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Multivariate Analysis of Water Quality in Rosario Islands National Park (Colombia)

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Abstract: *The objective of this study was to carry a rigorous analysis of the variation in the quality of the marine water in the natural park and in addition, carrying out the development of a multivariate model in order to have a tool that will allow the monitoring and minimization of the factors that distort the quality of water in the Islas del Rosario Natural Park. Parameters such as pH, salinity (SAL), dissolved oxygen (DO), total suspended solids (TSS), nitrate ($(NO_3^-$), total coliform (TC), total phosphorus (P), ammonium (NH_4^+), 5 days biochemical oxygen demand (BOD_5) and temperature have been measured during 14 years (2001-2014) in the natural park by local authorities. Temporal analysis indicates that 60% of variables degrade during rainy season due to Magdalena River fluvial contributions through inflows of the Canal del Dique. Salinity and total phosphorus parameters are over the recommended range in all sampling points, this poses a threat to coral reefs. Multivariable statistical analysis found a model with a statistical R^2 that explains 81,7% of the variability of the BOD_5 as a function of nitrates, dissolved oxygen and salinity. The results of this study may assist local decision makers in environmental management of this marine resource.*

Keywords: *Coral Reefs, Environmental Indicators, Environmental Pollution,Physico-Chemical Analysis, Water Quality*

I. INTRODUCTION

Coral reef ecosystems support millions of dollars for the tourism and fishing industry, vital to the sustainability of local economies. But, they are threatened by the rapid growth of the population in surrounding areas, climate change and the overexploitation of the resources (Maldonado et al., 2011; Yee et al., 2014). ThePark includes the most developed fraction of corals in the Caribbean Strip and is the only protected area of underwater nature in Colombia. Due to its particular characteristics, it is considered of special interest around the world. Thanks to its high biological variety and its scenic qualities, the Islands have become one of the main tourist attractions of the Colombian Caribbean. In addition, it receives more than 200,000 visitors per year, which has led to an accelerated process of deterioration of the ecosystems due to (a) the low effectiveness in the implementation of current environmental legislation and regulations, (b) the lack of planning and (c) the high influx of public (Gladstone et al., 2013).

The quality of the marine water in the Park has beenaffected by different river outlets of the Canal del Dique, which flow into the Barbacoas bay and surroundings. The Canal del Dique is a 114 km long man-made channel built by the Spaniards in order to communicate the city of Cartagena with the interior of the country through the Magdalena River. 21% of the stream of the Canal del Dique flows into the Barbacoas bay through CañoMatunilla; 5% through CañoLequerica and 14% through Caño Correa. 24% reaches the Cartagena Bay in its final estuary in the Pasacaballos district; the rest remains in the region's swamp system (Morenoet al., 2015).

Through CañoLequerica flows 19,85$m^3 s^{-1}$ of freshwater with average concentrations of solids of 219.66 $mg\,L^{-1}$; 4297,78 *NMP* for total coliform; nitrates 0,36 66 $mg\,L^{-1}$and total phosphorus, 0,1666 $mg\,L^{-1}$. Through Caño Matunilla, flows 83.37 $m^3 s^{-1}$ of freshwater with average concentrations of solids 360.41 $mg\,L^{-1}$, 16304.73*NMP* for total coliform; nitrates 0,34 66 $mg\,L^{-1}$and total phosphorus, 0,24 66$mg\,L^{-1}$. Through Caño Correa, flows 55.58 $m^3 s^{-1}$ of freshwater with average concentrations of solids of 122,17

66 mgL^{-1} ; total coliform, 1866,48 *NMP*; nitrates, 0,11 66 mgL^{-1} and total phosphorus 0,12 66 mgL^{-1}(Acevedo and Severiche, 2013; Acosta et al. 2014). Possible leaks from domestic sewage could impact the ecosystems of the reserve with bacteria and pathogens from wastewater. Pollution caused by sewage may negatively affect both the marine environment and human health (Lu*et al*., 2017). In this research, Temporal variability of marine water quality was analyzed during 14 years (2001-2014) using parameters such as: pH, salinity, dissolved oxygen (DO), total suspended solids (TSS), nitrates(NO_3^-), total coliform (TC), total phosphorus (P), ammonium (NH_4^+), biochemical oxygen demand (BOD_5) and temperature. In addition, we developed a multivariate model of water quality in order to provide better tools for the environmental management of this marine resource.

