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Oil and Grease as a Water Quality Index Parameter for the Conservation of Marine Biota

Mónica Eljaiek-Urzola [1,*], Nora Romero-Sierra [2], Laura Segrera-Cabarcas [2], David Valdelamar-Martínez [2] and Édgar Quiñones-Bolaños [1]

1 Faculty of Engineering, Universidad de Cartagena, Cartagena 130015, Colombia; equinonesb@unicartagena.edu.co
2 Faculty of Engineering, Civil Engineering Program, Universidad de Cartagena, Cartagena 130015, Colombia; nromeros@unicartagena.edu.co (N.R.-S.); lsegrerac@unicartagena.edu.co (L.S.-C.); dvaldelamarm@unicartagena.edu.co (D.V.-M.)
* Correspondence: meljaieku@unicartagena.edu.co; Tel.: +57-317-894-5305

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Abstract: Water quality indexes are a tool used to evaluate the physicochemical characteristics of a water body according to its use. The present study proposes the inclusion of oil and grease (OG) as a new water quality index ($ICAM_{PFF\text{-}GA}$) parameter for the preservation of marine biota in tropical areas, since it is a typical pollutant found and measured in water bodies, causing damage to the aquatic environment. The normalized curve for OG was defined based on the percentage of surviving microorganism under a lethal concentration exposure of OG. The $ICAM_{PFF\text{-}GA}$ suitability was evaluated by its application to analyze marine water quality in the area of the sea outfall in the city of Cartagena, Colombia and comparing the trends of the outfall flow and the rainfall for 2017. Physical chemical data analyzed for the year 2017 shows that OG varies from 0.0 to 3.8 mg/L. The results show that the water quality index increases when rainfall and flow values increase for the rainy season. The $ICAM_{PFF\text{-}GA}$ can be a tool to evaluate the water quality of marine waters affected by the discharge of waters with oil and grease.

Keywords: water quality index; marine water; oil and grease; marine biota

1. Introduction

Water quality indexes (WQI) have been widely used for decades as a tool to simplify the complex state of the physical, chemical and microbiological characteristics of surface waters in just one number, allowing engineers, scientists, non-scientists, general public, and decision-makers to develop appropriate strategies for the conservation and preservation of aquatic life and human health [1–3]. In the last 20 years, more than 5000 manuscripts and 200 doctoral dissertations have been published in topics related to the development, mathematical structure and application of water quality indexes worldwide [4]. One of the critical steps in developing WQI is the selection of the physical, chemical and microbiological characteristics of the surface water that could represents better the quality of the waters, for instance the WQI developed by the National Sanitation Foundation (NSF) in The United States of America [5], that is one of the most popular WQI worldwide to analyze water quality in rivers and lakes [6,7], considers only nine parameters: temperature, pH, turbidity, fecal coliform, dissolved oxygen, biochemical oxygen demand, total phosphates, nitrates and total solids. In Colombia, the Water quality index to preserve the marine biota ($ICAM_{PFF}$) developed by the Institute of Marine and Coastal Research (INVEMAR, due to its initials in Spanish), considers seven parameters: dissolved oxygen, nitrates and nitrites, total phosphates, total suspended solids, biological oxygen demand, fecal coliforms and pH, to study the impact of domestic contamination in marine waters [8]. Torres et al. [9], has reported that dissolved oxygen and pH are the two most (above 70 % of the times) common parameters selected in building water quality indexes, biological oxygen demand, nitrates, fecal coliforms, temperature, turbidity and total suspended solids are in the second place (between 30 and 70 % of the times). Other parameters are heavy metals, which are usually associated with the chemical risks of contamination of surface waters. It is interested to observe that most of the existing WQIs do not include oils and greases as a critical parameter in their analyzes, despite that the literature [10] has reported the presence of high oil and grease content in surface water and its toxicity to aquatic life, especially in marine waters [11]. Sewage oil and grease has been identified as a major component of material causing beach pollution both in Sydney and Australia [11]. As well, a study on the beaches of Cartagena de Indias showed that the coast line of the city was in poor environmental conditions due to the high amount of nutrients, oil and grease, hydrocarbons and total solids [12].

Oil and grease are present in wastewater in a 10% approximately [13], with a concentration range between 10 to 100 mg/L [14]. Petroleum oils, vegetable oils, and animal fats share common physical properties and produce similar environmental effects. Their constituents can cause devastating physical effects, such as coating animals and plants with oil and suffocating them by oxygen depletion; be toxic and form toxic products; destroy future and existing food supplies, breeding animals, and habitats; produce rancid odors; foul shorelines, clog water treatment plants, and catch fire when ignition sources are present; and form products that linger in the environment for many years [15]. The effect of these substances may be drowning of waterfowl because of loss of buoyancy; lethal effects on fish by coating epithelial surfaces of gills, thus preventing respiration; ·asphyxiation of benthic life forms when floating masses become engaged with surface debris and settle on the bottom; and adverse aesthetic effects of fouled shorelines and beaches [16]. Also, oily wastewater, which usually has as final disposal to the sea, contains toxic substances such as phenols, petroleum hydrocarbons, polyaromatic hydrocarbons, which are inhibitory to plant and animal growth, equally, mutagenic and carcinogenic to human being [17], and the presence of this, even the thinnest layer, will affect aquatic life by decreasing both the penetration of light and the oxygen transfer between air and water [18]. Also, oils of animal or vegetable produce similar effects to oils spills [19]. That is why the objective of this manuscript is to present a new water quality index, focused on the preservation of biota in marine waters considering oil and grease as a quality parameter ($ICAM_{PFF\text{-}GA}$—By its acronyms in Spanish). This new parameter proposed herein makes reference to a total measurement conducted by the gravimetric method that is one of the most used methods to quantify total oil and grease without providing details of the composition, in terms of animal, vegetable and hydrocarbon composition [10].

