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Characterization of seawater quality in stressed coastal zone of Iligan Bay

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Abstract. A small portion of the coastal zone along Iligan bay stretching from barangay Dalipuga to Kiwalan, was under stress brought about by rapid development of industries and growth of population. Seawater quality in this area was examined using 12 physico-chemical and biological variables. The prime object of the study was to characterize the seawater quality in the stressed coastal zone by specifically sorting and identifying most important variables that capture and could best describe the current seawater quality condition. The multivariate statistical approach was used to help discover the structure of variables needed for characterization. Principal Component Analysis effectively reduced the 12 variables into 3 component factors namely: PC 1 which is related to abundance of microbial contaminants has an eigenvalue of 2.54, hence declared as significantly different from the other variables; PC 2 pertains to phosphate loading with eigenvalue of 1.94 and PC 3 which is related to physical factors with eigenvalue of 1.16. Scatter plot produced from PCA revealed that the entire study area was generally uniform in characteristics. Based on PC 1, the seawater quality of the stressed coastal zone was characterized generally as poor, and therefore not safe for recreational and fishing activities.
Key Words: Multivariate analysis, principal component analysis, stressed coastal zone, seawater quality.

Introduction. Seawater quality in marine ecosystem changes and differs over time and space depending on a number of factors: anthropogenic influences, level of urbanization and development, and seasons or changes in weather. Thus, characterization and identification of factors affecting water quality including its structure causing spatial variations is imperative for making informed decisions concerning coastal management.

With increasing urbanization and development *e.g.* rapid increase of households coupled with industrialization, will inevitably cause changes in the nearby bodies of water. Goldberg (1995) pointed out that the primary factor driving ocean pollution is the increase in population, which uses more energy and material resources that eventually produce wastes that can enter the ocean in an unacceptable amount. The coastal zone in the study is not far from this reality. It is under stress brought about by industrial development and rapid growth of population, and thus assumed as being the reservoir of the continued influx of various contaminants coming from both point and non-point sources.

In Taihu watershed in China, Xiao-long et al (2007) identified that the anthropogenic factor is the cause of considerably unfavorable changes in the water quality *viz.* increase nutrient loading particularly nitrogen and phosphates, which lead to deterioration of water quality.

Many other similar reports firmly established the fact that urban communities are one of the major sources of faecal associated bacteria (Haller et al 2009; Mallin et al 2000). The industries as well is identified as a point source of organic chemical contaminants, various nutrient elements, PCB's, and pesticides (Xiao-long et al 2007; O'Connor & Hugget 1988) and metals from mining areas that runoff to seas (Levings et al

2005). The coastal waters receive variety of these contaminants that pollute seawater in which its horizontal distribution in space may not be uniformed.