II. MATERIALS AND METHODS

Study Area

Rosario Islands National Park is part of the Territorial Planning and environmental Land Use Unit. It is located in front of the Bolivar state - Colombia between 10° 15' and 9° 35' North latitude and is part of the coastal environmental unit of the Magdalena River (Restrepo*et al.*, 2006).

Figure 1: Sampling points and currents in the Colombian Caribbean

Sampling Procedure

The CorporaciónAutónoma Regional del Canal del Dique (Cardique) is the entity responsible for monitoring marine water quality in Rosario Islands since 2001 and its laboratory is ISO 17025 certified. Samples of marine water are taken twice a year (Dry and rainy season) in three sites within the natural park. Table 1 shows the global positioning system location of the sampling sites of marine water (Restrepo et al., 2006).

Table 1: Sampling stations in Rosario Islands (Cartagena de indias-Colombia)

Point	Locations	Coordenates
P_1	Grande island	10°11'07,9" N 75°43'41,5" W
P_2	Rosario Island	10°09'01,8" N 75°45'06,6" W
P_3	Coral reef – In front of Isla Arena	10°09'01,8" N 75°43'44,3" W

Marine Water samples (2000 mL in sterile plastic bottles) were taken at 50 cm deep, according to APHA water sampling protocols, at each point were measured *in-situ*: pH, salinity, and DO. Refrigerated samples were also taken for TSS, $BOD_5$and nitrates analysis; In addition, preserved samples with EDTA for total coliform tests and preserved with H_2SO_4 for phosphorus tests were collected. For all the trials were followed protocols established by APHA (Maldonado et al., 2011). After sampling, marine water samples were kept at 4 ºC in the dark and all analyses were performed within 48 h.

Sample analysis

Analytical methods were standard; APHA method numbers and other methods are cited in parentheses. Temperature (SM 2550-B), pH (SM 4500-H+), DO (SM 4500-O G) and Salinity (SM-2520-B) were measured in situ with the help of portable water analysis kit (multi-parameter - Hach 5465011 SensIon). To measure biochemical oxygen demand BOD_5, Winkler method (SM 4500-O G) was used, solids were measured by gravimetric analysis (SM 2540D). The method of multiple tubes (SM 9222B) was used for total coliform. Ammonium was determined by distillation-volumetric method (SM 4500-NH3 B, C). Cadmium Reduction method was used for nitrates (SM 4500-NO_3^-) and ascorbic method was used for total phosphorus (SM 4500-P B, E), both method using Varian Cary 100 UV-Vis spectrophotometer. Table 2. Shows the recommended values of water parameters for good quality of the resource, these values are in agreement with environmental Colombian law.

Table 2: Recommended values for Water Quality

Parameter	Permissible Value
P (mgL^{-1})	$<$ 0.003
TEMP (°C)	27 – 30
SAL(%)	33 – 36
SST (mgL^{-1})	$\leq$ 90
OD (mgL^{-1})	$\geq$ 4
DBO_5 (mgL^{-1})	$\leq$ 3
CTT (NMP)	$\leq$ 5000
NO_3^- (mgL^{-1})	$\leq$ 5
pH	6.5 – 8.5
NH_4^+ (mgL^{-1})	$\leq$ 1

Data analysis

Data was recorded in an Excel file, then migrated and analyzed using the *free Rsoftware*, version 3.2. Obtaining a matrix correlation and an ANOVA variance analysis; on the other hand, Statgraphics 17 statistical package was used to generate behavioral graphics on the variables of interest.

