

# Statistical analysis on physical and chemical parameters and heavy metal in marine water

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**Abstract.** The study attempts to determine the spatial distribution of heavy metal pollution and to identify the physical and chemical marine parameters with respect to water quality status along Straits of Johor from 2003 to 2014. There are several marine parameters considered which are temperature, salinity, electrical conductivity (EC), pH and dissolved Oxygen (DO), and heavy metals which affect the quality of marine water. Principal component analysis revealed that there are three main factors involved in identifying the water quality with the variation of 30.8, 18.9 and 11.4%. Cluster analysis showed that the stations can be categorized into 2 clusters with distinct characteristics of water quality parameters. Based on this study, salinity, temperature, Cadmium, Manganese, Nickel and Zinc contribute the most in the components of this study of heavy metal pollution distribution.

## 1. Introduction

Marine pollution has become a global concern due to the dumping of pollutants into the ocean at an alarming rate. Release of hazardous chemicals due to human activities and irresponsible acts have resulted in the accumulation of heavy metals and metalloids in the marine environment. It has become a serious issue due to its persistent toxicity and nature, especially in industrialized countries [1].

Heavy metals are naturally occurring elements with high atomic weight and density, at least 5 times greater than that of water [2]. Though heavy metals are essential to maintain the body metabolism, it is toxic at higher concentrations [3]. Its concentration in aquatic environment is a critical concern due to the toxicity of metal and its accumulation in aquatic habitats [4]. The excess amount of heavy metals are lethal to the organisms as they can bio accumulate in the organism [5]. Hence, this study is important to assist authorities in managing the amount of heavy metal in the straits of Johor, especially in controlling the pollutant sources.



Naturally metals are continuously released into the biosphere by volcanoes, natural weathering of rocks but also by numerous anthropogenic activities, such as mining, combustion of fuels, industrial and urban sewage and agricultural practices [6]. Various pollutants and toxic chemicals can also enter into the aquatic environments by several other routes. These routes are direct precipitation, surface water, runoff, sewage discharges and industrial wastewater outfalls [7]. A major environmental concern due to the spread of industrial and urban wastes generated by human activities result in the contamination of soil and water [8].

Release of pollutants streamed directly into the ocean or stream with no proper treatment and control result in harmful heavy metal contamination. According to the Department of Environment in 2008 [9], changes in land use and industrialization have prompted to an extreme increment in the release of heavy metals, for example, cadmium (Cd), copper (Cu) and Mercury (Hg), from the manufacturing sectors like Penang, Selangor and Johor and contributes to the wide variety of heavy metal pollutants into the marine environment. The introduction of natural pollutants (POPs) from petroleum spills or tanker wreckage also have polluted the seawater and sediment, leading to the accumulation of heavy metals in aquatic systems. The release of pesticides attributed to agricultural sector also contributes to heavy metal pollution in ocean. The toxicity of metal ions in mammals systems is due to chemical reactivity of metal ions on cellular structural proteins, enzymes and membrane system. The target organs of specific metals are usually the ones that accumulate the highest concentrations of metal in vivo [10].

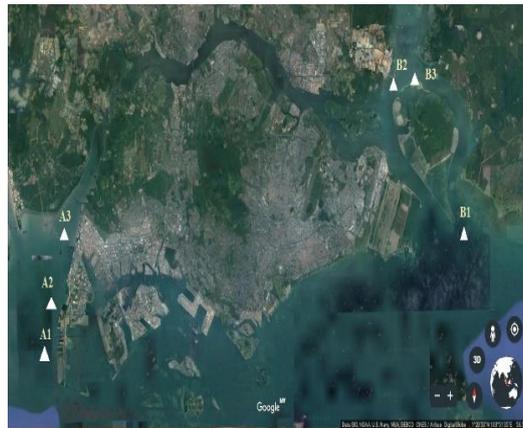
Based on previous research, there are several methods being conducted to evaluate the effect of pollution in sea water. [11] [12] evaluates the existing relationship between different pollutants using cluster analysis and principal component analysis. [13][14] also implemented the same method to evaluate geochemistry of sinking particles in the ocean. [15] evaluates the distribution of heavy metals along the southeast coast of India using the two multivariate approaches and [16] evaluates the relationship between water quality characteristics, nutrients and phytoplankton density and biomass. This method is also implemented to detect harbour pollution with various point sources as studied at Mediterranean Harbour [17]. This method is suitable to be implemented in marine problems as it reduces the number of data parameters, but in the same time does not reduce the information from the original observation [18].