The new WQI is proposed as a modification of the $ICAM_{PFF}$, that this is one of the regulatory indexes established by the Colombian government to control the use of marine waters at a national level. To evaluate the applicability of the new WQI, a water quality monitoring campaign was conducted in the marine area that could be affected by the discharge of the sea outfall of Cartagena de Indias, Colombia. The sea-outfall started operation in 2013 [20] and serves a population of approximately one million habitants [21]. The collected wastewater in the facility before discharge has an average flow of 202,169 m^3/day and an average concentration of 117.6 mg/L, 3.4×10^6 MPN/100mL and 30.75 mg/L for biological oxygen demand, fecal coliforms and oil and grease, respectively. It is important to mention that it is has been found in previous studies [22] that the dilution rate of pollutants is between 1:100 to 1:900 comparing the effluent characteristics obtained from the wastewater treatment plant facility and those determined for the near and far field marine water characteristics.

2. Materials and Methods

2.1. Water Quality Monitoring

A water quality analysis was carried out in the Caribbean Sea, near the city of Cartagena de Indias, in the area that could be affected by the sea outfall wastewater discharge, located (10°32′33.5″N

75°29′46.8′′W) close to the town of Punta Canoa in the province of Bolivar (Colombia). The discharge point is located 2.85 km from the coast line (Figure 1).

Figure 1. Location of the submarine outfall of Cartagena de Indias. Source: Google Earth.

The monitoring campaign was conducted by the water and wastewater work private company of the city of Cartagena (ACUACAR), during February, March and April (dry season, 2017) and August, September and October (rainy season, 2017), in 13 sampling points distributed throughout the area that could be influenced by the sea outfall wastewater discharge, where P2 is the final point of the pipeline (Figure 2). Water samples were taken from 7:00 am to 10:00 am, using a 5-liter Niskin Vertical bottle, performing two sets per sample. The parameters and the standard methods for the examination of marine water quality used herein are presented in Appendix A, Table A1.

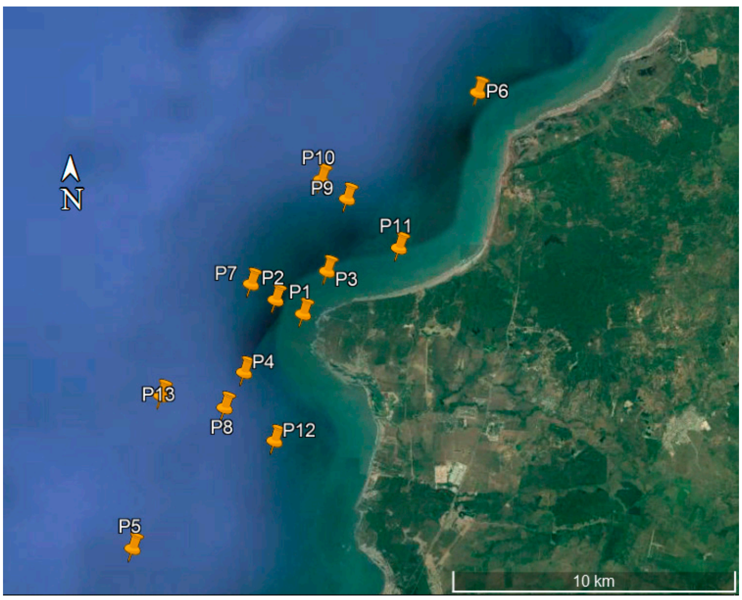


Figure 2. Sampling points in the study area. Source: Google Earth, 2018, modified by authors.

2.2. Methodology for the Development of the New $ICAM_{PFF\text{-}GA}$

The following methodology is proposed for the development of a new water quality index focused on the preservation of marine biota for marine waters affected by the discharge of domestic wastewater ($ICAM_{PFF\text{-}GA}$), which includes the concentration of oil and grease. First, the physical chemical parameters were selected which are dissolved oxygen, oil and grease, pH, biological oxygen demand, nitrates, total phosphates, fecal coliforms and total suspended solids. The importance of each parameter for marine biota is described as follows:

- Dissolved Oxygen is essential for the survival of the aerobic organisms present in the waterbody. In addition, microorganisms such as bacteria and fungi use the dissolved oxygen to decompose the organic material at the bottom of the water, which contributes to the recycling of nutrients [19]. The high values of dissolved oxygen suggest that more photosynthesis is being produced by the plants than microorganism's consumption, while the low values suggest that the oxygen is being consumed faster than it is produced, negatively affecting fish and invertebrate populations [23]. In addition, according to Torres, González, Díaz, Espinosa and Cantero [9], dissolved oxygen is one of the most affected parameters by oil and greases.
- The pH of the water is also critical and its measurement in coastal water is important since the acidification of the ocean continues to occur in the ocean basins [23]. The pH can be affected by the concentration of dissolved oxygen and determines which organisms can live and thrive. In addition to this, Knutzen [24] states that the pH tolerance of marine organisms indicates that there is little evidence of damage caused by a decrement in pH of 0.5 to 1.0 pH units.
- BOD is often used to predict the impact of an effluent discharged into the receiving bodies, such as rivers, lakes and the sea, because it indicates the amount of organic matter present in the waterbody [25]. For this reason, a low BOD is an indicator of good water quality, while a high BOD indicates contaminated water. Unpolluted waterbodies usually have BOD values of 2 mg/L or less, while waterbodies that receive sewage may have BOD values of up to 10 mg/L [26].
- Additionally, the abundance of nitrates and phosphorus improve the growth of algae and aquatic plant in the waterbodies. As a consequence, the oxygen concentrations that the aquatic species need to survive diminishes, causing damage to the waterbody [27].
- Fecal Coliforms are a biological contamination indicator, which despite having no value for the preservation of aquatic life, indicate the presence of pathogenic organisms that can pose a risk to human health. For this reason, this parameter was incorporated into the $ICAM_{PFF\text{-}GA}$ [28].
- The importance of the suspended solids lies in the fact that as the amount of sediment in the water column increases, the clarity of the water decreases, which makes it difficult for plants to perform photosynthesis. In addition, excessive amounts of suspended sediment can negatively affect animals by making it difficult for them to feed and find food [23].
- Finally, oil and grease have a very low biodegradability. It is for this reason that their release into the environment can affect the biosphere, causing lethal effects like drowning of waterfowl, fish asphyxiation or adverse aesthetic effects of fouled shorelines and beaches, even the thinnest layer of oil and grease will affect aquatic life [16,18]. Although oils of animal or vegetable origin are generally not chemically toxic to humans and aquatic life, such floating oil layers produce similar effects to oils spills [29]. Oils and fats are one of the most common types of water pollutants, which can cause damage to the aquatic environment and can come from different sources, such as wastewater effluents, where the concentrations of oil and grease have been increasing on the last years, because of the use of oil and grease in high-demanded oil-processed foods, establishment and expansion of oil mills and refineries worldwide, as well as indiscriminate discharge of oil and grease into the water drains, domestically and industrially, the spills oil that have been frequently reported in the past decades, caused by the oil production, transportation, bad storage, maintenance activities and offshore drilling [30,31].