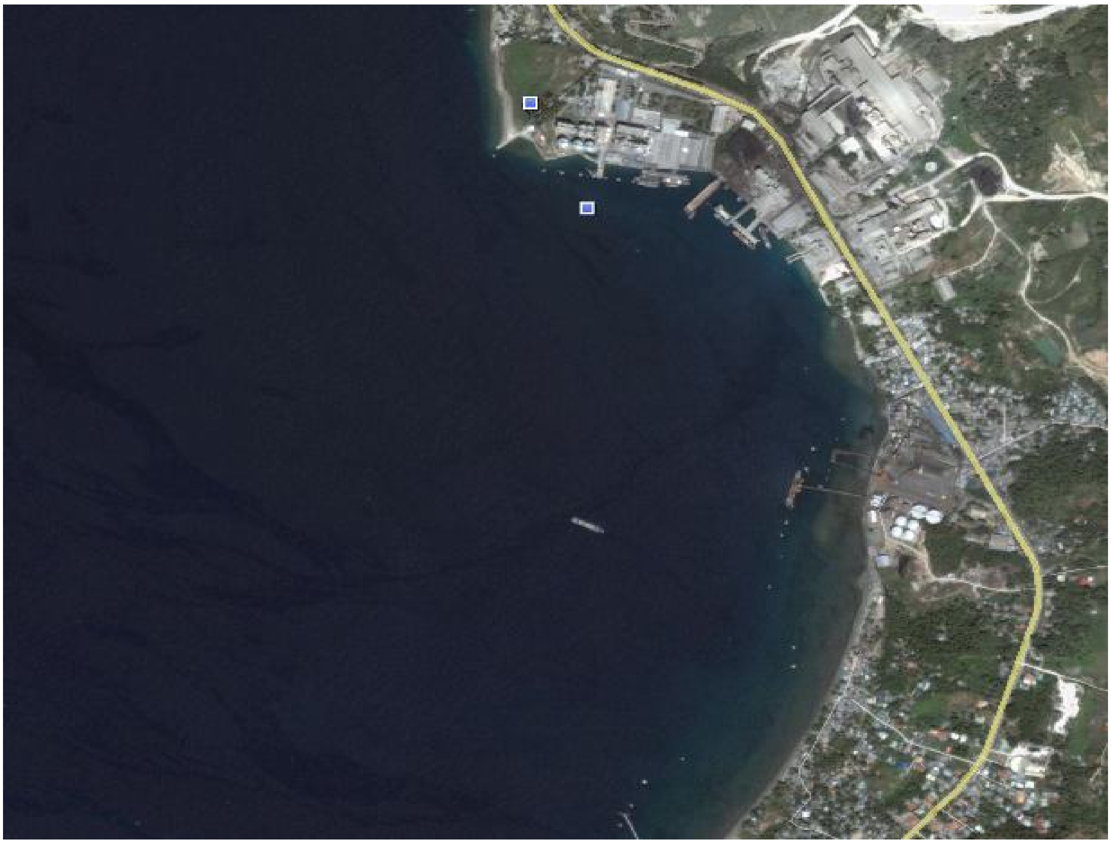

Figure 1. Portion of Iligan bay subjected to stress by industrial development and urbanization.

The study area in Figure 1, which is part of the Iligan bay stretching from Dalipuga to the outskirts of Kiwalan in Iligan city is a coastal zone spoiled by continuous influx of sewage through estuary, wastewater from industries and ballast water from ships at the industrial wharf.

The maintenance of seawater quality in this coastal zone is of paramount importance for sustaining the marine ecosystem and livelihood of some residents, and keeping the coastal area safe for recreational activities. Knowledge therefore on the character of seawater quality and the structure variables is important for effective interventions.

The present study characterized the seawater quality in the coastal zone using multivariate analysis involving 12 parameters combining physico-chemical and biological variables. It specifically aimed to determine the structure of the variables and to identify dominant factor causing large spatial variations of seawater quality. Since the study area it is used by some residents as a recreational area aside from fishing activities, biological parameters included were the presence and levels of faecal indicator bacteria (FIB). The assumption was that both the residents and industries contributed to biological contamination specifically bacteria of faecal origin. FIB is coliform and has been used effectively as bioindicator of water quality.

Material and Method

Study area. A small portion of Iligan bay, 20 to 50 meter from the coastline stretching from barangay Dalipuga (N 8^0 16.547”, E 124^0 15.698”) to the next barangay of Kiwalan (N 8^0 16.754”, E 124^0 15.752”) was selected. The selected coastal zone was under stress brought by the industrial development and rapid growth of population. Current usage of the coastal zone is for fishing and recreational activities. Industries were using the coastal zone as wharf areas for cargo ships where ballast water can be unloaded.

The entire study area was divided into 3 stations, each with 4 samples of seawater obtained at the surface. Station 1 was near an oil industry of San Miguel Corporation, station 2 was at the area fronting another oil industry (Granex) to the wharf area of Iligan Cement Corporation. The last is station 3, very near of a feed industry of Pilmico.

Sampling and sample analysis. Twelve cleaned and acid washed polypropylene bottles for physico-chemical analysis plus another 12 pre-autoclaved and sterilized bottles for microbial analysis were prepared in the laboratory and brought to the field. A total of 24 samples were obtained at the study area, 8 samples from each station which later divided into two groups, the first group of bottles was for microbial analysis while the second was for physico-chemical analysis. Surface water (~20 cm deep), was obtained manually and immediately secured in an ice bucket for delivery to the laboratory within 6 hours.

