



ISSN: 0975-833X

RESEARCH ARTICLE

APPLICATION OF MULTIVARIATE STATISTICAL ANALYSIS IN THE ASSESSMENT OF WATER QUALITY OF VLORA BAY, ALBANIA

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ARTICLE INFO

Article History:

Received 19th December, 2014

Received in revised form

25th January, 2015

Accepted 10th February, 2015

Published online 17th March, 2015

Key words:

Water quality,
Pollution,
Cluster Analysis,
Principal Component Analysis,
Vlora Bay.

ABSTRACT

Aiming to assess the water quality and to evaluate the environmental pollution caused by different anthropogenic factors on Vlora Bay, the physical and chemical parameters were determined at 15 sampling sites during the February 2013. The seawater samples were collected at 7 sampling sites among the bay and 8 sampling sites of Narta and Orikumi Lagoons that are positioned in the Bay. The seawater samples were analyzed for 12 physico-chemical parameters such as temperature, pH, total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), salinity, red/ox potential, conductivity, and nutrients content (N-NO₃⁻, N-NO₂⁻, N-NH₄⁺ and P-PO₄³⁻). The analytical data were entered into a data matrix and were statistically treated with Descriptive Statistics method and multivariate analysis by using MINITAB 15 software package. Based on the similarity regarding the environmental situation, the sampling stations were classified into 3 main clusters by grouping in the same cluster the stations of the same lagoon and the next one belongs to the samples of the Bay. The principal component analysis identified four principal components that distinguish different factors that affect the environmental situation of Vlora Bay coastal area.

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INTRODUCTION

The quality of water is identified in terms of its physical, chemical and biological parameters (Sargaonkar and Deshpande, 2003). The anthropological influences (i.e., urban, industrial and agricultural activities) as well as the natural processes (i.e., changes in precipitation amounts, erosion and weathering of crustal materials) degrade surface water quality and impair its use for drinking, industrial, agricultural, recreational and other purposes (Carpenter *et al.*, 1998). A particular problem in the case of water quality monitoring is the complexity associated with analyzing the large number of measured variables and high variability due to anthropogenic and natural influences (Saffran, 2001; Simeonov *et al.*, 2002). The application of different multivariate statistical techniques, such as Cluster Analysis (CA) and Principal Component Analysis (PCA), helps in the interpretation of complex data matrices to better understand the water quality and ecological status of the studied systems, allows the identification of possible factors/sources that influence water systems, and offers a valuable tool for reliable management of water resources as well as a rapid solution to pollution problems (Wunderlin *et al.*, 2001; Reghunath *et al.*, 2002; Simeonova *et al.*, 2003; Singh *et al.*, 2004; Shrestha and Kazama, 2007).

Multivariate data analyses have been revealed to reduce data without losing the original information (Vega *et al.*, 1998; Singh *et al.*, 2004; Mendes, 2011). Reducing the number of variables makes the assessment process more rapid. The reduction in variable number in the original data aids in the identification of the relationships between variables. The Bay of Vlora represents one of the most attractive coastal zones of Albania, and it has been defined as a top-priority tourism area. Unfortunately, this area has suffered from the significant population growth and the increase of human activities in recent years (Rivaro *et al.*, 2011). The marine and coastal environment of Vlora constitutes resources of high economic and ecological value for the country. Due to the mismanagement of these resources in past years, considerable amounts of wastes have been discharged directly or through river flows and atmospheric deposits into the sea (Corsi *et al.*, 2011).

From 1967 to 1992 (when the production stopped), a chloro-alkali plant (producing soda and polyvinyl chloride [PVC] using very outdated technology), lying 4 km to the north of Vlora city, discharged relatively large amounts of liquid wastes containing mercury and other pollutants directly into the sea. Moreover, the Vjosa River, which originates in Greece and runs through the whole southern part of Albania, flows into the north of the bay, transporting eroded suspended material containing relatively high levels of nickel and chromium as

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well as most urban and agricultural pollutants (Rivaro *et al.*, 2011). Water exchange in bays is often limited and shipping activities introduce contaminants, which include oil, trace metals, nutrients and organochlorine compounds (UNEP, 1990). Finally, the natural composition of the waters could be affected by human pollution through water discharges from the surrounding cities (Tursi *et al.*, 2011).