There is significant difference between PCA and factor analysis. Although the process to implement these two methods are similar, however, there is a significant fundamental difference, which the first one refers to linear combination of several variables, while the latter refers to measurement model of a latent variables. PCA process is to determine a single index variable, known as components, from a multiple set of variables. The process involves optimizing every possible point such as number of relevant variables and the optimal weight to class the index variable. The objective of the study is to identify spatial distribution of heavy metal pollution along Johor Straits and to determine the effect of physical and chemical parameters on heavy metal pollution using multivariate statistical analysis.

## **2. Materials and methods**

### *2.1 Study Area*

Johor straits is situated between latitude of 1.2719° N, and longitude of 103.5668° E, at the southernmost tip of Peninsular Malaysia. It is located between two powerful regional hubs, Johor and Singapore; the Straits of Johor is the only passageway by land between Malaysia and Singapore. The strategic geographic position of sampling station is on the world's busiest shipping routes, both eastbound and westbound [19].



**Figure 1:** Map of A1, A2, A3, B1, B2 and B3.

Johor Straits is a main area for fishing and aquaculture activities along the narrow straits separating Peninsular Malaysia and Singapore[20]. The eastern part of Johor Strait is located between the Causeway and Johor River estuary with a distance of about 20 km and the western part of Johor Straits is located between Causeway and Pulai River estuary, 33 km away with a minimum width of 632 m and a maximum width of 12440 m in the close estuary of Pulai[21].

### 2.2 Data preparation

The water samples for the study were collected from 6 different locations, which were categorized into two divisions: East and West as shown in Figure 1. The samples were collected from stations: B1, B2, B3, A1, A2 and A3 every month from 2003-2014. The data were supplied by the Earth Observation Centre (EOC) at the National University of Malaysia (UKM). Several major water quality parameters monitored in the study are temperature, salinity, electrical conductivity (EC), pH and dissolved oxygen (DO). Every parameter chosen in the study has exhibited potential relationship with heavy metal distribution. The physical parameters conducted were temperature, salinity and EC while chemical parameters were pH and DO.

pH measures the acidity or alkalinity of the solution. Chemical reactions inside aquatic organisms for survival and growth require a narrow pH range. DO represent the amount of oxygen which dissolved in water and is essential for aquatic organisms. Insufficient oxygen in water could trigger problems such as reduction in organism's growth or failure of eggs and larvae to survive. Some metals are essential for life, but some are highly toxic. The essential concentration of metals for some organism's might be toxic to others.

Temperature is the measure of average kinetic energy of water molecules. It is one of the most important water quality parameters as it influences the chemistry and the functions of aquatic organisms. Conductivity is the ability of water to conduct electrical current, and the dissolved ions are the conductors while salinity is a measure of the amount of salts present in the water. Because dissolved ions increase salinity as well as conductivity, the two measures are related to each other. Multivariate statistical techniques used helped to simplify and organize large set of data to provide meaningful insight[22].

### 2.3. Cluster Analysis

Cluster Analysis (CA) too is a multivariate technique to compartmentalize large set of data into various meaningful groups. By reducing the data into sub groups, it classifies data into more interpretable information in relative to individual original datum[23]. Prior to CA, it is unknown about which metals can be grouped together. The CA of the data groups the metals through an analysis of the data[24,25].

Squared Euclidean distance ( $D^2$ ) between location I and II is calculated by using Equation (1):

$$D^2 = (X_2 - X_1)^2 + (Y_2 - Y_1)^2 + \dots \quad (1)$$

where  $D^2$  is distance between locations 1 and 2, X and Y are constant values for particular parameters at location 1 and 2. The Euclidean distance usually gives the similarity between two samples, and a distance can be represented by the difference between transformed values of the samples[26].