Temperature and pH data were obtained *in situ* immediately after getting water samples. Nitrate concentrations of seawater samples was determined using Resorcinol method, in which 5.0 ml of a seawater sample was transferred into a 25 ml volumetric flask, and 0.6 ml of 2% (w/v) resorcinol solution was added. The flask was then swirled to mix the resorcinol with the sample. This was followed by carefully adding 5.0 ml of concentrated sulfuric acid. The flask was then closed with stopper and then gently swirled to mix the solution. The flask was placed in the dark and allowed to stand for 30 min. It was then placed in a water bath at room temperature for 5 min to ensure it reaches room temperature. The volume was adjusted to the mark with deionized water and the absorbance of the sample was observed by spectrophotometric method.

For nitrite determination, the Griess Reaction method was followed. A 50 uL seawater sample was poured into a well in which a sulfanilamide solution and NED solution was added using a multichannel pipettor. The solution was incubated for 10 minutes under dark condition until a magenta color developed. Absorbance was then measured and recorded.

Phosphorus was determined using Molybdenum Blue method. Water samples about 100 ug was transferred to a flask and added with water to give a volume of 5 mL. 1 mL of 1ON H_2SO_4 was added, mixed until the solution turned blue. 2 mL of Na_2SO_3 plus water to bring the volume to 10 mL, and absorbance was then measured.

For microbilogical analysis, the usual serial dilution was made and sample of water was added to a broth (Laurel sulfate broth, Brilliant Green Bile Broth, EMB). Appearance of gas in broth indicates presence of gas forming bacteria. Samples from it were plated in an agar, incubated and the colony forming units (cfu/100 mL) were determined and compared to the standard. For identification of specific group of bacteria, differential growth media were used *viz.* indole methyl red vogues praskeur (IMVIC), sulfide motility indole (SIM), and triple sugar iron agar (TSI). All approaches following the standard microbiological procedures.

Multivariate analysis. The structure of the water quality indicator was explored using multivariate analysis. Data on the 12 variables were pooled and subjected to Principal Component Analysis (PCA) to sort variables and identify the most important that best describe the character of seawater quality. Significant component factor was identified based on eigenvalue. Any principal component (PC) with eigenvalue >1.0 was considered significant following the procedudre of Xiao-long et al (2007). Multivariate analysis was implemented using PAST software version 1.78.

Non-normal distribution of data was log transformed before subjected to analysis of variance (ANOVA). The Analysis of variance was used to determine significant differences among stations, samples and variable. All these statistical operations were implemented using SPSS software version 12.

Results and Discussion

Physico-chemical parameters. Table 1 shows values for all 6 physico-chemical parameters per sampling point in all three stations. Average nitrate concentration in stations 1, 2 and 3 (not shown in Table 1) is 0.003 ppm, 0.005 ppm and 0.003 ppm respectively. Analysis of variance for nitrates in all 3 stations did not differ significantly ($p = 0.33$, $\alpha = 0.05$). The same pattern was observed for nitrites and phosphates in all the stations across 12 samples with $p = 0.9422$ and $p = 0.3596$ respectively at 5% level of significance.

Except for sample 8 in station 2 and sample 12 in station 3, with respective salinity values of 26.67 ppt and 31 ppt, all other samples in all 3 stations is 30 ppt. Since distribution of salinity values across all samples and stations is not normal, nonparametric test was used and it shows that all 3 stations did not differ significantly from each other. The same pattern was also observed in temperature that range from 28 to 29 degree centigrade in the entire study area.

Potential of Hydrogen (pH) value ranges from 6.52 in sample 7 located in station 2 to 9.05 in sample 3 located in station 1. Analysis of variance after log transformation of pH values revealed that all 3 stations across all samples is not significantly different ($p = 0.188$) at 5% level of significance.

