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ASSESSMENT OF RIVER WATER QUALITY VIA ENVIRONMENTRIC MULTIVARIATE STATISTICAL TOOLS AND WATER QUALITY INDEX: A CASE STUDY OF NAKDONG RIVER BASIN, KOREA

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Abstract: Nakdong River Basin has been extensively studied to assess the overall water quality and to identify the major variables responsible for water quality variations in the basin. A total of 14 sampling points were selected in the riverine network of the River Basin during the year of 2011. Specifically, the temperature, pH, DO, BOD, COD, TP, TOC, TSS, NH_4-N, NO_3-N, PO_4-P, Chl.α and Cl were investigated. Based on the WQI and NWQS, the river quality status for Nakdong River Basin falls under good to moderate class which indicate that, the water is suitable for industries and irrigation. Thus, they may not be suitable for recreational, water supply or fisheries purposes. Environmentric multivariate statistical tools of correlation matrix, factor analysis (FA) and cluster analysis (CA) revealed that the surface water quality was mainly controlled by anthropogenic activities. Therefore, the identification of the main pollution sources in the River Basin will help water authorities make better and more informed decisions on the improvement of Nakdong River water quality.

Keywords: Correlation analysis, Factor analysis (FA), Cluster analysis (CA), Water Quality Index (WQI)

1. INTRODUCTION

Rivers are important resources because they are directly used for drinking, domestic, agriculture, transportation, power generation, recreation, and other human activities including waste disposal. However, discharge of untreated or partially treated industrial effluent, municipal wastewater, as well as washing clothes and cattle bathing adversely affect river water. Human settlements and industries have long been concentrated along rivers, estuaries, and coastal zones owing to the predominance of water-borne trade. A river's water quality is the composite of several interrelated compounds, which are subjected to local and temporal variations and also affected by the volume of water flow (Mandal et al., 2010). Rivers constitute the main inland water body for domestic, industrial, and agricultural activities and often carry large municipal sewage, industrial wastewater discharges, and seasonal runoff from an agricultural field (Singh et al., 2004; Pradhan et al., 2009; Hu et al., 2011). The river waters have been contaminated as a result of the discharges of wastewater containing degradable organics, nutrients, domestic effluent, and agricultural waste (Dimitrovska et al., 2012). Anthropogenic influences such as urbanization, industrial and agricultural practices, chemical spill accidents, dam construction, and natural processes like erosion and climatic conditions, could each affect surface water quality. However, the degree to which each factor contributes to water quality is unclear (Zhang et al., 2009). Thus, in order to help managers prioritize and make rational decisions as to the best course of action for improving water quality, it is necessary to decrease this uncertainty by interpreting temporal and spatial variations in water quality (Wang et al., 2013) and identifying the latent pollution sources.

In recent years, there has been increasing awareness and concern about the surface water pollution all over the world, and new approaches toward the sources of pollutants and achieving sustainable exploitation of water resources have been developed. The combined use of environmentric tools such as multivariate statistical techniques and water quality index (WQI) enables the classification of water samples into distinct groups, source apportionments, relationship, and differences in the parameters used based on hydrochemical characteristics (Shrestha et al., 2008, Venkatramanan et al., 2012). They reflect more accurately the multivariate nature of the natural ecosystem, which provides a way to handle large datasets with a large number of parameters by summarizing the redundancy and provides a means of detecting and quantifying truly multivariate patterns of the datasets (McGarigal et al., 2000). The use of conventional techniques of descriptive analysis to interpret surface water quality has several limitations of not detecting the long-term correlation between variables and poor delineation in the source apportionments of the surface water quality variation. The use of environmetric techniques and water quality index (WQI) have several advantages to overcome these limitations (Ocampo Duque et al., 2006, Rosli et al., 2012, Iticescu et al., 2013, Kilic Taseli, 2013).

In Nakdong River Basin, however, the use of environmetric multivariate statistical tools and WQI is rather an emergent; consequently, not much work has been done to evaluate the relationship of physiochemical parameters and water pollution source apportionments, and very little work has been reported about the quality of the Nakdong River Basin. It is against this background that this study was carried out to provide an overview of the relationship between physiochemical parameters and the possible sources of water pollution in the river basin.