The second step after selecting the fundamental parameters for the preservation of marine biota was the assignment of the parameters weights according to the standards established in national regulations, the essential substances for aquatic life and the pollutants that negatively affect marine biota, in a round table expert-meeting. These weight factors have the aim of including the importance of each parameter for the quality of the water body and the marine biota conservation (Table 1).

Table 1. Weight factors for each parameter for the $ICAM_{PFF\text{-}GA}$.

Parameter	Units	Weight
DO	mg/L	0.17
OG	mg/L	0.08
pH	UpH	0.13
BOD_5	mg/L	0.15
NO_3	mg/L	0.10
FO_4	mg/L	0.10
FC	MPN/100mL	0.11
TSS	mg/L	0.16

Notes: DO—dissolved oxygen; OG—Oil and grease; BOD_5— 5-day biological oxygen demand; NO_3—Nitrate; FO_4—phosphates; FC—fecal coliforms; TSS—total suspended solids.

2.2.1. Selection of the Average Function

The third step is to select an appropriate method to group all the combined effects of each parameter in just one mathematical expression. The most common equations for calculating water quality indexes are the weighted geometric mean function (Equation (1)) and weighted arithmetic mean function (Equation (2)). These are based on a weighting factor (w) and a sub-index (q) defined by normalized concentration curves [32].

$$\text{Geometric mean function} = \left(\prod_{1}^{n} {q_i}^{w_i}\right)^{\frac{1}{\sum_1^n w_i}} \tag{1}$$

$$\text{Arithmetic mean function} = \left(\sum_{1}^{n} {q_i}^{w_i}\right)^{\frac{1}{\sum_1^n w_i}} \tag{2}$$

A sensitivity analysis was conducted for Equations (1) and (2), corresponding to the weighted geometric average and weighted arithmetic equations, respectively. Based on this analysis, the geometric average weighted method was chosen for further calculations of the proposed WQI.

2.2.2. Sub-Index Curves

The new water quality index for the preservation of biota in marine waters uses the sub-index curves of ICAMPFF, since the first one is a modification of the latter. These curves were developed by INVEMAR (Santa Marta, Colombia) [12], except for the oil and grease curve, which is not taken into account within ICAMPFF. The curve of oils and greases was built taking into account the percentage of microorganisms that survive when exposed to oil and grease lethal concentration. In the new water quality index, it was considered lethal concentrations and normalized curve for OG, based on acute toxicity studies that are already reported in the literature that has more affinity with the detected concentrations of oil and grease in marine impact and its toxicity. The National Academies of Science, Engineering and Medicine in USA has reported that the lethal concentration yielding 50% mortality over pre-determined exposure time of 96 hours for some selected microinvertebrates and fishes, such as grass shrimp, salmon fry, neanthes, cypronodon among others, are in the range of 2.0 to 28.0 mg/L [33]. It also was reported that for Red Swamp Crayfish, the lethal concentration is in the range between 100 and 400 mg/L [34]. For this reason, considering that the chemical composition of oil and grease is usually unknown, the standard methods (gravimetric) commonly used to determine oil and grease does not allow its chemical characterization, based on the literature review and the OG data reported for the Caribbean area of Cartagena, it was proposed to build the normalized curve for OG in a range between 0.14 and 14 mg/L that is the point in which more than 80 % species studied were drastically affected (Figure 3).

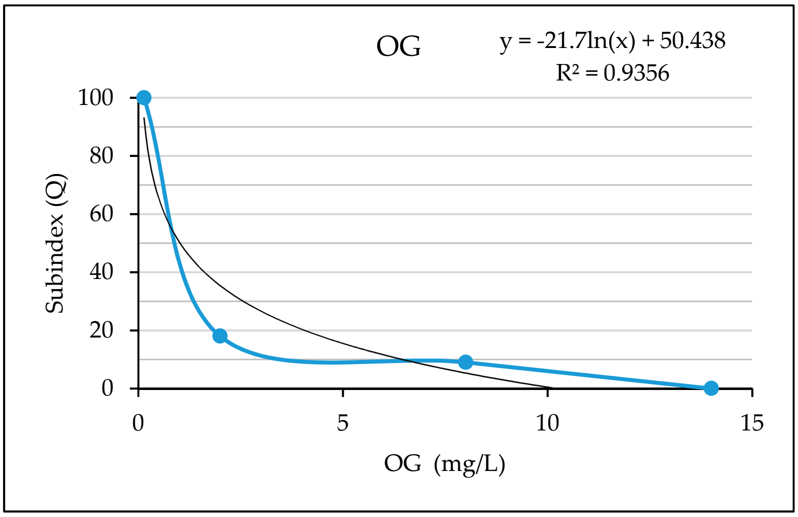


Figure 3. Sub-index values of OG.