The aim of this study was to assess the water quality of Vlora Bay and to evaluate the environmental pollution caused by different anthropogenic factors. For this purpose, the results obtained for the physico-chemical parameters and nutrients in water samples were statistically treated with descriptive statistics method and multivariate analysis; cluster and principal component analysis.

MATERIALS AND METHODS

Studied Area

Vlora Bay is a half-closed bay with a reduced water exchange with the Adriatic Sea throughout the mezo-channel inlet. It is positioned in the south part of Albania and faces to Karaburuni peninsula and Sazani Island. *Narta Lagoon*, with geographical coordinates: 40° 32' N latitude, 19° 28' E longitude (Lami, 2002), is located in the northwestern part of Vlora Bay. It is one of the biggest lagoons in Albania. *Orikumi Lagoon* is located in the southwestern part of Vlora Bay with geographical coordinates 40° 19' N latitude; 19° 25' E longitude (Phare, 2002). Figure 1 shows the map of the studied area and the positions of the sampling sites.



Figure 1. Network of sampling sites in Narta and Orikumi Lagoon and Vlora Bay

Sampling sites and methodology

Water samples were collected during the February 2013 according to a network of fifteen sampling sites positioned in the coastal area of Vlora Bay and two lagoons (Narta and Orikumi Lagoons) as is shown in Fig. 1.

The seawater samples were collected at 50 cm of deepness and about 50 m from the shore of the lagoons, while the seawater samples of Vlora Bay were collected at 150 cm of deepness and about 300 m from the shore. The sampling stations were selected in order to obtain a good assessment of the general environmental situation of Vlora Bay and to evaluate the probable polluting sources of the coastal area. Sample collection, transport and conservation were done according to the standard methods (APHA, 1998).

Water samples treatment

Water samples were collected in 1.5 liter PET bottles and were transported during the same day to the laboratory by refrigerated containers under the temperature of 4°C. The physico-chemical parameters of seawater samples were determined immediately in the laboratory. The seawater temperature, pH and red/ox potential were measured by using a pH meter (Model PHS-3BW). The conductivity (Cond) and total dissolved solids (TDS) were measured with a conduct meter (Model DDSJ 308A). Total suspended matter (TSS) was determined by pouring one liter volume of water through a pre-weighed filter of 0.42 µm pore size. The filter was weighted again after drying at 105°C for 2 hours till the constant weight. Winkler method was used for the determination of the concentration of dissolved oxygen (DO) content. Nutrients content (N-NO₃⁻, N-NO₂⁻, N-NH₄⁺, P-PO₄³⁻) was determined according to the APHA (1998) standard procedures by using the UV 2401 PC spectrophotometer for nitrogen compounds and PYEUNICAM SP-9 spectrophotometer for phosphate determination.

Statistical Analysis

To interpret the results and to explain the variations in the analytical data of 12 parameters and 15 sampling sites, the Descriptive Statistics method was applied. Finally, the data were processed by cluster analysis (CA) and principal component analysis (PCA) by using the MINITAB 15 software package. These statistical techniques have been widely used as unbiased methods in analysis of water quality data for drawing out meaningful conclusions (Simeonov *et al.*, 2003; Singh *et al.*, 2004) and to characterize and evaluate water quality for analyzing spatial and temporal variations caused by natural and anthropogenic processes (Helena *et al.*, 2000; Singh *et al.*, 2006; Bhat *et al.*, 2013). Multivariate data analyses have been revealed to reduce data without losing the original information (Vega *et al.*, 1998; Singh *et al.*, 2004; Mendes, 2011). Cluster analysis is used to detect the group of samples with similar patterns of the parameters and the parameters with reasonable similarity regarding the distribution among the different sampling sites. The numbers of the clusters and the most important principal factors related to the classification are after discussed. Cluster analysis is an important tool in multivariate

analysis. The levels of similarity at which observations are merged, form the dendrogram that provides a visual summary of the clustering process, presenting a picture of the clusters and their proximity with a dramatic reduction in dimensionality of the original data (Shrestha and Kazama, 2007). Principal component analysis (PCA) is used in this study. The loading plots of the PC's were used to show correlations between the original variables and the first two factors. It takes into consideration many variables, and explains them with a few "components" (Wunderlin *et al.*, 2001). The correlated variables are grouped together and separated from other variables with low or no correlation (Feoli and Orlęci, 1992).