2. SITE DESCRIPTIONS

The Nakdong River (Fig. 1), biggest river in South Korea. The length and total watershed of the Nakdong River are 525km and 24,000 km^2 respectively. It is divided into 8 main tributaries. The river in the study area is connected to the East China Sea. The River originates from Andong city, Gyongbuk province to the Busan Metropolitan city, Gyongnam province. Flood frequently happens in the study area in case of heavy rain in summer, and the many sediments and organics deposit in the study area. The delta deposits is about 60~90 m deep, and composed of backfill, upper clay, sand, lower clay and gravel in sequence. The sediments began to deposit from the late Pleistocene Epoch, i.e., the end of 4^{th} glacial period (Oh, 1994; Ryu et al., 2011). Basal gravel bed indicates an unconformity between delta sediments and bedrock. The bedrock consists of granite, andesite, and rhyolite. Geological sequence of upper clay ranges 5~10 m, sand 10~40 m, lower clay 10~30 m, gravel 5~40 m, respectively. The upper clay is relatively soft and loose, but lower clay is relatively stiff and dense. An unconfined aquifer of sand layer and a confined aquifer of gravel layer co-exist in the study area. The industrial complex is located beside the right side of the Nakdong River in the study area, and many factories are managed at the upstream of the Nakdong River. Many rice paddies, and greenhouses of fruits and vegetables are also managed in the delta as well as its upstream area. Many houses, roads and airport are also located in the deltaic region. Thus, some contaminants such as nitrate, phosphate, and some inorganic and organic materials comes into the Nakdong River, even though the city controls the contaminants well. The mouth of the Nakdong River is connected to East China Sea. By the way, the barrage constructed at the river mouth prevents seawater intrusion. Thus, the influence of seawater is very limited in the study area.

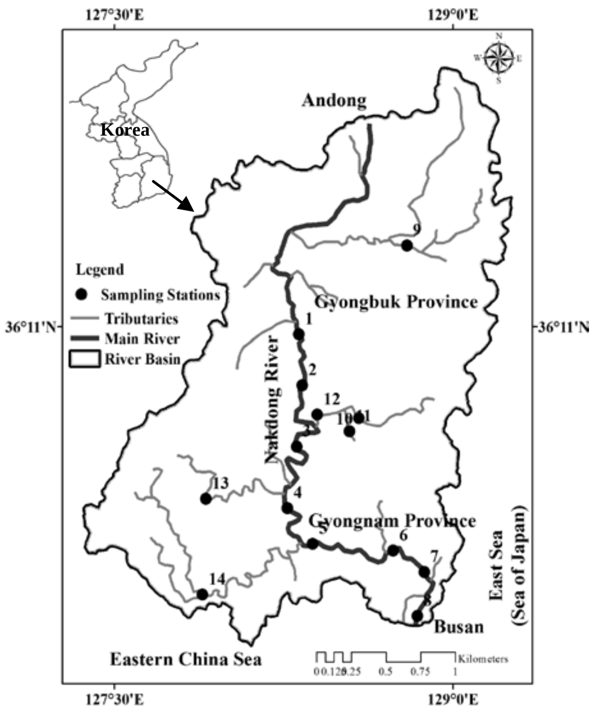

Figure 1. Map showing Location of the Study Area.

3. MATERIALS AND METHODS

3.1. Sampling and analytical procedures

The total 14 water samples were collected below the water surface using 200 ml polyethylene bottles. The surface water samples were collected during the month of July 2011. Prior to sampling water, the bottles were rinsed with the water to be sampled, and the samples were preserved by acidifying to pH 2 with HNO_3 and kept at 4°C until analysis. Temperature, pH and DO were checked in situ with a portable meter Horiba U-51, Japan. BOD, COD, TP, TOC, TSS, NH_4-N, NO_3-N, PO_4-P, Chl.α and Cl were measured by complying standard procedures (APHA, 1998). The collected water samples were filtered using a pre-conditioned plastic Millipore filter unit equipped with 45 ㎛ cellulose nitrate membrane filter for further chemical analyses.