2.2.3. Water Quality Classification

Table 2 shows a proposed classification to analyze the state of the water quality for the preservation of marine biota, according to the possible results that can be obtained with the proposed $ICAM_{PFF\text{-}GA}$ index. They are similar to those used for the $ICAM_{PFF}$ (Table A8). Table 2 also shows some actions that can be implemented to monitor and develop contingency plans.

Table 2. Options of actions to adopt [28].

Water Quality	Value	$ICAM_{PFF\text{-}GA}$ and $ICAM_{PFF}$ Options of Actions to Adopt
Optimum	91–100	Characterization, diagnosis and verification.
Adequate	71–90	Monitoring and evaluation: physicochemical and toxic parameters biannual.
Acceptable	51–70	Monitoring, bioassay, control actions and supervision. Evaluate: physicochemical and toxic parameters and make a contingency plan quarterly.
Inadequate	26–50	Monitoring and supervision, bioassay. Evaluate: physicochemical and toxic parameters, contingency plan and application of shock measures quarterly.
Poor	0–25	Water with many restrictions that do not allow proper use.

2.3. Suitability of Application of the Proposed WQI

The suitability of application of the proposed $ICAM_{PFF\text{-}GA}$ WQI was evaluated by first comparing rainfall behavior with the numerical results of the $ICAM_{PFF\text{-}GA}$ for the year 2017 that was the time considered for the monitoring campaign in this study. It has been demonstrated that as the precipitation increases, the contaminants in the combined collected sewer system are more diluted leading to a lesser water quality impact and better WQI when is discharged in the marine water. Similar approach of verification has been applied in previous studies [35]. In concordance with this, a tendency between wastewater flow registered in the wastewater treatment plant, rainfall precipitation and the index result was conducted, with the aim to analyze the behavior of the index according to each phenomenon. Rainfall precipitation data were taken from the multiannual analysis presented by IDEAM (Instituto de Hidrología, Meteorología y Estudios Ambientales, Bogotá, Colombia) for the city and the flow of the submarine outfall was provided by ACUACAR (Cartagena, Colombia) (Table 3).

Table 3. Rainfall of Cartagena and flow of the submarine Outfall.

Season	Date	Rainfall (mm)	Flow (m^3/day)
Dry	7 February	1	215,348
	15 March	2	205,118
	18 April	22	213,692
Rain	9 August	129	248,099
	12 September	144	243,549
	4 October	239	257,545

To observe also the suitability of application of the proposed $ICAM_{PFF\text{-}GA}$, three water quality indexes were chosen for comparison with the new index, in order to observe how the performance of the results depends on the concentrations of oil and fats in marine waters. Table 4 shows the main information about each index. In addition, all the procedure for each water quality index is contemplated in the Appendix A, their parameters, individual weights, additional considerations and the meaning of the result.

$$WQI\ CCME = 100 - \left(\frac{\sqrt{F_1{}^2 + F_2{}^2 + F_3{}^2}}{1.732} \right) \tag{3}$$

$$WQI_{HL} = \left(\prod_1^n q_i{}^{w_i} \right)^{\frac{1}{\sum_1^n w_i}} \tag{4}$$

$$ICAM_{PFF} = \left(\prod_1^n X_i{}^{w_i} \right)^{\frac{1}{\sum_1^n w_i}} \tag{5}$$

Table 4. Water quality indexes.

Index	Acronym	Developed by	Equation	Classification	
Water Quality Index proposed by the Canadian Council of Ministers of the Environment	WQI CCME	Canadian Council of Ministers of the Environment	Equation (3)	Excellent Good Acceptable Marginal Poor	95–100 80–94 65–79 45–64 0–44
Water Quality Index developed in coastal area of Ha-Long Bay, Vietnam	WQI_{HL}	Loan, Đ.; Nguyên, N.T.; Hồi, N.	Equation (4)	Excellent Good Medium Bad Very bad	97–100 92–96 70–91 35–69 1–34
Water Quality Index of Marine and Coastal Waters for the preservation of Marine biota	$ICAM_{PFF}$	INVEMAR	Equation (5)	Optimum Adequate Acceptable Inadequate Poor	97–100 92–96 70–91 35–69 1–34

Table 4 presents the WQI_{HL} proposed for marine and coastal water quality indexes in Taiwan (CWQI) where it is concluded that due to the high assimilation capacity of seawater, the geometric weighting method is not sensitive [36], in Ha-Long Bay, Vietnam (WQI_{HL}) where the index is developed according to the standards of Asian Region and the nature of coastal zone [32]. Also in coasts of Cuddalore and Puducherry in India (MWQI) nine related parameters were integrated towards evaluation of specific oceanographic parameters through the development of Marine Water Quality Index in Geographic Information System for Surface water quality [37]. The Water Quality Index developed by the Canadian Council of Ministers of the Environment (WQI CCME) has been used on different water bodies such as lakes and estuaries. On the estuarine water of Aucklans, New Zealand, this index is used to analyze the water quality for the monitoring program installed in 1987 [23]. It also has been used in the waters of the new Tongyang Chanel in China [38].

3. Results and Discussion

3.1. Water Quality Data

Table 5 shows the collected data at each sampling point for 14 physical, chemical and microbiological parameters from February to April (2017) and August to November (2017), which represent the dry and rain season, respectively. It is observed that the pH varies from 7.69 to 8.34, which is a typical range for seawater, indicating a slightly alkaline state. The average temperature is 28.8 °C and the variation between the seasons is not significant, with a standard deviation of 1.86. In the case of Dissolved Oxygen, the lowest value observed was 4.85 mg/L for P1 in April and the highest value was 7.47 mg/L for P11 in October, which meets with the lower limit (4 mg/L) established by the Colombian standard for the preservation of Marine biota in marine waters (Table A3).

Table 5. Average values of water quality parameters along the water column in the area affected by the discharge of the Cartagena submarine outfall in 2017.