RESULTS AND DISCUSSION

All the analytical data were entered into a data matrix, and the Descriptive Statistics method was applied to the physico-chemical parameters and nutrients concentration data to interpret the results, to explain the variations in the data, or to predict the future data (Table 1).

Table 1. Statistical data of physico-chemical parameters

	pH	E (mV)	Temp (°C)	Cond (mS/cm)	TDS (g/L)	Sal (‰)	TSS (mg/L)	DO (mg/L)	NO ₃ -N (mg/L)	NO ₂ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	PO ₄ ³⁻ -P (mg/L)
Mean	8.033	-56.8	8.94	49.76	25.66	33.31	90.56	8.672	0.0348	0.009	0.043	0.008
Median	8.07	-60.4	8.9	52.8	25.2	39.6	102.7	9.08	0.029	0.007	0.033	0.005
St.Dev.	0.177	8.940	0.297	17.97	9.825	11.74	44.23	1.295	0.020	0.006	0.032	0.010
Sample Variance	0.031	79.92	0.088	323.1	96.52	137.9	1955	1.675	0.0004	3.55	0.001	0.0001
CV%	2	16	3	36	38	35	49	15	57	67	74	125
Kurtosis	-0.84	0.009	0.188	-1.281	-0.985	-1.537	-1.052	-0.870	1.518	-0.103	0.370	13.57
Skewness	-0.369	1.065	-0.620	-0.175	0.345	-0.726	-0.243	-0.506	1.456	1.163	1.225	3.626
Min	7.72	-66.4	8.3	22.6	12.16	15.1	21.6	6.42	0.016	0.004	0.014	0.004
Max	8.28	-37.2	9.4	76.3	41.8	45.4	165.3	10.6	0.084	0.02	0.112	0.045
Sum	120.49	-852.3	134.1	746.4	384.89	499.6	1358	130.08	0.522	0.14	0.645	0.122
Conf.Lev(95.0%)	0.098	4.951	0.164	9.954	5.441	6.503	24.49	0.717	0.011	0.003	0.017	0.005

Most of the data of the physico-chemical parameters under investigation (except red/ox potential) followed the normal distribution, by means that the water system of Vlora Bay was stable regarding the different monitoring points of the Bay. The nutrients data were characterized by moderate and high values of the variance and were positively skewed. PO₄³⁻-P was characterized by high value of variance, and high values of Skewness and Kurtosis by indicating the strong influence of different factors (Qarri *et al.* 2014).

Multivariate analysis

Cluster Analysis

Aiming to distinguish the similar patterns of the seawater parameters, the Cluster Analysis of the observations was done using the computer program MINITAB 15.

Cluster analysis of the sampling sites

The sampling sites can be grouped into clusters of similar water quality features. The dendrogram of the correlation coefficients distance of sampling sites of Vlora Bay, Narta and Oriki Lagoon, obtained from Cluster Analysis, is presented in Figure 2.

