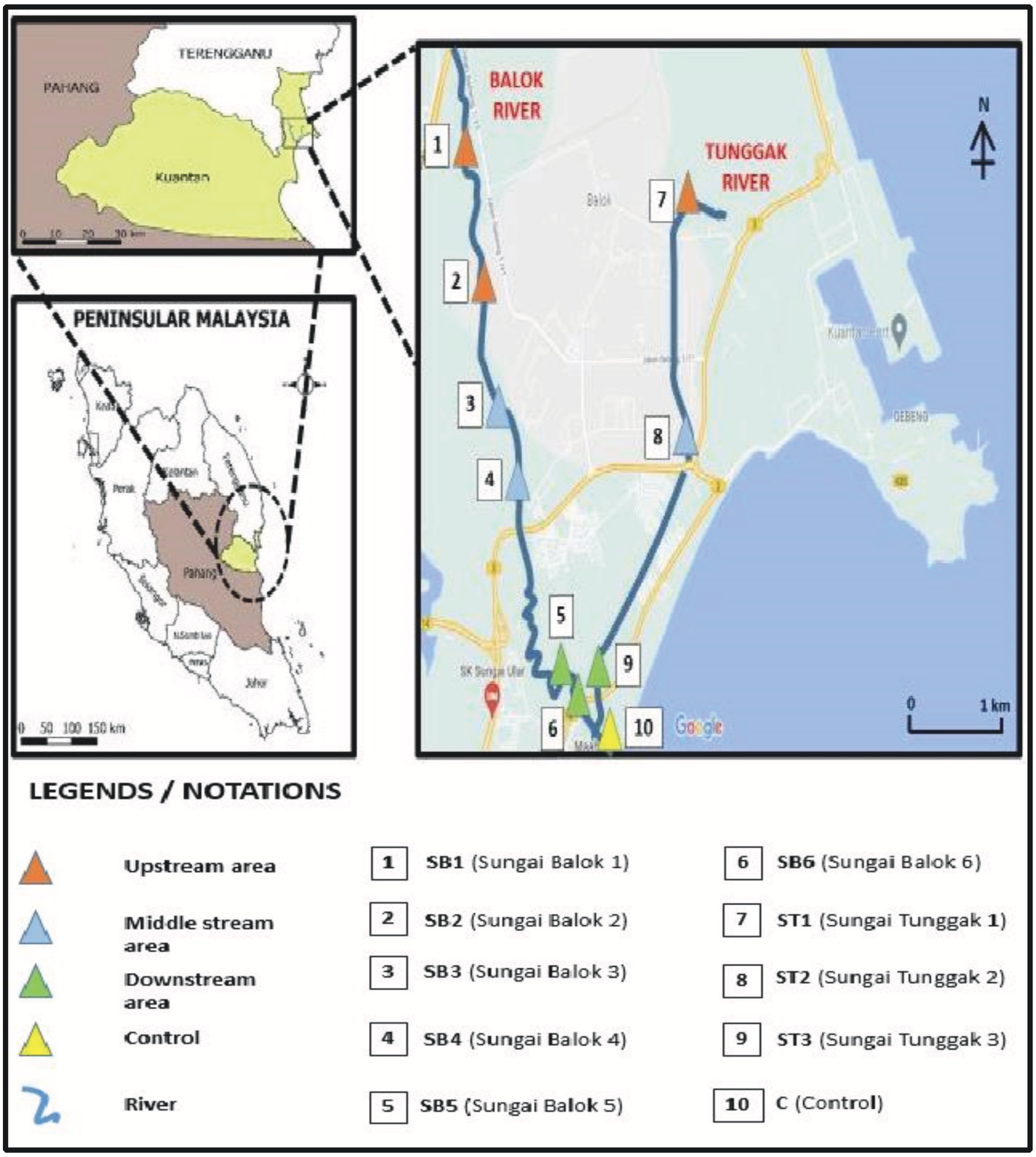

Figure 1. Map of the sampling area along Balok and Tunggak River

2.2. Water Quality Parameters Reading and Samples Collection

The physicochemical parameters that were examined on-site *(in-situ)* were temperature, turbidity, salinity, pH, dissolved oxygen (DO), and specific conductivity (SC). All readings were taken triplicate using Hydrolab DS5 Multiparameter Sonde (refer to figure 2 (a)). The water samples for *ex-situ* analysis (heavy metals and radioactive elements) were collected using a Van Dorn water sampler (refer to figure 2 (b)) and there were three replicates of water samples were taken for each of the sampling points, followed the study by [18] and [19]. The water samples were then kept in Polytetrafluoroethylene (PTFE) bottles for each sampling point before being temporarily placed in an ice box during transportation to the laboratory to retain the water's natural characteristics. Because the midpoint area of both the Balok and Tunggak Rivers is deeper than the river bank and has less-muddy water, sampling of surface water (0-20cm depth) was done at the midpoint of the river width in this study. It is critical to collect less murky water in order to assist and speed up the filtration process in the laboratory. Since this study involves heavy metals and radioactive elements sampling, safety precautions were implemented, such as donning gloves and wearing protective clothing.

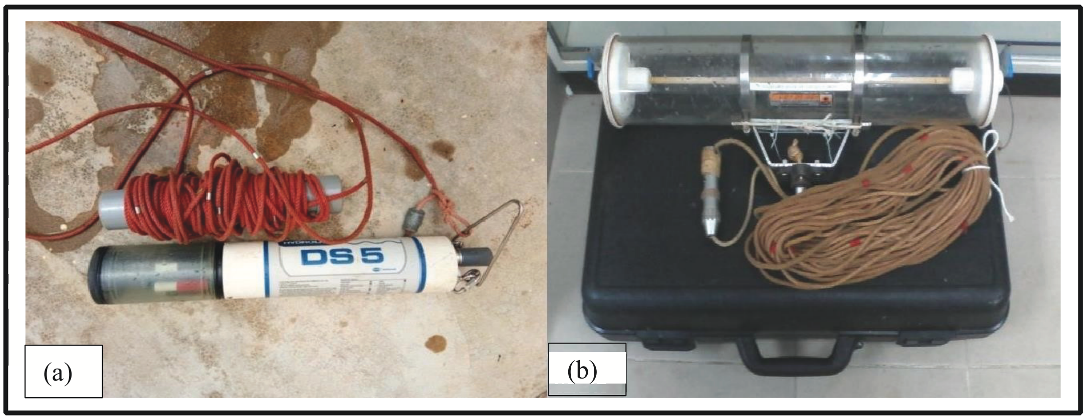

Figure 2. The equipment used for taking (a) water quality parameters reading and (b) samples collection

2.3. Samples preparation and analysis