Date	Station	pH (UpH)	Temp. (°C)	D.O. (mg/L)	D.O. %sat.	Turb. (UNT)	Oil and Grease (mg/L)	BOD5 (mg/L)	TSS (mg/L)	Phenols (mg/L)	TP (mg/L)	NH4 (mg/L)	PO4 (mg/L)	NO3 (mg/L)	F. Coli (MPN/100mL)
7 February	P1	8.04	27.00	5.87	90.00	25.05	0.60	1.75	32.94	<0.1	0.81	<0.28	<0.46	x	2.00
	P2	8.23	26.50	6.195	94.05	8.82	2.80	1.28	11.78	<0.1	0.05	<0.28	<0.46	x	49,000.00
	P3	8.24	26.40	6.3	95.40	6.19	2.00	1.97	12.97	<0.1	<0.05	<0.28	<0.46	x	<1.8
	P4	8.24	26.90	6.19	94.75	12.70	2.50	1.08	15.80	<0.1	<0.05	<0.28	<0.46	x	230.00
	P7	8.23	26.40	6.315	95.55	6.90	1.30	1.33	9.44	<0.1	<0.05	<0.28	<0.46	x	<1.8
	P11	8.18	26.70	6.165	94.00	13.05	2.80	0.89	16.96	<0.1	0.41	<0.28	<0.46	x	<1.8
15 March	P1	7.69	26.90	6.07	92.90	33.55	2.10	2.45	27.89	0.15	0.01	<0.57	0.05	0.08	2.00
	P2	8.17	26.70	6.275	95.70	7.59	0.90	2.17	13.05	0.38	0.15	<0.57	<0.04	0.07	49,000.00
	P3	8.18	26.80	6.36	97.25	31.20	1.50	2.37	5.91	0.10	0.04	<0.57	<0.04	0.11	2.00
	P4	8.16	26.70	6.26	95.40	9.50	0.00	2.49	16.04	0.10	0.05	<0.57	<0.04	0.05	5.00
	P7	8.19	26.80	6.345	97.00	3.57	0.60	2.84	6.77	<0.10	0.16	<0.57	<0.04	0.03	5.00
	P11	8.02	26.90	6.255	95.65	16.88	2.00	2.90	23.52	0.21	0.03	<0.57	<0.04	0.25	23.00
18 April	P1	7.85	27.50	4.845	72.70	5.96	1.20	1.00	9.02	<0.10	0.01	<0.57	<0.04	0.55	8.00
	P2	8.14	27.25	5.03	76.95	3.38	1.20	1.85	2.21	<0.10	0.03	0.58	<0.04	0.12	700,000.00
	P3	8.17	27.85	5.215	80.75	3.87	2.30	1.07	2.01	<0.10	0.03	<0.57	<0.04	<0.0104	5.00
	P4	8.18	27.50	5.195	80.10	3.22	1.90	1.28	2.26	<0.10	0.07	<0.57	<0.04	0.34	8.00
	P7	8.18	27.95	5.235	80.90	2.04	1.30	5.04	2.92	<0.10	0.32	<0.57	<0.04	1.24	33.00
	P11	8.18	28.00	5.065	77.80	2.02	1.70	1.29	3.05	0.12	0.83	<0.57	<0.04	0.09	70.00
9 August	P1	8.19	31.05	5.485	89.40	3.26	2.10	1.45	3.80	<0.1	0.14	<0.28	<0.46	x	23.00
	P2	8.17	30.95	5.765	93.85	4.09	2.00	1.83	3.20	<0.1	0.05	<0.28	<0.46	x	79.00
	P3	8.22	31.40	5.045	81.95	1.84	3.10	1.55	2.50	<0.1	0.02	<0.28	<0.46	x	490.00
	P4	8.23	31.15	5.41	87.40	3.36	1.80	1.35	2.40	<0.1	0.06	<0.28	<0.46	x	23.00
	P7	8.21	31.30	5.045	82.25	1.75	2.70	2.25	3.00	<0.1	0.04	<0.28	<0.46	x	1100.00
	P11	8.23	30.95	5.74	93.10	3.44	1.50	3.70	2.95	<0.1	0.07	<0.28	<0.46	x	0.00
12 September	P1	8.30	30.30	5.485	87.75	1.34	2.81	2.20	2.71	<0.1	0.24	<0.28	<0.46	x	33.00
	P2	8.20	30.25	5.65	87.95	1.88	2.58	2.70	3.44	<0.1	0.19	<0.28	<0.46	x	8.00
	P3	8.33	30.45	5.42	87.10	1.15	2.13	1.75	2.23	<0.1	0.12	<0.28	<0.46	x	33.00
	P4	8.34	30.40	5.425	86.15	1.18	2.02	2.40	2.50	<0.1	0.05	<0.28	<0.46	x	23.00
	P7	8.28	30.25	5.43	87.85	1.36	2.32	1.70	2.60	<0.1	0.03	<0.28	<0.46	x	13.00
	P11	8.29	30.40	5.34	85.05	1.92	1.91	2.65	3.65	<0.1	0.00	<0.28	<0.46	x	0.00
4 October	P1	8.30	29.95	5.675	66.80	1.33	3.80	1.07	2.65	<0.1	0.24	<0.28	<0.46	x	13.00
	P2	8.25	29.95	5.68	66.80	1.14	3.19	2.52	2.55	<0.1	0.19	<0.28	<0.46	x	8.00
	P3	8.29	30.10	6.905	81.25	1.76	3.00	2.24	2.85	<0.1	0.12	<0.28	<0.46	x	5.00
	P4	8.22	29.90	6.365	74.90	1.56	3.50	2.33	3.15	<0.1	0.05	<0.28	<0.46	x	13.00
	P7	8.29	29.80	5.75	67.65	1.62	2.60	3.36	3.00	<0.1	0.03	<0.28	<0.46	x	17.00
	P11	8.27	30.35	7.47	87.85	2.20	1.86	3.28	4.00	<0.1	0.00	<0.28	<0.46	x	0.00

x = Not available data.