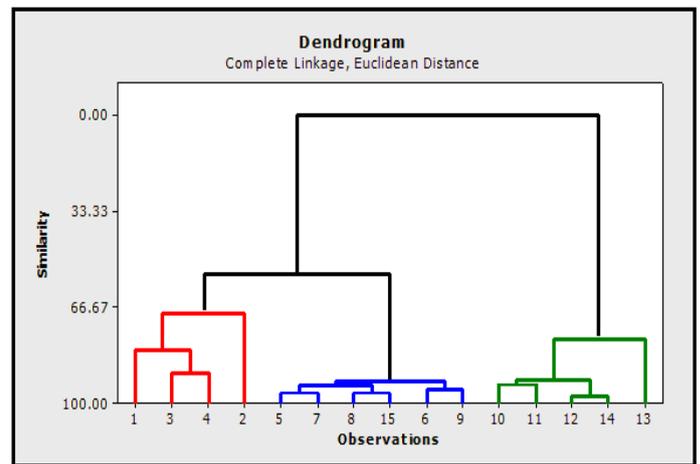


Figure 2. The dendrogram of cluster analysis based on the correlation coefficients distance of the dataset of the seawater samples of Vlora Bay. Final Partition: Cluster 1: St. 1, 2, 3 and 4; Cluster 2: 5, 6, 7, 8, 9 and 15, Cluster 3: St. 10, 11, 12, 13 and 14

The dendrogram of cluster analysis based on the correlation coefficients distance (see Figure 2) of the dataset of the seawater samples shows that the stations under investigation can be divided into three main clusters (complete linkage; correlation coefficients distance; similarity level 70 %, see Figure 2).

Cluster 1 represents a similarity level higher than 80% by grouping together the sampling sites St. 1, 3 and 4 of Narta Lagoon that are clustered together with the station 2 with a similarity level of about 70 %. The association of these stations in the same Cluster is due to their similar characteristics in the terms of the correlation coefficients distance of their physico-chemical parameters. The depth of Narta Lagoon (known as a shallow lagoon with 0.70 m to 1.50 m of deepness) and the urban wastewater discharges have a strong influence on the parameters under investigation of Narta Lagoon. The sampling site St. 2 is positioned close to the drainage channels of Panaja. St. 2 is associated with the other stations of Narta Lagoon with a similarity of 70% that is probably affected from the discharges of the Panaja drainage channels.

Cluster 2 is associated with the sampling sites St. 5, 6, 7, 8, 9 and 15 that are positioned in Vlora Bay and represents a high similarity level (>95%). The high similarity level of the stations of Vlora bay is probably related to the similar pollution sources at the open sea. The most probable pollution sources of Vlora Bay are the urban wastewater discharges from the surrounding cities (Tursi *et al.*, 2011), maritime traffic, fishing activity etc.

Cluster 3 is associated with the sampling sites St. 10, 11, 12, 13 and 14 that are positioned in Orikumi Lagoon. This association is probably influenced by the discharges of urban wastewaters and agricultural runoff discharged from the surrounded areas, causing a higher nutrient content compared to other studied areas. The sampling sites St. 10, 11, 12 and 14 represent a similarity level higher than 95%, while the sampling site St. 13 appear a similarity of about 80% with the St. 10, 11, 12 and 14. St. 13 is positioned in the southwestern part of the Orikumi Lagoon and very close to the spring of fresh water from the bottom of the lagoon. The mixing of the lagoon's water with the fresh water in this station causes the reduction of salinity and normal physico-chemical parameters and nutrients content by decreasing the similarity level of St. 13 from the St. 10, 11, 12 and 14.

Cluster analysis of physico-chemical parameters and nutrients

The dendrogram of the correlation coefficients distance of the physico-chemical parameters and nutrients content in seawater samples of Vlora Bay is presented in Figure 3. Based on their similarity levels between the parameters under investigation, it is possible to identify the problematic parameters that affect the environmental situation of the bay.