The water samples for the direct method were analyzed following the previously published method [20]. This method was applied to the samples from the upstream and middle stream area because this area had salinity lower than 4.35% [21]. First, the samples were filtered (0.45 µm filter paper) on a vacuum filtration system. Then, 20 mL of water samples were topped up to 40 mL with 2% nitric acid. Then, the prepared samples were stored in the refrigerator (–20°C) before being analyzed with the inductively coupled plasma mass spectrometry (ICP-MS) as described previously in [22, 23] with some modifications. While for the downstream area, the method for pre-concentration water analysis was used following the [24] and [2] with some optimization because this area had salinity higher than 4.35%, and the direct method was not suitable to be used. ICP-MS was the best machine used to measure both heavy metals and radioactive elements content in the surface water collected from this study since it can measure multiple elements of both heavy metals and radioactive elements for a large number of samples at the same time. Before the analysis, the data were quantified using a calibration curve produced from serial dilutions of multi-element calibration standards 2 and 3 (Merck). Diluting the stock solution to 1.0 ppb, 2.0 ppb, 5.0 ppb, 10.0 ppb, 50.0 ppb, 100.0 ppb, 300.0 ppb, and 500 ppb yielded a standard calibration curve. Finally, the formula was used to compute the amount of heavy metals and radioactive elements present in surface water:

$$\text{Total metal content} = \frac{[\text{ICP-MS reading (sample – blank) (ppb)}] \times \text{markup volume} \times \text{dilution factor (if any)}}{\text{Dry weight (g)} \times 1000}$$