#### 2.4 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is a multivariate technique used to analyse large set of data is categorized into various intercorrelated dependent variables. It extracts significant information from the data and reduces to new orthogonal variables called principal components. By displaying pattern of similarity in the observed data set as points in map[27][28,29], it helps reduce large data set of parameters to important observations without losing much of information. It is a widely used technique in environmental management and protection[30][31].

Based on PCA of heavy metals, variables with eigenvalue  $>1.0$  are considered important. PCA can be expressed as the following equation (2):

$$L_{ij} = a_{i1}X_{1j} + a_{i2}X_{2j} + \dots + a_{ik}X_{kj} \quad (2)$$

where  $L_{ij}$  is the principal component,  $a_{ij}$  is the component loading, X is the measured original variables,  $i$  is the component number and  $k$  is the number of original variables.

### 3. Results and Discussion

#### 3.1. Cluster Analysis (CA)

In the study, sampling site classification was performed by the use of cluster analysis. Hierarchical CA was performed on the factor scores obtained from factor analysis using Ward's method with squared Euclidean distances as a measure of similarity. Cluster analysis from factor scores of stations reduce the clustering error caused by data error or multi-collinearity. Ward's method uses analysis of variance (ANOVA) to calculate the distances between clusters to minimize the sum of squares of any two possible clusters at each step. The results of cluster analysis are represented using dendrogram. The distance in dendrogram is equal to  $(D_{link}/D_{max}) \times 100$ , which represents the quotient between the linkage distances for a particular case divided by the maximal linkage distance. The quotient is then multiplied by 100 as a way to standardize the linkage distance [32,33].

In the dendrogram of six sampling stations (B1, B2, B3, A1, A2 and A3), water sampling stations are classified into two clusters at  $(D_{link}/D_{max}) \times 100 < 25$  as shown in Figure 3.

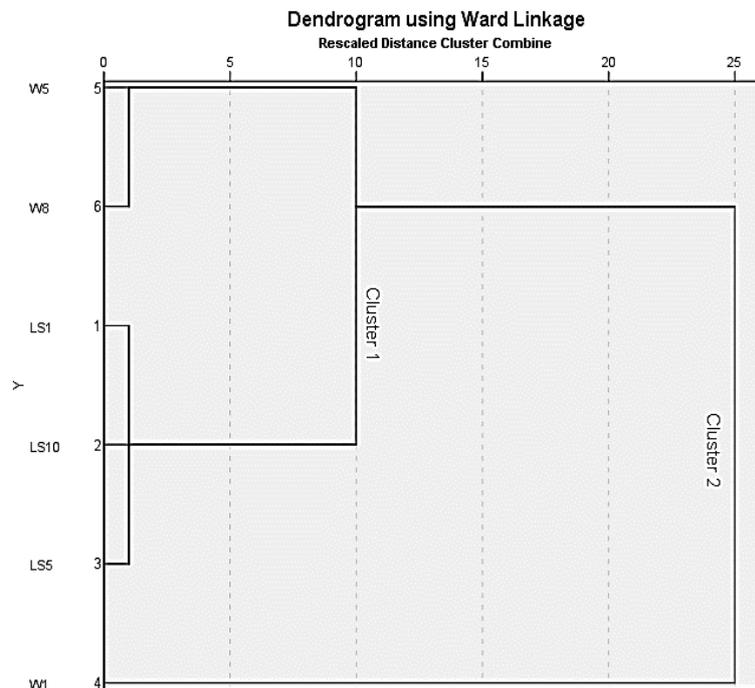


Figure 2: Dendrogram using Ward Linkage of six sampling stations

On the basis of cluster analysis, stations of same clusters have similar water quality pattern are divided as follows:

Cluster I : Station B1, B2, B3, A2, A3

Cluster II: Station A1

DO, Electrical Conductivity, pH, Manganese, Nickel and Cadmium are the highest recorded in cluster 1. Oxygen is more available in cooler water temperatures[34]. Thus, hot water tends to have lower DO saturation level than cold water[35]. Johor Bahru is the second largest city in Malaysia after Kuala Lumpur and the area is rapidly developing to accommodate large population. Similar sources of pollution at the cluster might result from rapid land use, construction and also dense population in Johor Bahru. Most of the sampling station at cluster 1 is located near to Singapore. Pasir Gudang port is known as one of the busiest ports in the world. The Singapore port is among the busiest free port in the world, and it also contributes to the pollution by oil spills from ships[36].