3.2. Environmetric statistical tools

Data analysis was conducted using Pearson's correlation, factor and cluster analyses, which is an important source identification technique. All statistical calculations were performed using the STATISTICA Ver.8 statistical software package. Factor analysis was performed by varimax orthogonal rotation (Howitt & Cramer, 2005), which minimized the number of variables with a high loading on each component. Pearson's correlation matrix was also used to identify the elements relationship. Cluster analysis was applied to identify groups of samples with similar water quality parameters (Kumari et al., 2013). It was formulated according to the Ward-algorithmic method, and the rescaled linkage distance was employed for measuring the distance between clusters of similar heavy metal contents. Cluster analysis was used to determine the association of different physicochemical parameters and metals, and the association of different sediment and water samples.

3.3. Water quality Index

The WQI is obtained by adding the multiplication of the respective weight factor by an appropriated quality-value for each parameter. The WQI index consists of parameters: DO – Dissolved Oxygen (0.22), BOD – Biological Oxygen Demand (0.19), COD – Chemical Oxygen Demand (0.16), NH_4-N – Ammonium Nitrogen (0.15), NO_3-N – Nitrate Nitrogen (0.10), TSS – Total Suspend Solids (0.16), pH (0.12), TP – Total Phosphorus (0.10), TOC – Total Organic Carbon (0.32), Cl – Chloride (0.16) and temperature (0.1) based in the concept developed by U.S. National Sanitation Foundation (NSF, 2007). In parentheses are given the weight factors according to the importance of the parameters. Other indices are also used at regional level to evaluate water quality. All the data obtained to calculate the water quality index where this water quality index plays an important role in evaluating the water quality status and classification of the rivers. Then, from the WQI, the water quality is classified according to National Water Quality Standards (NWQS, primary criteria) for Korea are shown in table 1. Eleven water quality parameters that involved in the WQI formula (Eq. 1)

$$WQI = [0.22*SIDO] + [0.19*SIBOD] + [0.16*SICOD] + [0.15*SINH_4\text{-}N] + [0.16*SISS] + [0.12*SIpH] + [0.10*SINO_3\text{-}N] + [0.16*SITSS] + [0.10*SITP] + [0.32*SITOC] + [0.16*SICl] + 0.1*SITemp] \ldots\ldots\ldots\ldots\ldots (1)$$

The WQI was classified into five groups based on the calculating values such as 0-30 (good), 30-60 (moderate), 60-90 (bad) and 90-120 (very bad).

Table 1. National river quality standards (Korea)

Designated best use	**Quality Class**	**Primary water quality criteria**
Water source for municipal use	I	pH between 6.5 and 8.5 Dissolved oxygen > 7.5 mg/L Biochemical oxygen demand < 1mg/L TSS < 25 mg/L
Outdoor bathing and fisheries	II	pH between 6.5 and 8.5 Dissolved oxygen 5mg/L or more Biochemical oxygen demand 3 mg/L or less TSS < 25 mg/L
Industrial use	III	pH between 6.5 and 8.5 Dissolved oxygen 5mg/L or more Biochemical oxygen demand 3 mg/L or less TSS < 25 mg/L
Irrigation and Industrial uses	IV	pH between 6 and 8.5 Dissolved oxygen 2mg/L or more Biochemical oxygen demand 8 mg/L or less TSS < 100mg/L
3rd grade industrial use and conservation of municipal living environment	V	pH between 6 and 8.5 Dissolved oxygen >2mg/L or more Biochemical oxygen demand <10mg/L

4. RESULTS AND DISCUSSION

4.1. Descriptive statistics

The statistical summary of the selected parameters of the Nakdong River Basin water samples are presented in table 2. All parameters that showed spatial and temporal variations were illustrated graphically through box–whisker plot (Fig. 2). A total of 13 physicochemical variables were analyzed from 14 sampling stations in the Nakdong River Basin. Water temperature varied from 25°C in sampling station 1 to 30°C in sampling station 13, which is within the portable range of 25–32°C by the World Health Organization.