2.4. Environmetric Analysis

Using IBM SPSS Statistics 20, environmetric analysis such as CA and PCA was applied to examine water quality parameters [25]. Hierarchical cluster analysis (HCA) was performed in this work to find the similarities between the mean values of the parameters of all sampling locations. Ward's method was used to apply HCA, with squared Euclidean distances as the measure of similarity [26, 27, 28]. To guarantee normal distributions for the HCA, all studied data was uniform to z scores. In addition, PCA was utilized in this research to track out the major pollutant sources in both rivers. Instead of using the mean, the whole data set was used to increase the variability and data size, resulting in a better result.

Essentially, PCA approaches have been used in a wide range of environmental applications, and this analysis was hailed as the most effective way to avoid misinterpretation of vast volumes of complicated environmental monitoring data [2, 29]. The correlation matrix was used to normalize the data. Varimax rotation was used to improve the data interpretation [30] because it can be extended to PCA to simplify the problem structure and make interpretation easier. A straightforward solution here indicates that each factor has a small number of large loadings and a large number of zero or small loadings [31]. It is because each original variable will tend to be connected with one or a small number of factors after this rotation, and each factor reflects only a limited number of variables, the interpretation will be simplified.

3. Results and Discussion

In this study, the spatial and temporal pattern was investigated. The spatial pattern was mostly related to the anthropogenic activities, particularly land pollution input. *In-situ* water quality parameters readings were taken on-site afore and in the Covid-19 pandemic to analyze the data using CA and PCA, and the results are displayed in Table 1 from March 2019 to October 2020. This study involved data on heavy metals and radioactive elements since these pollutants are also important to be taken into the consideration especially for industrial areas such as Gebeng.

Table 1. *In-situ* water quality parameters analysis during the sampling period.

Parameters		Temperature (°C)	Specific conductivity (mS cm–1)	pH	Salinity (PSS)	Turbidity (NTU)	DO (mg L–1)
from March 2019 to October 2020							
SB1	Mean	28.69278	0.625361	7.327222	0.305556	102.1861	4.375278
	Std. Dev.	1.457188	0.302202	0.64614	0.150086	58.19685	1.887891
SB2	Mean	27.90222	0.580278	7.519722	0.303056	109.4528	4.684444
	Std. Dev.	2.330684	0.302952	0.679544	0.1513	60.90075	1.909055
SB3	Mean	28.48056	0.434	4.999722	0.265306	100.9	2.521111
	Std. Dev.	1.018172	0.74144	0.860974	0.385376	36.23598	1.797346
SB4	Mean	29.62278	15.1055	6.421944	6.840278	71.67778	3.281667
	Std. Dev.	1.174558	9.311864	0.826744	6.146156	35.80661	1.257664
SB5	Mean	28.64556	6.075944	7.3525	6.736944	80.18889	2.613889
	Std. Dev.	1.308373	3.155304	0.559648	3.970942	35.20416	0.701109
SB6	Mean	28.94778	31.15583	7.885	21.775	55.17222	3.600000
	Std. Dev.	1.439308	17.9462	0.722822	11.73968	25.69361	1.500835
ST1	Mean	27.39061	1.173697	7.370303	0.623333	91.09394	0.847879
	Std. Dev.	0.831395	3.25949	0.767408	1.720491	35.15242	0.839619
ST2	Mean	28.62222	0.982972	8.396667	0.512222	62.42222	3.369444
	Std. Dev.	0.892713	0.423784	0.594619	0.213041	15.64218	2.022241
ST3	Mean	28.96944	34.00917	7.995	25.82639	51.76111	3.735278

	Std. Dev.	1.334094	17.5918	0.58602	11.17229	13.10994	1.654567
C	Mean	28.92833	31.37389	8.117222	22.435	305.9333	3.777222
	Std. Dev.	0.763369	14.28624	0.73176	11.59794	33.85702	1.299147