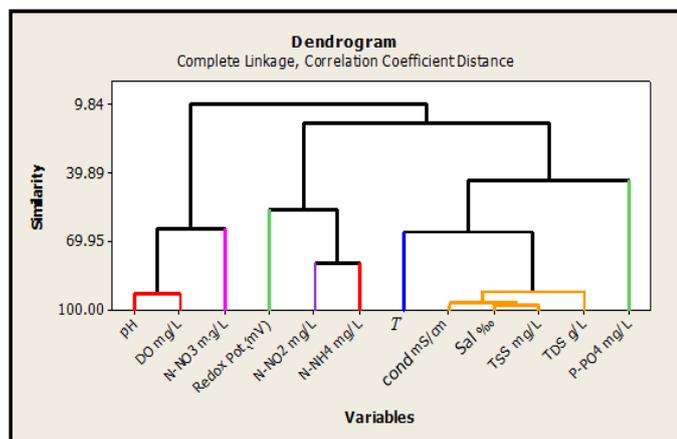


Figure 3. The dendrogram of cluster analysis based on the correlation coefficients distance of the parameters under investigation. Final Partition: Cluster 1: pH, DO; Cluster 2: Temperature; Cluster 3: red/ox potential; Cluster 4: TSS, TDS, salinity and conductivity; Cluster 5: N-NO₃⁻; Cluster 6: N-NO₂⁻; Cluster 7: N-NH₄⁺; Cluster 8: P-PO₄³⁻

Eight individual clusters were obtained from cluster analysis based on the correlation coefficients distance of the parameters under investigation.

Cluster 1 appears a similarity level higher than 95% and is associated with the pH and DO. This association is probably

affected from the diurnal fluctuation pattern of these parameters with the intensity of photosynthesis process in the water system. The carbon dioxide CO₂ that is required during the photosynthesis causes pH to peak up in the afternoon, while the accumulation of CO₂ during dark causes the decrease of the pH to be at its minimum before dawn (<http://www.neospark.com>). Both parameters (DO and pH) are affected by the photosynthesis process in seawater.

Cluster 2 includes temperature, a very important parameter of water quality. A number of parameters are depended from the temperature. Some important parameters like the TSS, TDS, salinity and electrical conductivity (Cluster 4), show a similarity of 70% with temperature (Cluster 2). The DO is also affected by the water temperature; as the temperature and the salinity increases, the solubility of oxygen in the water decreases (PHILMINAQ, <http://www.aquaculture.asia>).

Cluster 3 is associated with the red/ox potential which is the activity or strength of oxidation and/or reduction process in seawater. Negative values of this parameter in all stations, indicates the reducing properties of seawater (Bellingham, <http://www.stevenswater.com>). The red/ox potential show a similarity of 55% with Cluster 6 and 7 (nitrite and ammonium). It is probably associated with the reducing properties of seawater that may inhibit the oxidation of ammonium in nitrite and nitrate. On the other hand it may allow the reduction of nitrite and nitrate to ammonium.

Cluster 4 is associated with the parameters of the conductivity, salinity, TSS and TDS that appear a similarity higher than 95%. These parameters resulted to be stable and to have a similar view, regarding the results obtained (see Table 1). The conductivity is often referred to the water quality parameters like salinity and TDS. The TDS and the salinity are associated with the presence of the dissolved inorganic ions such as Mg⁺⁺, Ca⁺⁺, K⁺, Na⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and CO₃²⁻ (Bellingham, <http://www.stevenswater.com>). This might be the reason of the high similarity between these parameters. The TSS and TDS are important parameters for evaluating the water quality. These parameters are also affected by the photosynthesis processes in water (PHILMINAQ, <http://www.aquaculture.asia>).

Cluster 5 is associated with the nitrates that are one of the common forms of nitrogen in natural waters. Nitrate levels over 5 mg/L in natural waters normally indicate man made pollution, such as fertilizers, livestock, urban runoff, septic tanks, and wastewater discharges (Bellingham, <http://www.stevenswater.com>). Nitrates in Narta and Orikumi Lagoon and Vlora Bay are mainly of natural origin. The high content of nitrates in sampling sites St. 7 and 12 is probably associated with the anthropogenic sources of origin. High levels of nitrates cause the eutrophication of the water, which stimulates the growth of algae and reduces the amount of dissolved oxygen in the water.

Cluster 6 is associated with the nitrites, which are found as an intermediate compound obtained from microbial reduction of nitrates or ammonium oxidation. This is why nitrite and ammonium (*Cluster 7*) show a similarity level higher than

75%. The phytoplankton and wastewater discharges are another probable source of nitrites in the water. Meanwhile, high level of ammonium is a reliable indicator of sewage discharges and livestock liquid wastes.

Cluster 8, with less than 50% of similarity with other parameters, is associated with the phosphates ($P-PO_4^{3-}$). Low content of phosphates was found at all sampling sites. Low content phosphates are determined as the limiting element of the eutrophication of the seawater of Vlora Bay and both lagoons.