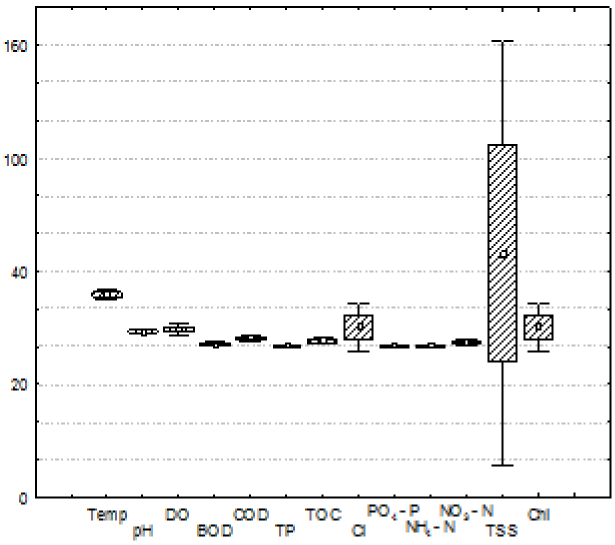

Figure 2. Box plot for physicochemical parameters

The value of pH is within the acceptable limit of 6.5–8.5, varying between 7.2 and 9.3, with the maximum limit of 9.3 at sampling point 13. The pH affects chemical and biological processes and temperature affects the availability of oxygen concentration in the water (Kowalkowski et al., 2006). BOD, COD, and NH_4-N of the water samples varied from 0.5 to 2.6 mg/L, from 2.8 to 6.2 mg/L, and from 0.026 to 1.14 mg/L, respectively. These concentrations must reflect anthropogenic influences since majority of the sampling points are located in the most industries and cultivation area, where the rivers are polluted by industrial wastewaters. BOD is a measure of the quantity of oxygen consumed by microorganisms during the decomposition of organic matter. BOD is an indicator of organic pollution. BOD is the most commonly used parameter for determining the oxygen demand on the receiving water of irrigation and industrial discharge. These organic compounds are indicators of organic pollution; un- polluted natural water has a BOD value of < 5 mg/L. (Schulze et al., 2001).

The concentration of COD in all the sampling points indicates the presence of organic compound in water under normal conditions supports the growth of bacteria and other microorganisms, which may enhance the concentration of BOD, COD, and NH_4-N. DO drops to alarming levels from upstream to downstream of Nakdong River Basin, the minimum and maximum concentrations of DO between 7.7 and 13.2 mg/L. DO content, which plays a vital role in supporting aquatic life in running water, is susceptible to slight environmental changes (Iticescu et al., 2013). Very low DO may result in anaerobic conditions that cause bad odors. The DO in water can be depleted as it is used in the oxidation of organic matter. The concentration of NO_3-N, PO_4-P, TOC and TP ranged from 0.79 to 4.25 mg/L, 0.003 to 0.22 mg/L, 1.69 to 5.04 mg/L and 0.01 to 0.26 mg/L respectively. The concentrations of these parameters were below the threshold limits of the WHO. The concentrations of these parameters were from a common source of origin (Onojake et al., 2011) and might be due to a high amount of dissolved ions in the Nakdong River Basin. The concentration of Cl ranged from 4.2 to 26.4 mg/L. Thus Cl might have been derived from irrigation and industrial discharge and subsequent mixing with surface water. Chl.α value of the present study ranged from 2.3 to 23.5 mg/L. The discharge of nutrients contribute to the high value of Chl.α in the sampling point. The excess concentration of Chl.α affected the bio-living of the river system. The concentration TSS of the samples between 5.7 and 227 mg/L.

Table 2. Descriptive statistics of the physicochemical parameters

Parameters	Mean	Median	Minimum	Maximum	Std.Dev.	Kurtosis
Temperature	27.6	27.5	25.0	30.0	1.3	0.4
pH	8.1	7.8	7.2	9.3	0.7	-1.4
Dissolved Oxygen	9.0	8.4	7.7	13.2	1.5	4.5
Biological Oxygen Demand	1.2	1.0	0.5	2.6	0.5	2.5
Chemical Oxygen Demand	4.4	4.5	2.8	6.2	0.9	0.4
Total Phosphors	0.1	0.1	0.0	0.3	0.1	0.3
Total Organic Carbon	2.9	2.8	1.7	5.0	0.8	2.6
Chloride	10.5	8.1	4.2	26.4	6.5	1.5
Phosphate Phosphors	0.1	0.0	0.0	0.2	0.1	0.8
Ammonium Nitrogen	0.2	0.1	0.0	1.1	0.3	11.9
Nitrate Nitrogen	2.2	2.1	0.8	4.2	1.0	1.0
Total Suspend Solids	49.4	25.1	5.7	227.1	57.4	7.5
Chlorophyll.α	10.1	8.2	2.3	23.5	6.6	0.7