III. RESULTS AND DISCUSSION

Physicochemical parameters

The parameters that describe the water quality in the three points of study are found in Table 3. It shows the average, minimum and maximum-recorded values of the variables in the period 2001-2014. Dissolved oxygen is one of the most important factors associated with aquatic life, since it affects almost all the chemical and biological processes. DO measurement is widely used as an indicator of the organic pollution level, the rate of degradation of organic and inorganic substances likely to be oxidized and self-purging capacity of surface currents (Keeling *et al.,* 2010). Table 3 shows that the average of this parameter in the water resource is greater than 6 mg/L for all sampling points in rainy and dry seasons; in this way, they exceed the minimum value of 4 mg/L set by the Ministry of environment and sustainable development in Colombia. Low levels of dissolved oxygen concentration occur in dry season that extends from December to April (Acevedo and Severiche, 2013).

Biochemical oxygen demand (BOD_5) is one of the most used parameters to measure the water quality, since it directly affects the amount of DO present in the water resources. An increase of this parameter represents a decrease in dissolved oxygen as a result of its consumption in the oxidation of organic matter (Jouanneau*et al*., 2014). The average values measured in this study do not exceed the 2 mg/L in all sampling points, which indicates low levels of water pollution by organic matter; in this way, meets Colombian regulations for this parameter. The three stations met the pH parameter in both rainy and dry season. In Grande Island a pH range of 7.99 $\pm$ 0.12 was recorded in rainy season and 7.97 $\pm$ 0.62 in dry season. In the coral reef, a pH range of 8.02 $\pm$ 0.17 in rainy season and 7.97 $\pm$ 0.59 in dry season was measured. Finally, in the Rosario Island, the registered pH range was 7.91 $\pm$ 0.57 in dry season and 8.07 $\pm$ 0.18 in rainy season.

Table 3: Results of water quality parameters at the three stations during 2001-2014

Rainy Season Parameters									
	P_1 - Grande island			P_2- Rosario Island			P_3- Coral reef – In front of Isla Arena		
Parameter	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
P (mg/L)	0.07	0,13	0,03	0,09	0,21	0,03	0,11	0,16	0,03
NH_4^+ (mg/L)	0,18	0,74	0,07	0,27	0,74	0,07	0,24	0,60	0,07
NO_3^- (mg/L)	0,226	1,27	0,012	0,13	0,66	0,012	0,25	1,45	0,012
pH	7,99	8,12	7,82	8,07	8,28	7,79	8,02	8,20	7,80
Temp(ºC)	30,4	31,6	29,4	30,0	31,2	28,7	30,5	31,8	29,4
SAL (%)	24,42	34.00	0,10	22,22	32.00	0,10	22,22	30.00	0,10
OD (mg/L)	6,47	7,53	5,93	6,65	8,69	5,95	7.00	8,90	6,06
DBO_5 (mg/L)	1,57	3,00	0,38	1,54	4,00	0,57	1,47	4,00	0,59
CTT (NMP)	19,62	43,00	1,80	499,98	2400,00	1,80	29,86	93,00	3,00
SST (mg/L)	64,90	304,00	2,60	6,50	13,00	3,00	6,96	14,00	2,00
DrySeasonParameters									
	P_1 - Grande island			P_2- Rosario Island			P_3- Coral reef – In front of Isla Arena		
Parameter	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
P (mg/L)	0,07	0,16	0,03	0,05	0,12	0,03	0,07	0,11	0,03
NH_4^+ (mg/L)	0,77	5,08	0,07	0,11	0,24	0,07	0,33	1,68	0,07
NO_3^- (mg/L)	0,03	0,12	0,012	0,028	0,13	0,012	0,032	0,137	0,012
pH	7,97	8,39	6,46	7,91	8,43	6,56	7,97	8,48	6,61
Temp(ºC)	28,5	30,2	27,2	28,2	29,5	27,6	28,5	29,7	27,0
SAL (%)	28,92	38,00	0,10	28,38	38,00	0,10	27,98	37,00	0,10
OD (mg/L)	6,86	7,31	5,21	7,22	7,39	5,90	7,43	7,53	6,18
DBO_5 (mg/L)	0,58	1,20	0,31	0,76	2,00	0,31	0,82	3,00	0,31
CTT (NMP)	8,31	23,00	1,80	3,01	4,50	1,80	7,81	36,00	1,80
SST (mg/L)	36,57	79,00	12,00	32,17	103,00	7,00	39,78	118,00	11,50

Total Solids mean levels remained below the maximum standard permissible 90 mg/L, as stipulated by the Ministry of environment of Colombia in the resolution 0631 of 2015. The highest point in rainy season was measured on Grande Island with 304 mg/L in 2002; during dry season, it was recorded at 118 mg/L in the coral reef in 2010. The main contributions of fluvial waters that influence the study area come from the Canal del Dique, which provides fresh water and sediments to the Caribbean Sea and from there to the natural park by the Panama-Colombia countercurrent (Moreno *et al*., 2015).