The turbidity in the dry season varies from 2.02 to 33.55 NTU. These values are higher than those obtained for the rain season (between 1.14 and 4.09 NTU). This behavior is similar to that observed for TSS in both seasons. These differences in turbidity and TSS can be attributed to the transport of sediments coming from the north, in which the mouth of the Magdalena River is located, contributing with a TSS load of 2.82×10^6 tons per year [39]. The transport of sediments from the north is, in accordance with the observed wind direction and speed in the area of study, around 7.25 m/s during the dry season and 1.3 m/s during the rainy season.

The concentrations of oil and grease ranged similarly between 0 and 3.8 mg/L during both seasons. Most of these values exceed the higher limit established by some international standards such as ASEAN (Table A3). The BOD_5 showed concentrations between 0.89 and 5.04 mg/L, Colombian standards do not include a maximum limit of BOD_5 for the marine biota conservation. In terms of oil and grease, the Colombian standard establishes a limit of 0.1 of the lethal concentration. However, there are no studies to determine the lethal concentration.

In the case of phenols, 83.33% of the selected tests were below the detection limit of the equipment (<0.10 mg/L), complying with the maximum permissible concentration that is 0.12 mg/L. Unlike phenol concentrations, 94.4% of ammonium tests measured concentrations lower than 0.57 and 0.28 mg/L, whilst the higher concentration limit established by regulations is 0.07 mg/L.

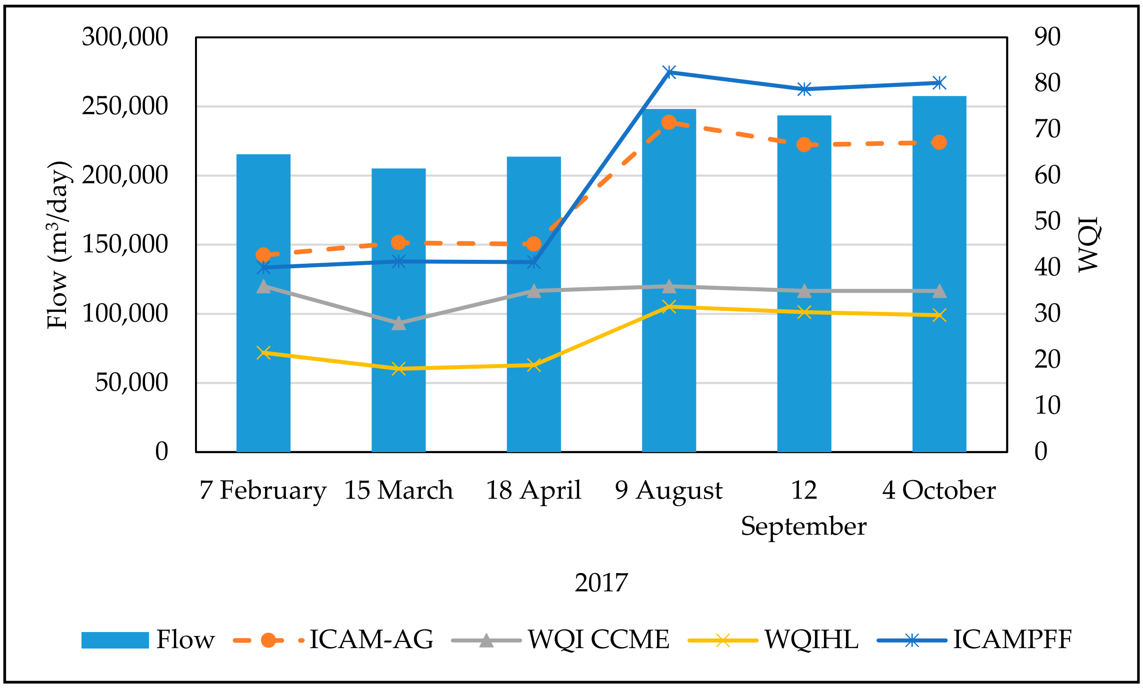
The Colombian standard for phosphates and nitrates does not specify a limit concentration for the marine biota conservation, but it does specify the criteria proposed by ASEAN. Phosphates have values below 0.46 mg/L (Equipment detection limit) and for nitrates there is an average value of 0.18 mg/L for March and April. There are no available records for other sampling dates. In the dry season, Fecal Coliforms concentrations were higher at the discharge point P2, with values of 49.000 and 70.000 MPN/100 mL. In the rainy season the values were lower, which could result from an increment in rainwater flow. Rainfall exceeding 28.5 mm were reported in the Colombian Caribbean Bulletin of the DIMAR for this season, favoring the dilution process of pollutants.