Table 3. Pearson correlation coefficient of physicochemical parameters

Parameters	T	pH	DO	BOD	COD	TP	TOC	Cl	PO_4-P	NH_4-N	NO_3-N	TSS	Chl
T	1.00												
pH	0.64	1.00											
DO	-0.57	0.66	1.00										
BOD	-0.15	0.23	0.13	1.00									
COD	-0.49	-0.07	-0.08	0.48	1.00								
TP	-0.12	0.28	0.40	0.51	0.36	1.00							
TOC	-0.18	-0.19	-0.07	0.12	0.81	0.26	1.00						
Cl	0.15	0.39	0.57	0.35	0.35	0.86	0.34	1.00					
PO_4-P	-0.02	0.43	0.52	0.54	0.35	0.97	0.27	0.90	1.00				
NH_4-N	0.02	0.51	0.31	0.75	0.35	0.58	-0.09	0.34	0.62	1.00			
NO_3-N	-0.10	-0.02	0.19	0.00	0.24	0.60	0.50	0.76	0.59	-0.23	1.00		
TSS	0.19	-0.29	-0.18	-0.17	0.12	0.08	-0.10	0.16	-0.02	-0.05	0.03	1.00	
Chl	0.32	0.69	0.80	0.63	0.12	0.57	-0.06	0.63	0.69	0.65	0.12	-0.25	1.00

T-Temperature; pH; DO – Dissolved Oxygen; BOD – Biological Oxygen Demand; COD – Chemical Oxygen Demand; - TP - Total Phosphors; TOC - Total Organic Carbon; Cl – Chloride; PO_4-P - Phosphate Phosphors; NH_4-N – Ammonium Nitrogen; NO_3-N – Nitrate Nitrogen; TSS – Total Suspend Solids; Chl - Chlorophyll.α.

The high TSS concentrations are observed at sampling station 1 draining areas of poorly permeable, easily eroded soils in both agriculture and urban areas of the present study. The net result of nutrient inputs and transport through the Nakdong River Basin were elevated nutrient concentrations at the most-downstream site in the study area.

4.2. Physicochemical parameters relationships

The Pearson's correlation matrix is presented in table 3. The correlation between the physiochemical parameters under study showed a significant positive relationship between DO and Chl-α (r = 0.80), COD and TOC (r = 0.81), TP and Cl (r = 0.86), PO_4-P (r = 0.97), Cl and PO_4-P (r = 0.90). This is indicate that DO in water break into positively and negatively charged ions, which increases the concentration of Chl-α (Mustapha et al., 2013). (r=0.66) at $p<0.01$. The close relation between these parameters reveal that they have similar anthropogenic sources mainly industries and agriculture field that discharge their effluent into the river water. However, only BOD with PO_4-P (r = 0.54), NH_4-N (r = 0.75), Chl.α (r = 0.63) were significantly correlated with BOD. This indicates the presence of bio-degradable organic matter in the sampled water. BOD is a measure of the amount of oxygen that is consumed by bacteria during the decomposition of organic matter under aerobic conditions, whereas COD is a measure of the total quantity of oxygen required to oxidize organic materials into carbon dioxide and water under strong oxidants (Mandal et al., 2010). The degradation of organic matter in the water consumes the available DO, leading to the rapid depletion of available DO in water, resulting in high BOD, NH_4-N and PO_4-P. The positive correlation of PO_4-P with NH_4-N (r = 0.62), NO_3-N (r = 0.59), Chl.α (r = 0.69) was reported. The positive correlation was also observed between TP and NH_4-N (r = 0.58), NO_3-N (r = 0.60), Chl.α (r = 0.57). Similarly, a significant correlation of DO with pH (r = 0.66), Cl (r = 0.57), Temp between pH (r = 0.64) and Cl with NO_3-N (r = 0.76), Chl.α (r = 0.63) were also observed. The good correlations between these parameters indicate that they have similar anthropogenic sources, mainly represented by small-scale industries located in and around the Nakdong River Basin. The negative correlation of DO with Temp (r = -0.57) was observed. These findings may indicate that an increase in temperature leads to the reduced dissolution of ambient oxygen into the river water.