The wider range of salinity registered was during dry season in Grande Island, with 28.9 $\pm$ 20.1, and the lowest average registered was in rainy season, with 22.2 $\pm$ 15.7; which means that high flows of Caño Correa, Lequerica, and Matunilla, caused by precipitations may have negative effects on the salinity of the park water. This problem has been aggravated since 1980, when the expansion of the canal delDique began and this increased the discharges of fresh water from the Magdalena River into the Caribbean Sea. These sudden changes in salinity cause stress in corals, which leads to the death of many species.

The presence of coliform groups is an indication that water may be contaminated by sewage or other decomposing waste. Coliform contamination is one of the main sanitary risks in water, since these pathogens could cause a number of diseases in human health (Bachoon et al., 2010). All stations meet Colombian regulations for this parameter during the period 2001-2014. The highest value was recorded in rainy season of 2002 (2400 NMP/100 mL) and could have been caused by Canal del Dique flows or septic tanks leaks due to high tourism in the park and poor maintenance of wastewater systems.

Nutrients

In the coral reefs ecosystems, the nitrification may create an imbalance in the exchange of nutrients between symbiotic algae and the coral host. Also, it could reduce the penetration of light to the reef, due to nutrient-induced phytoplankton growth and also may improve the growth of algae and the proliferation of seagrass. To prevent the enrichment of nutrients in coral reefs, the biologically available nitrogen (nitrate and ammonium) must be below 0.014 ppm and the biologically available phosphorus must be less than 0.003 ppm (Gavius*et al*., 2010). Nowdays pollution of groundwater by nitrates is a growing problem, since high levels could have an impact on the community health and pose a threat to the flora and fauna of the water resource (Zhang *et al*., 2014; Kim *et al*., 2015). The Colombian regulation sets a maximum value of 5 mg/L of (NO_3^-); As shown in table 3, the nitrate average concentrations in the period from 2001 to 2014 do not exceed this limit, which remained at 0.03 mg/L in all places during dry season. However, outliers of 1.27 mg/L at Grande Island, 0.66 mg/L in the Rosario Island and 1.45 mg/L in the coral reef were found in rainy season; This indicates that plumes from the polluted Barbacoa Bay represent a contribution to this variable, in addition to the possible leaks in the septic tanks of the community.

Ammonium is a micronutrient for microorganisms and algae, Its presence in water favours their multiplication. Once they die the NH_4^+ moves into the sediments, which compromises the quality of water resources (Severiche and Barreto, 2014; Oku et al., 2014). In the three points of study the parameter met the law for this variable, however, in April 2010, a maximum value of 5.08 mg/L, well above the allowable maximum of 1 mg/L was recorded. In the same way, in table 3 the averages of NH_4^+ can be seen, which are higher in dry season; this increase can occur by the large influx of people during the tourism season, that leads to the increase of wastewater in the park. High concentrations Phosphorus may represent a threat to corals, since this nutrient is limiting the growth of algae and sea grass. Therefore, its accumulation can represent a real problem for this ecosystem (Worsfold*et al*., 2016). In the period 2001-2014 the limit for this parameter was exceeded, as shown in table 3. Average values of 0.07 mg/L were recorded in dry and rainy season in Grande Island. In coral reef, average values of 0.11 mg/L were measured in rainy season and 0.07 mg/L in dry season. Finally, at Rosario Island, an average of 0.05 mg/L was found in dry season and 0.09 mg/L in rainy season.