Although the entire study area has long been a reservoir of various contaminants from different sources *i.e.* households, oil industry, cement and feed milling industry; uniformity of seawater quality in terms of physico-chemical factors is still observed. This pattern of contaminant distribution in space is different from that observed in Taihu watershed in China in which there is much variation affected by differences in anthropogenic activities (Xiao-long 2007). Comparing the spatial coverage of both study areas, Taihu watershed covered large area encompassing two large provinces of Jiangsu and Zhejiang plus the municipality of Shanghai. The stress coastal zone of Iligan bay on the other hand, covered only two small adjacent barangays of Dalipuga and Kiwalan. Thus the physico-chemical characteristic pattern observed in the present study could be related to distance. Furthermore, the long continuous loading of nutrients in the coastal area coupled with seawater current and activities of man may have been the caused of spread of nutrient contaminants and uniformity of seawater quality.

Biological parameters. All 3 stations in the selected coastal area have been contaminated by microbiological organisms of fecal origin *viz. Enterobacter, Citrobacter, Kleibsiella,* and *E. coli* (Table 1). Stations 1 and 2 have the human pathogen *Salmonella*, except station 3 near an oil industry. The most common bacteria present belong to *Enterobacter* group followed by *E. coli*. The lowest was *Salmonella* since it did not occur in station 3.

All samples in 3 stations have considerably high MPN index, indicating high level of population abundance compared to the US and EU standard (Mallin et al 2000). The results obtained clearly suggest seawater pollution in the stressed coastal zone of Iligan bay caused by microbial organisms. There are various sources of these contaminants classified as point and non-point sources. Mallin et al (2000), considered the presence of canals and impervious land surfaces in the adjacent industries and household communities as a non-point source. He further indicated that these non-point sources are highly correlated to the presence and abundance of fecal indicator bacteria (FIB). The growing number of households at the seashore is considered as a point source of FIB. Mailo & Tschetter (1981) have already indicated the high correlation between population factor and presence as well as abundance of FIB.

Based on the biological data obtained, the seawater at the coastal zone is characteristically poor in quality. Fishing activity and recreation may be risky since direct contact with contaminated seawater and consumption of fishes may lead to human illness (Epstein 1998). The MPN values of $\geq$1600 or cfu/100 mL in the seawater samples, indicates that it is not even fit for swimming based on EU fecal coliform standard of 100 MPN (Haller et al 2009; Rees et al 1998).

Table 1

Physico-chemical concentrations, MPN index and presence/absence of bacterial groups per station and sample

Station (sample #)	*Nitrate (ppm)*	*Nitrite (ppiom)*	*Phosphate (ppm)*	*Salinity (ppt)*	*Temperature (^0C)*	*pH*	*MPN index*	*Enterobacter*	*Citrobacter*	*Kleibsiella*	*E. coli*	*Salmonella*
Station 1 (1)	0.004	1.000	0.400	30.00	29	8.36	≥1600	1	1	0	0	0
Station 1 (2)	0.001	0.600	0.500	30.00	29	8.72	≥1600	1	0	1	0	0
Station 1 (3)	0.005	0.600	1.500	30.00	28	9.05	≥1600	1	0	0	1	0
Station 1 (4)	0.002	0.633	0.300	30.00	28	8.06	≥1600	0	1	0	1	1
Station 2 (5)	0.003	0.733	5.000	30.00	28	8.27	≥1600	1	0	1	1	0
Station 2 (6)	0.004	0.633	1.400	30.00	28	8.30	≥1600	1	1	1	0	0
Station 2 (7)	0.004	0.667	1.367	30.00	28	6.52	≥1600	1	1	0	0	0
Station 2 (8)	0.007	0.800	0.400	26.67	28	8.50	≥1600	1	0	0	1	1
Station 3 (9)	0.004	0.600	0.500	30.00	28	8.92	≥1600	1	0	1	1	0
Station 3 (10)	0.003	0.700	1.167	30.00	28	8.75	≥1600	0	1	0	0	0
Station 3 (11)	0.003	1.133	3.233	30.67	29	8.64	≥1600	1	0	1	1	0
Station 3 (12)	0.003	0.600	0.500	31.00	29	8.59	≥1600	1	1	0	1	0

1 and 0 values for bacterial groups indicate its presence and absence in stations and samples.

Table 1 shows that all the microorganisms found in the current study belong to an enteric group of bacteria, and are used widely as indicator of microbial pollution (An et al 2002; Noble et al 2003; Owili 2003; Kashefipour et al 2002; Hughes & Thompson 2004). It was reported that the presence and abundance of these organisms is highly correlated to wastewater (Noble et al 2003) and human illnesses (Haile et al 1999).