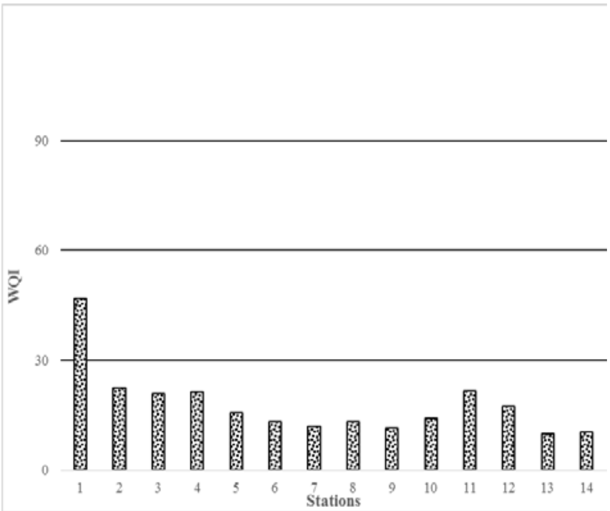

Figure 3. WQI values of physicochemical parameters

4.3. River quality identification (WQI)

The WQI and degree of pollution at every sampling point are illustrated in figure 3. The results revealed that 13 sampling points are classified under Class I (good) and except station 1. It is fall in class II (moderate) sector. The degree of pollution for these points is moderate and this might be caused by the location of the rivers that is from the anthropogenic activities such as irrigation and industries. On the other hand, the remaining sample points which are

classified under Class I which is good. The major contribution of the river pollution comes from the daily routine activities either from the upstream or downstream of the river. According to NWQS (primary criteria), all the sampling points are only suitable for industries and irrigation, thus they are may not fit for recreational, water supply or fisheries purposes.

4.4. Water pollution source identification using FA and CA

The FA and CA could be considered appropriate and useful to provide significant reduction in data dimensionality. To obtain more reliable information about the relationships among the variables, FA/CA was applied to the datasets to explore the extent of the physiochemical relationship and water pollution source identification. Varimax rotation method was used to maximize the sum of the variance of the factor coefficient, which better explained the possible group/sources that influenced the water chemistry in the Nakdong River Basin. The factor loadings were ranked following the correlation coefficient matrix between the variables. Table 4 summarized the FA results including the loadings, eigenvalues, variance of each factor, and the overall cumulative variance of the variables. In this study, a factor with an eigenvalue > 1 was considered for subsequent discussion, two independent varimax factors were extracted, which explained 63.59 % of the total variation of water quality in the Nakdong River Basin. The first F1 explained 40.84 % of the total variance and was best represented by DO, TP, Cl, PO_4-P, NH_4-N and Chl.α. This factor represents a pollution source from agricultural and industrial activities along the Nakdong River. This is evident as farmers are practicing irrigation activities around the area. The most common form of stream pollution associated with agricultural activities is the increased concentrations of soil particles washed into the stream by land clearing and farming activities.

The leaching of these parameters from the irrigation field and the return flow from irrigation water are the possible principal contributors that control the largest variation of water in the Nakdong River. The higher value of DO was mainly controlled by Chl.α. concentration of the present study. F2 had a strong loading on Temp, pH, BOD, COD, TOC and explained 22.75 %. This may be attributed by particles suspended in water may absorb heat in the sunlight, hence raising water temperature.