3.2. Suitability of Application of the Proposed WQI

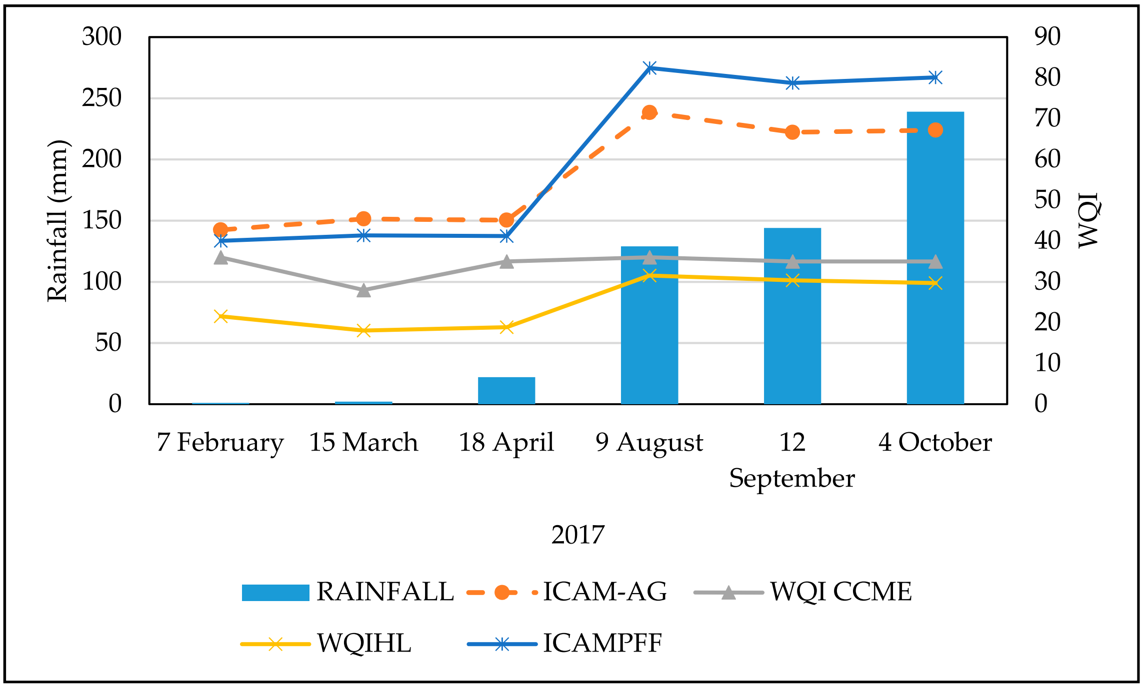
Figure 4 shows the variation of the rainfall (Figure 4A), the flow (Figure 4B) of the submarine outfall and the results of each WQI for P2 (dumping point of the submarine outfall). In both cases, there is an increase in the values for the rainy season, which means that when the rain occurs in the city and the flow increases, the quality of the water in the discharge zone improves product of the dilution.

$ICAM_{PFF\text{-}GA}$

Based on the proposed methodology for the index and the application of the weighted geometric mean function, it was found that the values were between it was found that the values were between 38.48 and 81.65 (Table 6). Most of them were in the category "Acceptable" and "Adequate", which indicates that water needs monitoring, bioassay, control actions and supervision on the body of water should be adopted, evaluating physicochemical and toxic parameters and make a contingency plan quarterly to improve the water quality of the study area and ensure that prevention measures taken in the area of the discharge are having a positive effect on the ecosystem studied and monitoring and evaluation: physicochemical and toxic parameters biannual to increase the quality of the zone, respectively (Table 2). The highest value of the index was observed in March (Dry season), in the point P4, which obtained an "Adequate" classification, it means that the water presents good conditions for aquatic life. For this date, most of the parameters had values with good results. In addition, the water quality index values for P2 were lower than all the other points, which can be because P2 is the point where the discharge of the outfall occurs. This behavior in March can be associated to the effects of the currents and tides of the zone; nevertheless, monitoring and evaluation of physicochemical and toxic parameters biannual is recommended for the "Acceptable" classification.



(**A**)



(**B**)

Figure 4. Variation of the WQI for the dumping point (P2) of the submarine outfall and: (**A**) Flow of the submarine Outfall (**B**) Rainfall.

Table 6. $ICAM_{PFF-GA}$ results.

Sampling Point	ICAM$_{PFF-GA}$ 2017 7 February		15 March		18 April		9 August		12 September		4 October	
P1	72.96	A	69.64	Ac	77.44	A	74.01	A	68.29	Ac	74.37	A
P2	42.73	I	45.45	I	45.13	I	71.53	A	66.67	Ac	67.20	Ac
P3	72.31	A	74.21	A	77.46	A	58.92	Ac	71.70	A	71.83	A
P4	69.74	Ac	81.65	A	77.06	A	74.86	A	67.98	Ac	69.68	Ac
P5	76.34	A	75.59	A	78.20	A	72.72	A	78.15	A	75.37	A
P6	77.22	A	71.91	A	74.58	A	71.57	A	71.92	A	69.76	Ac
P7	77.80	A	73.10	A	76.28	A	38.48	I	72.40	A	63.94	Ac
P8	65.38	Ac	43.66	I	77.34	A	70.70	A	65.26	Ac	71.68	A
P9	75.69	A	72.25	A	75.98	A	71.07	A	69.17	Ac	78.79	A
P10	79.16	A	72.73	A	72.59	A	72.30	A	73.62	A	70.07	A
P11	75.83	A	67.91	Ac	75.19	A	65.94	Ac	66.66	Ac	68.23	Ac
P12	66.35	Ac	76.11	A	77.96	A	66.32	Ac	77.17	A	70.02	A
P13	69.17	Ac	77.47	A	73.77	A	67.56	Ac	73.43	A	67.05	Ac

Notes: O—Optimum; A—Adequate; AC—Acceptable; I—Inadequate; P—Poor.

One of the parameters that most affected the results of the index was OG because in most of the samples it exceeds the upper limit designated in the sub-index curve. Another parameter that influenced the results of the dry season was the concentration of fecal coliforms, which presented values higher than 10,000 MPN/100 mL, corresponding to water of the "Inadequate" water quality category.

3.3. Comparison of Water Quality Indexes

To make the comparison between the indexes, it was considered that the $ICAM_{PFF-GA}$, $ICAM_{PFF}$ and WQI_{HL} and six points were selected. On the other hand, the WQI CCME allows choosing the parameters according to the normativity of the country or region that regulate the water body, without assigning a weighing factor to each parameter.

Likewise, the parameters involved in the calculation of the indexes are different for each methodology, as can be observed in Table 7. In the case of the $ICAM_{PFF}$, the methodologies does not consider the concentrations of ammonium, oils and greases, which are the ones that influence in the negative result of the WQI CCME, WQI_{HL} and the $ICAM_{PFF-GA}$.

Table 7. Physicochemical parameters considered in the quality indexes.