Among 5 microbial groups identified, *Enterobacter* is present in almost all samples indicating widespread spatial distribution. This pattern may be related to its surviving ability, for example the high vulnerability to sunlight degradation of *E. coli* than to enteroccoci - *Enterobacter* (Sieracki 1980). Furthermore, *E. coli* has been observed to survived only in 0.8 d than to enterococci which survive up to 2.4 d in marine water (Hanes & Fragala 1967).

Structure of seawater quality variables. To understand the character of seawater quality, it is necessary to sort and structure indicator variables and identify the most important factor that capture and best describe its current condition. Brogueira & Cabeçadas (2006) used multivariate statistical approach to solve this problem. Similarly, Xiao-long et al (2007) used specifically the Principal Component Analysis (PCA) coupled with cluster analysis (CA) in exploring variables that best characterized water quality of 19 tributary rivers of Taihu watershed in China. In the present study, the 12 variables were successfully reduced into 3 factor components *viz.* PC 1 which is related to microbial abundance significantly differ from the other variables (Figure 2).

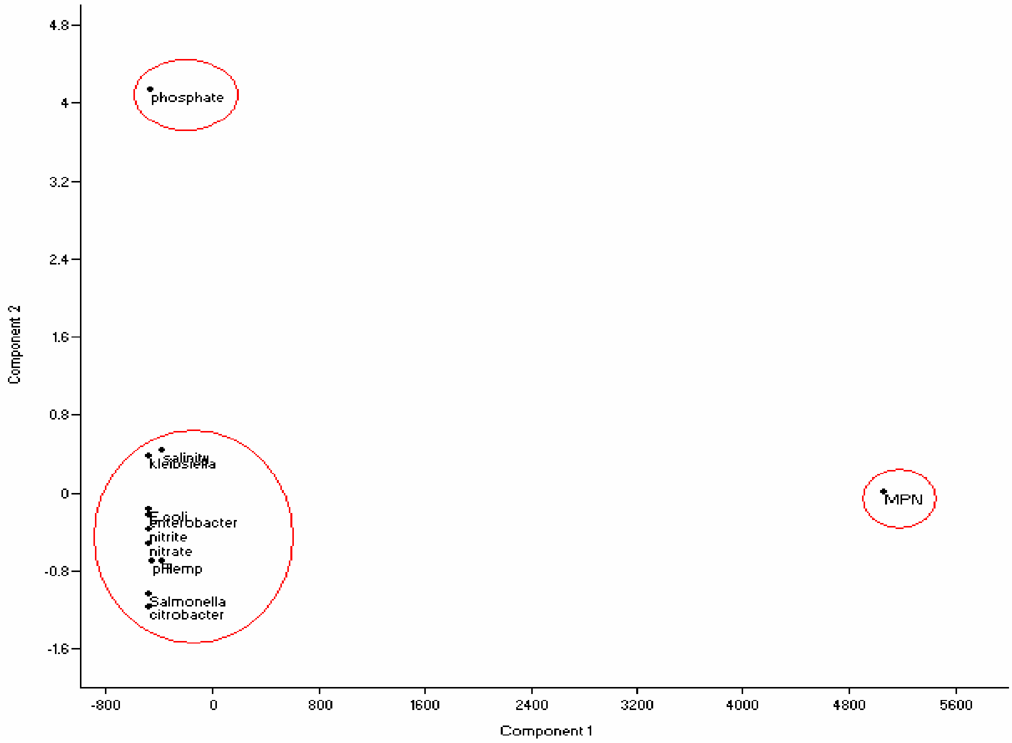

Figure 2. Scatter plot produced from principal component analysis (PCA) separating variable into 3 groups.