Behavior of the Biochemical Oxygen Demand

A hypothesis test was proposed considering the three sampling points, in order to prove that average levels of BOD_5do not depend on the sampling point, i.e.:

$$H_0: \mu_{rosarioisland} = \mu_{grandeisland} = \mu_{coralreef}$$

$$vs$$

$$H_1: \mu_i \neq \mu_j forsomei \neq j$$

In order to analize the data, statistical software R was used (Adamu et al., 2013). Table 4 shows an ANOVA variance analysis; the place of sampling is considered a factor with three levels: Rosario Island, Grande Island and Coral Reef, which results in a statistic F-test with value of 0.51 and P-value of 0,6004. Therefore, concludes that there is no significant statistical difference between the averages of BOD_5 (mg/L) from one place to another, with a 95% confidence level.

Table 4: ANOVA for BOD_5 (mg/L) by sampling site

Source	Square Sum	Degree of Freedom	Square Medium	statistic F	P-Value
Betweengroups	3.21062	2	1.60531	0.51	0.6004
Intragroups	168.339	54	3.1174		
Total (Corr.)	171.55	56			

Fig. 2 shows the spatial distribution of biochemical oxygen demand in the three sampling points, where outliers for all sites can be observed. In Coral Reef and Grande Island the distribution tends to be symmetrical, while in Rosario Island, is asymmetrical and negative, which implies a negative skew.

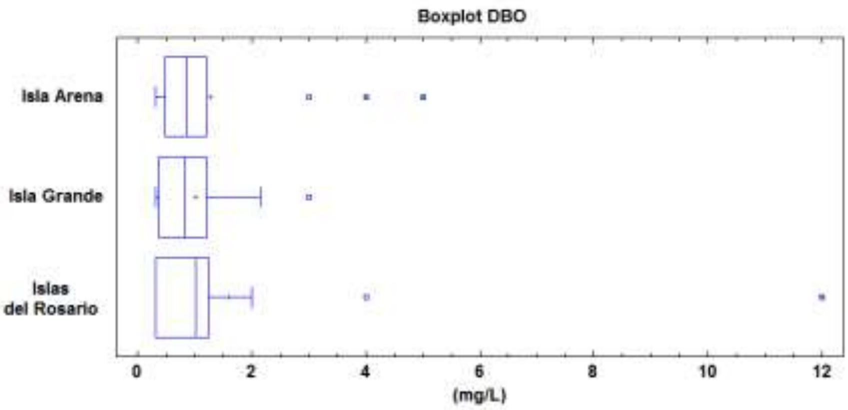

Figure 2:BOD_5Boxplot and whisker diagrams in sampling points

To establish the incidence of the properties in the Rosario Islands water quality, a predictive model was done. The aim of this model is to take corrective and preventive measures for the recovery, development and permanence of the marine ecosystem. Table 5 shows the Pearson correlation coefficient, which seeks to establish the relationship between the variables of interest (Lin *et al*., 2017).

Table 5: Matrix of Correlations

	BOD_5	NO_3^-	DO	pH	TSS	SAL	TC
BOD_5	1						
NO_3^-	0,76	1					
DO	-0,3	-0,01	1				
pH	0,04	-0,14	-0,07	1			
TSS	0,57	0,82	-0,18	-0,16	1		
SAL	-0,62	-0,35	-0,15	-0,1	-0,04	1	
TC	0,25	0,41	0,35	-0,1	-0,12	-0,46	1

In this case, the Biochemical Oxygen Demand (BOD_5) is directly related to nitrate(NO_3^-) and total suspended solids (TSS), while the BOD_5 has an inverse relationship with salinity and dissolved oxygen (DO). It also shows a strong positive relationship between solids (TSS) and nitrates (NO_3^-). Known the initial dependency between variables, was needed a model that allows predicting the average population value of a dependent variable on the basis of known or fixed values of one or more independent variables. To do this, the following equation was used:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_n X_n$$

Yrepresents the variable BOD_5; $\beta_i \in \mathbb{R}$ and X_i are the explanatory variables.

In Table 6 is depicted the outcomes of the best-fitting model to a multiple linear regression with DBO_5as the response variable in terms of TC. TSS. NO_3^-. pH. DO and SAL as predictive variables. (Viswanath et al., 2015).

Table 6: Multiple linear regression model.