3.1. Cluster Analysis

The function of hierarchical cluster analysis (HCA) was to group or cluster sampling stations based on their similarity. Figure 3 shows a dendrogram that divides all ten stations into three statistically significant groupings. SB1, SB3, SB2, and ST1 are in Cluster 1, SB6, ST3, SB4, SB5, and ST2 are in Cluster 2, while C is in Cluster 3. Cluster 1, Cluster 2, and Cluster 3 correspond to highly polluted (HPS), moderately polluted (MPS), and less polluted (LPS), respectively, in terms of similarity characteristic between the water quality parameters, heavy metals, and radioactive elements data [30]. Ward's hierarchical cluster approach uses squared Euclidean distances as an indicator or index to evaluate similarity using an error sum of squares criterion that minimises the 'loss of information.'

The readings were heavily influenced by spatial variation among stations, based on the clusters created. C that represents Cluster 3 is the control area of both Balok and Tunggak rivers and is located near to the sea, whereas SB1, SB2, and ST1 are in the upstream area. C was in a cluster by itself. ST1 that represents Cluster 1 may have not only shown the most hostile water quality in the data but also represented it in the observations. As a result, it was labeled as HP. Oil contamination was severe in ST1, possibly as a result of anthropogenic activities such as the dumping of industrial effluents and the discharge from car washes and workshops nearby. The upstream area was connected to the industrial area, and away from domestic influence. Therefore, most of the factors contributing to the pollution were the result of industrial activities such as effluents discharge, and human activities such as river banks excavation for piping purposes [11].

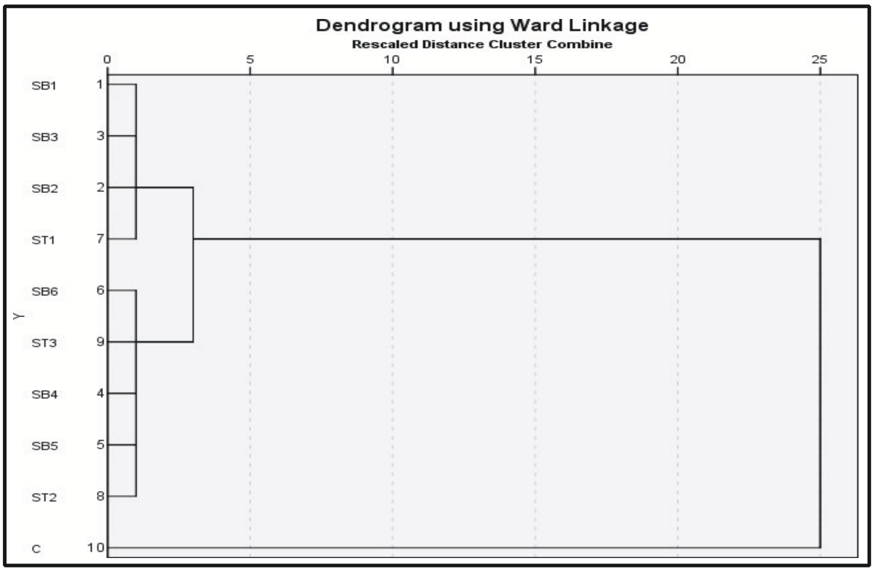

Figure 3. A dendrogram from HCA at upstream until downstream of Balok and Tunggak Rivers.

3.2. Principal Component Analysis

The principal component analysis (PCA) was applied to water quality information to find out, by reducing but not losing the entire meaning as possible, which parameters were the most significant to contribute to water quality, heavy metals, and radioactive elements variations in both rivers [32] and to summarize the statistical correlation among those parameters [27, 33].

From the scree plot, four principal components with eigenvalues bigger than one, totaling 90.68% of the total information variance were found (figure 4). Table 2 shows the corresponding components, variable loadings, and variance. Component 1 explains the overall variance in 33.69% and has substantial positive specific conductivity, salinity, and Uranium in the meantime as shown in Table 3; component 2 explains 24.78% of the total variance and has robust positive loadings on dissolved oxygen. While Component 3 explains the overall variance in 19.17% and has substantial positive loadings on Arsenic and component 4 explains 13.05% of the total variance and has robust positive loadings on turbidity.