PC 2 pertains to phosphate loading, is also significantly different from the other variables with eigenvalue of 1.94 (Table 2). PC 3 relates to the physical aspect (Figure 3) with eigenvalue of 1.16 (Table 2), hence declared as significant. It can be observed from table 3 that PC 1 effectively separates MPN from the rest of variables since it is the only one with positive PC loading. In PC 2, phosphate has the highest positive loading followed by salinity and presence of *Kleibsiella*. PC 3 has positive loading for both physical variables salinity and temperature, except the presence of *Citrobacter*. In the implementation of principal component analysis, any factor component with eigenvalue greater than unity (eigenvalue >1) is statistically, considered as significantly different from the rest (Xiao-long et al 2007). From among the principal components, only the first 3 PC's were found to be significantly different from the rest of the variables, hence construed as the most important factor capturing the character of seawater quality.

Table 2

Eigenvalue and variance per Principal Component (PC)

PC	*Eigenvalue*	*% Variance*
1	2.54E+06	100
2	1.94343	7.65E-05
3	1.16036	4.57E-05
4	0.53843	2.12E-05
5	0.308349	1.21E-05
6	0.180049	7.09E-06
7	0.159373	6.27E-06
8	0.0868911	3.42E-06
9	0.0187409	7.38E-07
10	0.0114773	4.52E-07
11	0.0027459	1.08E-07
12	8.05E-28	3.17E-32

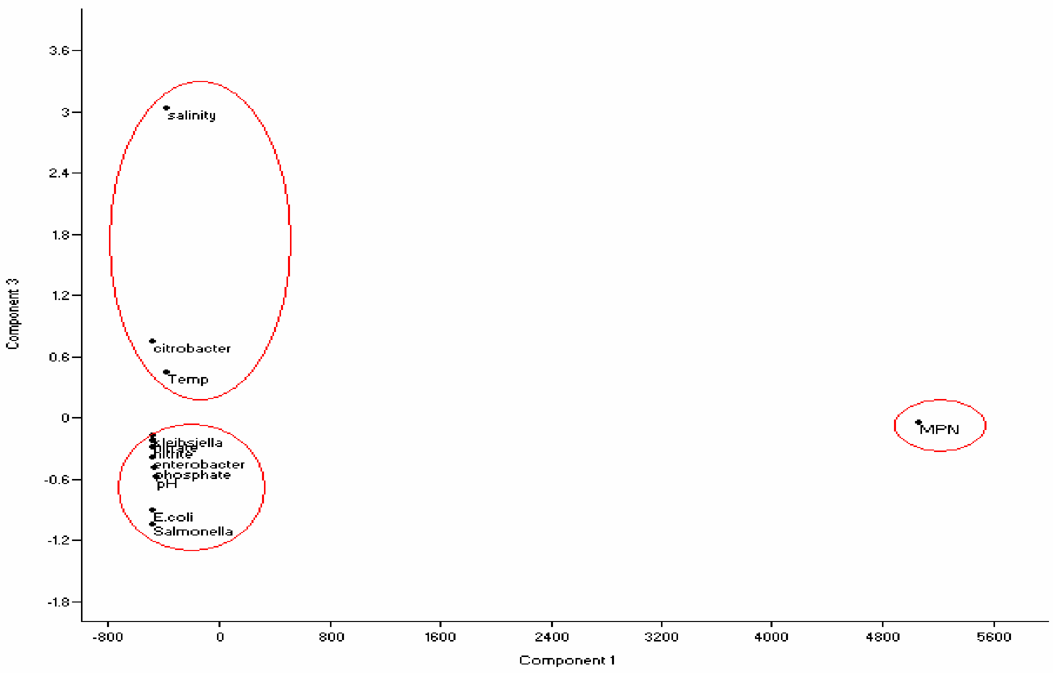

Figure 3. Scatter plot of principal component analysis (PCA) showing PC1 and PC2.

Figure 4 illustrates the effects of the first 2 principal components on the distribution of samples and stations on the planar plot. Although PC1 and PC2 accounts for most of the variations of samples, surprisingly majority of the samples in 3 stations tend to coalesce together indicating that seawater quality in the coastal area is generally uniform. The separation of the samples 5 and 8 in station 2 and sample 11 in station 3 could be attributed to random effect.