	Estimate	Std. Error	t value	Pr(>|t|)
Intercept	4.06869	0.74310	5.475	0.000142
NO_3^-	0.92497	0.18276	5.061	0.000279
DO	-0.17697	0.05375	-3.293	0.006427
SAL	-0.06787	0.01758	-3.862	0.002261

Adjusted R-squared: 0.8167 p-values: 2.727e-05

It was found a statistical R^2 which indicates that the well-adjusted model explains 85,34% of the variability of the BOD_5, while the adjusted statistical R^2, which is more appropriate to compare models with different number of independent variables has a value of 81,67%. Initially were considered six variables but using stepwise regression with backward selection method at the end only three variables remain in the model. To optimize the model were eliminated from the analysis the outliers of the variable TC. The equation of the fitted model is:

$$BOD_5 = 4.069 + 0.925 * NO_3^- - 0.177 * DO - 0.068 * SAL$$

Since the P-value in the ANOVA table 4is less than 0.05, there is a statistically significant relationship between variables with a level of confidence of 95.0%; this suggests that the model is adequate. The standard error of the estimated model shows that the standard deviation of the residues is 0,227.

According to the model Nitrates (NO_3^-), Salinity (SAL) and the Dissolved oxygen (DO) explains approximately 81,7% of the variations in BOD_5. Regardless of the NO_3^-, SAL and DO, the average value of the BOD_5 is 4,069 mg/L. NO_3^-has a direct relationship with the BOD_5, per each mg/L increased of it, BOD_5 increases in 0,925 mg/L, keeping SAL and DO as constant. DO has an inverse relationship with the BOD_5, since maintaining $NO_3^-$and SAL constant, per each mg/L that DO increases BOD_5 decreases in 0,068 mg/L. SAL also has an inverse relationship with BOD_5, for each unit that SAL increases BOD_5 decreases in 0,068 mg/L, if keeping $NO_3^-$and DO constant,In the equation NO_3^-has a direct relationship with BOD_5, high concentrations of this nutrient in the water produces an excessive growth of algae, which represent a high content of organic waste which consume dissolved oxygen; in this way, increases the value of BOD_5. This explains the inverse relationship between these two variables in the equation (Zhang et al., 2017). Fig. 3 shows that for nitrates formation, oxygen is consumed, which leads to an increase in the BOD_5.

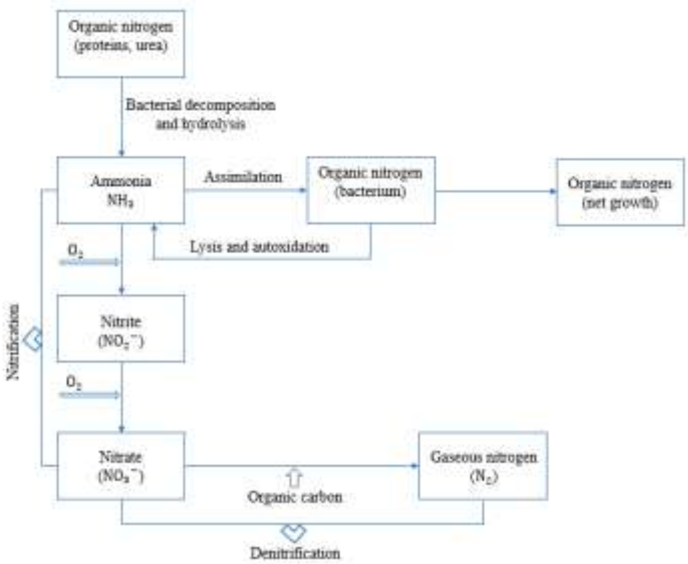

Figure 3: Nitrogen Cycle

Due to its high concentrations salinity affects inversely theBOD_5, it is bactericidal and has an influence on certain organisms that may elevate the value ofBOD_5. Correlation matrix shows the inverse relationship between Total coliforms and Salinity Finally, in order to validate the obtained multiple linear regression model were checked, the assumptions of no multicollinearity among explanatory variables, the independence of errors, the homoscedasticity and the normality of the distribution of the errors with zero mean term (Lee et al., 2017). According to data in table 5 shows No correlation among the variables NO_3^-, DO and SAL. Additionally, a Durbin-Watson analysis showed a value of 2.4848, with a P-value of 0.8403, which is greater than 0.05. Indicating No autocorrelation in the residues with a confidence level of 95%. In Figure 4. Q-Q Plot shows that points tend to align themselves to the straight line, which proves the normality of the residues of the model. Analytically, Shapiro-Wilks test confirms this, the P-value found was 0.8398. This means that there is insufficient evidence to reject the null hypothesis of normality with a significance level of 5% (Razali and Wah, 2011).