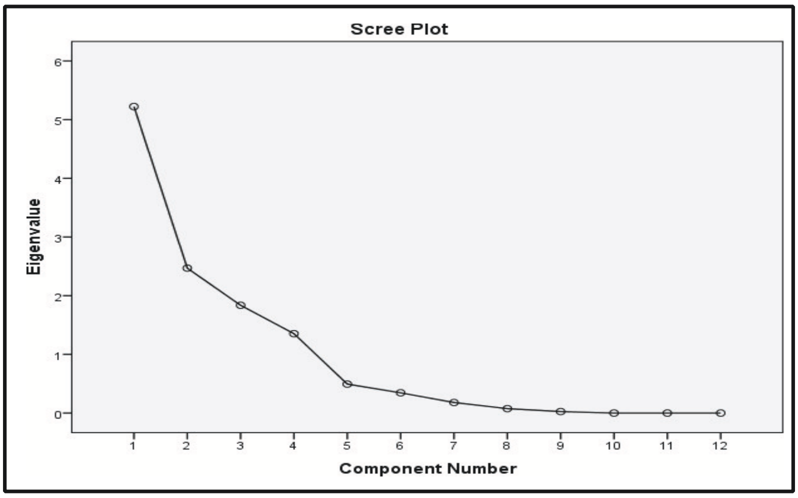

Figure 4. Scree plot for variables studied.

Table 2. Extraction values of the total variance for water quality, heavy metals, and radioactive elements parameters

Component	Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	Percentage of variance (%)	Cumulative %	Total	Percentage of variance (%)	Cumulative %
1	5.224	43.530	43.530	4.042	33.687	33.687
2	2.470	20.581	64.110	2.974	24.782	58.469
3	1.836	15.302	79.412	2.300	19.169	77.638
4	1.353	11.272	90.684	1.566	13.046	90.684

[a]Only the first four components were shown since their eigenvalues >1.0.

Table 3. Rotated component matrix for water quality, heavy metals, and radioactive elements parameters

Parameters	Component			
	1	2	3	4
Temperature	0.461	0.454	0.673	-0.109
Specific conductivity	**0.965**	0.183		
pH	0.352	0.455	-0.706	
Salinity	**0.970**	0.175		
Turbidity	0.188	0.104		**0.901**
DO		**0.941**		
Ferum	-0.403	-0.810	0.129	-0.114
Lead	0.729			0.660
Cadmium	-0.363	-0.156	0.582	0.517
Arsenic	0.135		**0.964**	
Thorium		-0.940	0.207	
Uranium	**0.971**	0.142		

[a]Extraction method: PCA.

[b]Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 6 iterations.

The large difference in variability between the fourth principal components indicates that all the components carried almost different weights in contributing to the water quality, heavy metals, and radioactive element variations for the whole sampling period. The specific conductivity, salinity, and Uranium parameters showed a strong correlation among themselves in Component 1. Briefly, the specific conductivity and salinity are affected by the number of ions available in the water.

4. Conclusion

Based on water quality, heavy metals, and radioactive element characteristics, the CA assisted in clustering the ten sampling stations for both the Balok and Tunggak Rivers into three clusters (HPS, MPS, and LPS) of similar characteristics. As a result, the few locations in the upstream area with high levels of heavy metals and radioactive elements, as well as hostile levels of physical water quality indicators like SB1, SB3, SB2, and ST1 require additional attention for successful pollution control mitigation. The PCA revealed significant evidence for variations in river water quality, with strong positive loading of several pollutants at ten sampling points, based on the findings. In summary, the four varifactors or components derived from the principal component show that the parameters governing the quality of the Balok and Tunggak Rivers are mostly contaminated by both point and non-point pollution sources. Therefore, environmental impact assessors and policymakers should take note of this first-hand approach that uses water quality, heavy metals, and radioactive elements pollutants to plan the future urban dynamics accordingly. Authorities' strong legislative backing, together with ongoing monitoring of river water bodies in Gebeng, would pave the way for the sustainable use of water resources in supporting the sustainable development goals.

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