Station A1 in cluster 2 is located at western end of the Straits of Johor and is closer to the shipping routes. Within this cluster, A1 recorded highest temperature, salinity and also Zinc. There are many cruise ships in the territorial waters between Johor and Singapore. Lots of waste production is discharged into the sea without being treated.

### 3.2 Principal Component Analysis (PCA)

Before conducting PCA, the Kaiser-Meyer-Olkin (KMO)[37] and Bartlett's sphericity tests[38] were performed on the parameter correlation matrix to check the validity. Based on the data, three factors which explain about 61 % of the total variance, was estimated on the basis of Kaiser criterion with the eigenvalues greater or equal 1 and from a Cattell scree plot[39]. A scree plot in Figure 2 shows the eigenvalues sorted from large to small as a function of the factor number. After the third factor, starting the elbow in the downward curve, other components can be omitted. Factor was extracted by principal component method and rotated by Varimax. Based on the figure, scree plot shows that it starts to form a straight line after third principal components.

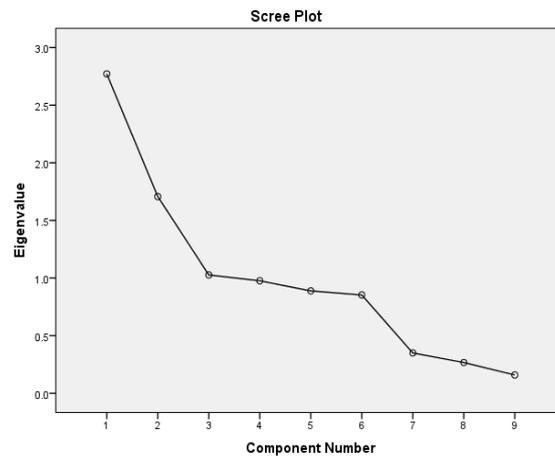


Figure 3: Scree plot of the eigenvalues

Principal component analysis was conducted on the raw data set. Three components (Eigenvalue > 1) accounted for 30.796%, 18.969% and 11.409% of the total variance from Table 1.

**Table 1:** Weight of three principal components of seawater quality parameters (Eigenvalue > 1)

Parameter	Principal Component		
	1	2	3
Temperature (°C)	-0.240	-0.105	<b>0.603</b>
Salinity (ppm)	-0.511	<b>0.799</b>	0.007
Dissolved Oxygen (mg/L)	0.388	0.035	-0.066
Conductivity (µS/cm)	-0.328	<b>0.885</b>	0.140
pH	-0.429	0.052	0.007
Manganese (mg/L)	<b>0.783</b>	0.281	0.027
Nickel (mg/L)	<b>0.805</b>	0.336	0.103
Zinc (mg/L)	-0.095	0.149	<b>-0.791</b>
Cadmium (mg/L)	<b>0.861</b>	0.238	0.051
Initial Eigenvalues	2.772	1.707	1.027
Percentage of Variance (%)	30.796	18.969	11.409
Cumulative Percentage of Variance (%)	30.796	49.766	61.175

Parameters were grouped based on the factor loading and following factors were indicated:

Factor 1: Mn, Ni, Cd.

Factor 2: Salinity, conductivity

Factor 3: Temperature, Zn

Manganese, Nickel and Cadmium marked factor 1, which explained 30.8% of the variance. The weight of three principal components of seawater quality parameters are shown in Table 1. Factor 1 has high positive loading in Manganese, Nickel and Cadmium which are 0.783, 0.805 and 0.861 respectively. High positive loadings indicated strong linear relationship between the factor and parameters. The release of metals is governed factors such as pH, salinity etc. Hence, their effect of overlying water might have influenced the metals to be released together. Sea water might have influenced the metal ions of Mn, Ni and Cd to release better in the presence of metal ionic conductivity.