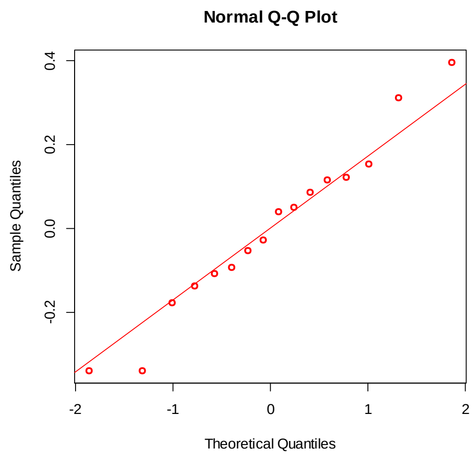

Figure 4: Normality plot of the residues of the model

To test constant variance and independence of errors, the residues vs adjusted values chart was used. Figure 5 shows a pattern of randomness, which guarantees the suitability of the model.

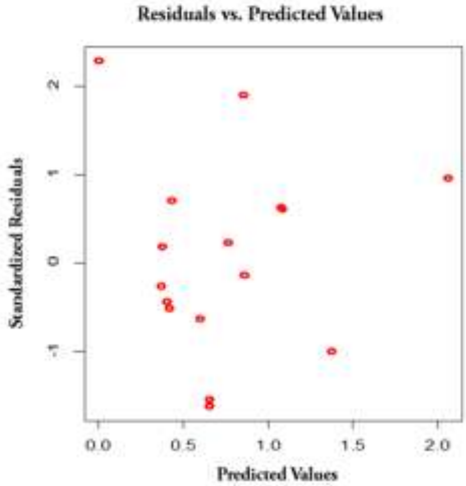

Figure 5: Residues vs Predictions Plot

IV. CONCLUSION

The data reveals that marine water of the Rosario Islands National Park shows signs of nitrification due to high levels of phosphorus principally, which may threaten coral reefs. One of the sources of these nutrients may be the Canal del Dique runoffs that are transported by the Panama-Colombia countercurrents to the waters of the natural park. In addition, wastewater from the Islands also acts as a source of nutrients, since excessive tourism and low maintenance cause leaks of septic tanks that pollute the water in the region. Total coliform in the reserve is at permissible levels for secondary contact, but sometimes it presents outliers above allowed limits for the primary contact. This can impact negatively on the tourism industry associated to the Park.

The sedimentation linked to solids and inherent to the Canal del Dique is associated to deep changes in the coral structures that do not grow enough and reduces their capacity for survival. The correlation matrix showed that solids might increase the value of nitrates, which decrease the quality of water. Changes in the salinity of the water in the natural park, product of the contributions of fresh water from the Canal del Dique, is a stressor for coral reefs, since this modifies the metabolic function of corals and their symbionts algae, resulting in the whitening of coral and also increasing the concentration of Total coliforms.

A statistical R2 of 0.8167 was determined. This indicates that salinity, nitrates, and dissolved oxygen explained about 81,7% of the variation in the biochemical oxygen demand. Multivariate linear regression model suggests that the quality of water in Rosario Islands National Park depends greatly of the level of nitrates in water. It is possible that the sources of this pollution nutrient are sewage, fertilizers and industrial effluents that can be dissolved in discharges from the Canal del Dique. It is important to control this parameter, since certain bacteria convert nitrates to nitrites and the latter are hazardous to human health. Local authorities must establish rigorous controls on septic tanks maintenance in tourist centers, which are sources of nitrates that may be easily handled. In Rosario Islands National Park, due to the large influx of tourism and huge inflow of highly turbid freshwater with high concentrations of nutrients from the Canal del Dique, favorable environmental conditions for possible bleaching and other diseases in coral reefs are given.

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