Principal Component Analysis (PCA)

Through the results of Principal Component Analysis (PCA), the principal components were extracted, and interpreted as source categories contributing to parameters level at the sampling sites. The results of the PCA analysis are shown in Table 2.

Table 2. The results of principal component analysis

Variable	PC1	PC2	PC3	PC4
pH	-0.109	0.871	-0.099	-0.337
Red/ox Potential (mV)	0.013	-0.937	0.050	-0.117
T(°C)	0.411	0.133	0.112	-0.089
Conductivity (mS/cm)	0.899	-0.194	-0.195	0.205
TDS (g/L)	0.868	-0.379	-0.171	0.112
Salinity (‰)	0.918	0.019	-0.173	0.048
TSS (mg/L)	0.893	-0.169	-0.238	-0.039
DO (mg/L)	-0.381	0.891	-0.025	-0.139
N-NO ₃ (mg/L)	-0.438	0.161	-0.040	0.041
N-NO ₂ (mg/L)	-0.503	-0.210	0.504	0.253
N-NH ₄ (mg/L)	-0.370	-0.097	0.905	-0.125
P-PO ₄ (mg/L)	0.121	-0.136	-0.076	0.976
Variance	4.1252	2.7571	1.2590	1.2470
% Var	0.344	0.230	0.105	0.104

Four principal factors (PC) were extracted through the PCA analysis that represent a total variance of 78.3%.

PC 1 is the strongest PC that represents 34.4% of the total variance. It is associated with high loads of TDS, Salinity, TSS and Conductivity. The marine currents are the main factor that may cause the variability of these parameters. The Bay receives particulate matter, nutrient and other dissolved element inputs from Vjosa and Shushica rivers, as well as from industrial, urban and agricultural activities along these rivers and the estuary around the Vlora Bay (Qarri *et al.*, 2014). TDS, Salinity, TSS and Conductivity values decrease as the distance from the delta of Vjosa River is increased. As it expected, the lowest values of these physico-chemical parameters resulted in Orikumi lagoon due to the mixing of lagoon water with fresh water (near Marmiroi Church)

PC 2 is the second strongest PC with 23 % of the total variance. It is associated with high loads of pH and DO. The variability of pH and DO is mainly affected by photosynthesis. In this study, pH and DO resulted in higher levels in Orikumi Lagoon.

PC 3 represents 15% of the total variance. This PC is associated with high loads of NO₂-N and NH₄⁺-N. The reduction conditions of seawater cause the transformation of

nitrites to ammonium. The high level ammonium is a reliable indicator of sewage discharges and livestock liquid wastes from the surrounded populated areas, by indicating an anthropogenic factor.

PC 4 represents 10.4% of the total variance. This PC is associated with phosphates which in general resulted in low content in the both lagoons and in the sea stations. The phosphate contents are mainly generated by urban discharges such as phosphate fertilizers and detergents.

Conclusion

Physico-chemical parameters content in combination with the multivariate analysis is successfully used in this study to assess the water quality of Vlora Bay. Three main clusters resulted from the cluster analysis of the dataset of the investigated samples by clustering together in a reasonable way the sampling sites under investigation. Cluster 1 and 3 grouped together the sampling sites of the same lagoon and the next cluster was formed with the sampling sites of the Bay, by indicating a high similarity of environmental situation of each ecological system; Vlora Bay, Narta Lagoon and Orikumi Lagoon. Eight reasonable clusters resulted from the cluster analysis of the dataset of the investigated physico-chemical and nutrients parameters. The classifications were based on the similar characteristic features regarding their distribution in water samples under investigation. The PCA analysis identified four important PC's and the main pollution sources were identified. The variability of the parameters is mainly caused by the marine currents and the particulate matter, from Vjosa and Shushica Rivers inputs in the north of the bay. The discharges from the shipping activity in the bay as well as the industrial, urban and agricultural activities along these rivers and the estuary around the Vlora Bay are distinguished as the main factors affecting the environmental situation of the Bay and the two lagoons.

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