Table 4. Varimax factor matrices

Parameters	**Factor 1**	**Factor 2**
Temperature	0.19	**0.79**
pH	0.65	**0.77**
Dissolved Oxygen	**0.70**	-0.39
Biological Oxygen Demand	0.63	**0.76**
Chemical Oxygen Demand	0.33	**0.74**
Total Phosphors	**0.85**	0.33
Total Organic Carbon	0.17	**0.84**
Chloride	**0.86**	0.25
Phosphate Phosphors	**0.93**	0.23
Ammonium Nitrogen	**0.70**	-0.10
Nitrate Nitrogen	0.42	0.51
Total Suspend Solids	-0.11	0.13
Chlorophyll.α	**0.88**	-0.30
Eigen Value	5.31	2.96
% total variance	40.84	22.75
Cumulative %	40.84	63.59

The strong loading on these parameters could have been due to anthropogenic activities through clearing of lands, runoff, and erosive processes taking place near the study area. This factor explains the biological processes due to phytoplankton productivity and more production of organic matter resulting in more microorganism activity, which in turn increases the concentration of BOD. A high concentration of organic matter in water may consume large amounts of available DO which undergoes anaerobic fermentation processes, leading to the formation of NH_4-N and organic acid. High loading on organic compounds in the water body indicates that the river is heavily polluted with both oxidizable organic and inorganic pollutants (Otokunefor & Obiukwu, 2005). The direct dumping of waste and the dis- charge of industrial effluent into the river have been identified as the main contributing factors enhancing BOD, COD and NH_4-N. DO may be consumed by the bioxidation of nitrogenous materials in water; the continual depletion of DO in surface water can encourage microbial depletion.

CA is an unsupervised pattern recognition technique that classifies variables based on their similarities. CA is considered to be a better approach than other techniques such as principal component analysis because it identifies the underlying factor in data without the need for any pre-assumption or a null hypothesis, and no simplification of data is required (Hill & Lewicki, 2007; Otto, 2007; Vega et al., 1998). Cluster analysis was performed by Ward's method using squared Euclidean distances as a measure of similarity (Massart & Kaufman, 1983).

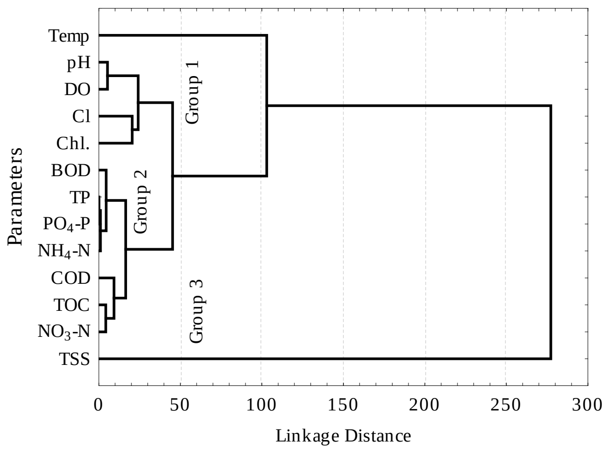

Figure 4. Dendrogram based on the cluster analysis.

In Ward's method, the proximity between two clusters is defined as the in- crease in the squared error that results when two clusters are merged. This is the preferred method because it more accurately classifies the groups (Willet, 1987). As shown in dendrogram (Fig. 4), the three groups obtained were:

Group 1: Temp, pH, DO, Cl, Chl.α
Group 2: BOD, TP, PO_4-P, NH_4-N
Group 3: COD, TOC, NO_3-N, TSS

Temperature, pH, DO, Cl and Chl.α were in Group 1, the close relation between these parameters were related with each other. Whereas Group 2 and 3 parameters reveal that they have anthropogenic sources mainly industries and agricultural field and that discharge their effluent into the river water.

5. CONCLUSION

In this case study, different multivariate statistical techniques and WQI were successfully used to assess the surface water quality of the Nakdong River Basin and identify the main contaminants and their sources of the sampling sites. The results of the environmetric statistical techniques and WQI used in this study seem to give evidence on the reasons behind the water quality variations in the Nakdong River Basin. The application of FA and CA on the available data indicated that the water quality variations are mainly due to anthropogenic (industries, irrigation agriculture, construction, cleaning of land, and domestic waste disposal) and natural processes (erosion and runoff). From the WQI, it clearly indicates that the good to moderate quality of water has already appeared. Hence, the water is suitable for industries and irrigation. Thus, they may not be suitable for recreational, water supply or fisheries purposes. These environmental tools provided more objective interpretation of surface-water physicochemical parameters and identification of water pollution source apportionment as a part of the effort toward the sustainable management of a river basin.

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