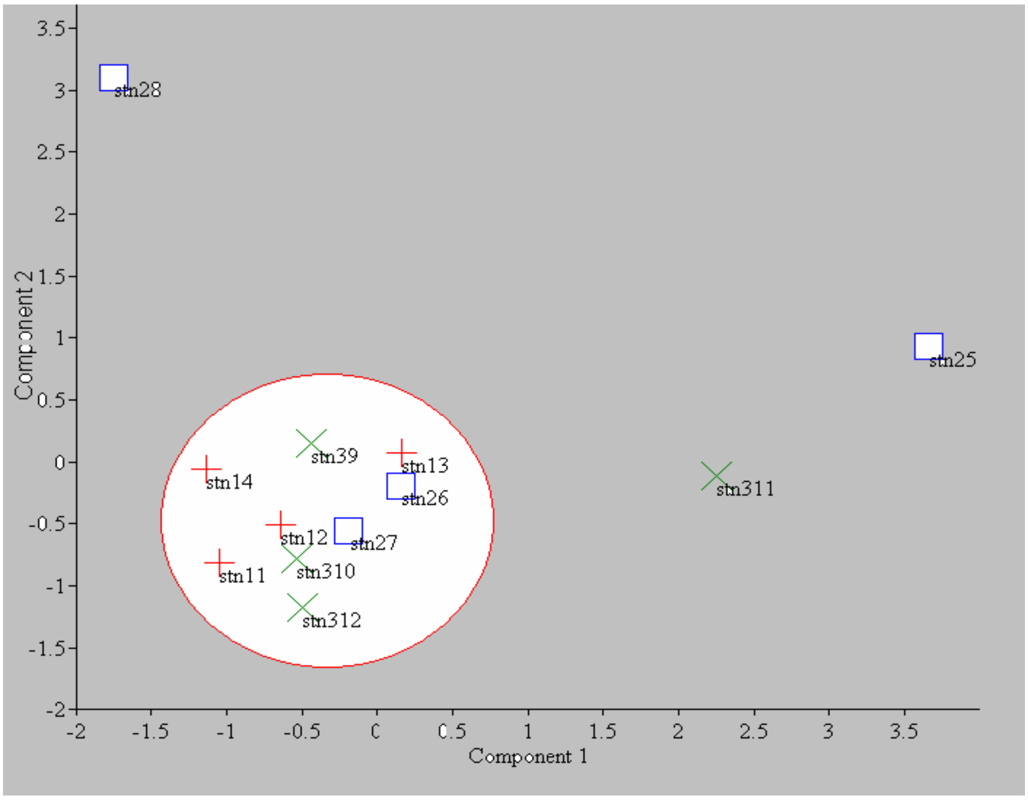

Figure 4. Scatter plot illustrating the effect of first 2 components on all 12 samples in 3 Stations.

PC 1 in Table 3 is a factor component related to MPN index accounts perfectly the variations among 12 variables. Since its eigenvalue of 2.54 is >1, its variation from the rest of the variables is significant. It means therefore that PC 1 is important and could be used as a new character to describe seawater quality. The rest of variables are less important in a sense.

The results of the present study happen to appear that only PC 1 is an important factor component. This circumstance may be attributed to distance and compactness of the study area. It is therefore recommended that the method be applied in a larger scale to discover spatial variations in seawater quality when two or more factor components play an important role.

Table 3

Principal component loading matrix

Variables	*PC1*	*PC2*	*PC3*
Nitrate	-482.41	-0.52619	-0.23124
Nitrite	-479.91	-0.37493	-0.29157
Phosphate	-477.73	4.1322	-0.50241
Salinity	-378.98	0.43884	3.0293
Temperature (^{0}C)	-384.28	-0.71002	0.43344
pH	-453.36	-0.70715	-0.57996
Enterobacter	-479.54	-0.23118	-0.40016
Citrobacter	-480.69	-1.1746	0.74049
Kleibsiella	-480.98	0.36948	-0.17914
E. coli	-480.4	-0.17915	-0.90917
Salmonella	-481.85	-1.0426	-1.0495
MPN	5060.1	0.005327	-0.06015

Conclusions. To understand seawater quality several variables are involved. Determination of its structure and identifications of the most important component factor can effectively be done by multivariate analysis, specifically Principal Component Analysis (PCA). The factor component or PC's will serve as a new character to describe seawater quality and by using the important components to plot the data or attributes, spatial variations may be discovered.

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