The second principal component (PC2) contributed 18.969% of total variance attributed to salinity and conductivity with positive correlation of 0.799 and 0.885 respectively. Salinity and conductivity measure the water's ability to conduct electricity, which provide a measure of what is dissolved in water. A higher conductivity value indicates that there are more chemicals dissolved in the water. Conductivity measures the water's ability to conduct electricity. It is the opposite of resistance. Pure, distilled water is a very poor conductor of electricity. When salts and other inorganic chemicals dissolve in water, they break into tiny, electrically charged particles called ions. Ions increase the water's ability to conduct electricity. Common ions in water that conduct electrical current include sodium, chloride, calcium, and magnesium. Since dissolved salts and other inorganic chemicals conduct electrical current, conductivity increases as salinity increases.

Organic compounds, such as sugars, oils, and alcohols, do not form ions that conduct electricity. It has been observed that an increasing level of salinity may be correlated with an increasing level of metals, but causation has not been established [40]. Different types of water have different characteristics of salinity and conductivity. Spikes outside this range may indicate a pollution event, such as an overdose of fertilizers or illegal chemical dumping. Conductivity and salinity explain how freshwater and seawater mix in saltwater estuaries, or how stream water and lake water mix in freshwater estuaries.

The third component only explains 11.409% of the total variance attributed to temperature and zinc which 0.603 and -0.791 respectively. Water temperature is a degree of heat present in the marine water and is responsible in controlling the aquatic life. Environmental temperature plays a key role in the physiology of ectotherms, as their body temperature changes according to the environment, which result in corresponding alterations of the rates of all physiological and biochemical reactions and stability of biological molecules [41]. The contamination of zinc in marine water results from the release of industrial wastewater containing zinc from galvanic industries, battery production and etc. Zinc leaks from zinc pipes and rain pipes, resulting circulation of carbon rich water. Car tires containing zinc and motor oil from zinc tanks release zinc compounds on roads. Zinc compounds are present in fungicides and insecticides, and consequently end up in water.

Due to inadequate safety measures, zinc may be emitted from chemical waste dumps and landfills or from dredge mortar. However, Zn is not a good indicator of pollution because it is an essential element for animal metabolism and can exist at temporarily high concentrations in tissues [42]. The result in Table 1 indicates that the water quality along Straits of Johor is mainly influenced by physical parameters such as temperature, salinity and EC, and chemical parameters in the water which are Manganese, Nickel, Cadmium and Zinc.

#### 4. Conclusion

The first objective had been achieved to identify spatial distribution of heavy metals using cluster analysis. According to the result generated using cluster analysis technique, the six stations can be group into two, based on the similarity of water quality in the area. Cluster 1 consist of Station A1 and the other cluster consists of the other five stations. Study on distribution of heavy metal pollution in Straits of Johor, Malaysia along 2003-2014 indicates Station A1 is exposed to high values of Zinc, temperature and salinity due to the location in the western end of Johor Straits, near to the shipping routes which prone to the pollution. The second objective conducted in this study involves identification of the effect of physical and chemical parameters on heavy metals along Johor straits using PCA, a multivariate approach which is commonly applied in environmental study. Based on PCA, the nine parameters known as conductivity, salinity, pH, temperature, dissolved oxygen, cadmium, manganese, nickel and zinc, are converted into three index variables, which explained the data set with minimum information loss. The first factor explained 30.8% of the total variance, the second and third factor explained 18.9 % and 11.4% of total variance respectively. The first index variable is grouped under chemical parameters factor, followed with physical variables as second index variables. In conclusion, the salinity, temperature, Cadmium, Manganese, Nickel and Zinc contribute the most in the components of this study of heavy metal pollution distribution. The issue regarding pollution along Johor straits is a continuous problem. The on-going activities around the area should be closely monitored. If there were recent collected data, it will be validated with the collected in-situ data between 2003 to 2014.

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