Parameters	ICAM$_{PFF-GA}$	WQI CCME	WQI$_{HL}$	ICAM$_{PFF}$
FC	✔		✔	✔
Oil and greases	✔	✔	✔	
vpH	✔	✔		✔
NO_3	✔	✔		✔
TSS	✔		✔	✔
NH_4		✔	✔	
PO_4	✔	✔		✔
TP			✔	
BOD_5	✔		✔	✔
DO	✔	✔		✔
DO% sat.			✔	
Temperature deviation				
Turbidity				
Phenols		✔		
Hydrocarbons			✔	✔

Notes: ✔—The index takes into account the parameter; DO% sat.—Dissolved Oxygen Percent Saturation.

Likewise, because the methodologies of each index are quite similar, the results can be close if all the parameters are available.

Table 8 shows the results of each index for each selected point in the study area. For the $ICAM_{PFF}$, on average the water quality classification is "Adequate"; in contrast, the WQI CCME, WQI_{HL} and $ICAM_{PFF\text{-}GA}$, resulted in "Poor", "Very Bad" and "Acceptable", respectively, remaining in the lowest range in the first two cases.

Table 8. Values of water quality indexes for the monitoring points.

Season	Date	Station	$ICAM_{PFF\text{-}GA}$		WQI CCME		WQI_{HL}		$ICAM_{PFF}$	
Dry	7 February	P1	73	Adequate	37	Poor	24	Very Bad	82	Adequate
		P2	43	Inadequate	36	Poor	22	Very Bad	39	Inadequate
		P3	72	Adequate	36	Poor	31	Very Bad	83	Adequate
		P4	70	Acceptable	35	Poor	32	Very Bad	79	Adequate
		P7	78	Adequate	36	Poor	32	Very Bad	89	Adequate
		P11	76	Adequate	35	Poor	31	Very Bad	90	Adequate
	15 March	P1	70	Acceptable	26	Poor	29	Very Bad	78	Adequate
		P2	45	Inadequate	28	Poor	18	Very Bad	39	Inadequate
		P3	74	Adequate	36	Poor	28	Very Bad	81	Adequate
		P4	82	Adequate	60	Marginal	76	Medium	82	Adequate
		P7	73	Adequate	49	Marginal	27	Very Bad	81	Adequate
		P11	68	Acceptable	36	Poor	29	Very Bad	78	Adequate
	18 April	P1	77	Adequate	37	Poor	30	Very Bad	85	Adequate
		P2	45	Inadequate	35	Poor	19	Very Bad	39	Inadequate
		P3	77	Adequate	43	Poor	30	Very Bad	87	Adequate
		P4	77	Adequate	34	Poor	28	Very Bad	88	Adequate
		P7	73	Adequate	32	Poor	26	Very Bad	86	Adequate
		P11	68	Acceptable	36	Poor	22	Very Bad	85	Adequate
Rain	9 August	P1	74	Adequate	36	Poor	31	Very Bad	84	Adequate
		P2	72	Adequate	36	Poor	32	Very Bad	80	Adequate
		P3	59	Acceptable	35	Poor	32	Very Bad	70	Adequate
		P4	75	Adequate	36	Poor	32	Very Bad	86	Adequate
		P7	38	Inadequate	35	Poor	21	Very Bad	36	Inadequate
		P11	66	Acceptable	36	Poor	31	Very Bad	76	Adequate
	12 September	P1	68	Acceptable	35	Poor	30	Very Bad	78	Adequate
		P2	67	Acceptable	35	Poor	30	Very Bad	75	Adequate
		P3	72	Adequate	36	Poor	31	Very Bad	81	Adequate
		P4	68	Acceptable	36	Poor	31	Very Bad	79	Adequate
		P7	72	Adequate	36	Poor	33	Very Bad	85	Adequate
		P11	67	Acceptable	36	Poor	33	Very Bad	78	Adequate
	4 October	P1	74	Adequate	35	Poor	31	Very Bad	88	Adequate
		P2	67	Acceptable	35	Poor	30	Very Bad	77	Adequate
		P3	72	Adequate	35	Poor	31	Very Bad	83	Adequate
		P4	70	Acceptable	35	Poor	31	Very Bad	83	Adequate
		P7	64	Acceptable	35	Poor	32	Very Bad	76	Adequate
		P11	68	Acceptable	36	Poor	33	Very Bad	80	Adequate

The classification categories for WQI CCME and WQI_{HL} are stricter than those of the $ICAM_{PFF}$, and $ICAM_{PFF\text{-}GA}$, because the range of the lower categories are wider than the upper ones. In the first two, to be classified as "acceptable", values around 65 and 70 are required, while the last two need values around 51 as it can be seen in the Table 4.

According to the results, it could be inferred that the reason of the difference between them is the parameters that each index use for their calculation. An example of this, is the result of the points P4 and P7 in March, where most of the parameters has good quality values and most of the indexes obtained better results in that date than in the rest of dates.

March was the only month where the oil and greases does not exceed the limit purposed by $ICAM_{PFF\text{-}GA}$, WQI CCME and WQI_{HL}. It means that they help to increase the results at this date for these indexes. In the first index the established limit is 14 mg/L, for the second was 0.14 mg/L and for the last one is 0.3 mg/L. The concentrations presented at the study zone were ranged between 0.6 and 3.8 mg/L. These concentrations compared with the admissible value of the Asian standard may have been caused by the absence of a removal system of oils and greases in the domestic wastewater treatment plant.

When analyzing the parameters that use the $ICAM_{PFF}$, Dissolved Oxygen is the most influential parameter because it is given the highest weighting factor for the calculation (Table A7) and by these concentrations (4.8–7.5 mg/L) and saturations (66%–95%) has a positive effect on the indicator's results. On the other hand, one of the parameters that negatively affected the result of the indexes was the fecal coliforms, because it is high values in the dry season.

Other parameters that affected the results between the indexes were the ammonium and the phosphates. These values were below the detection limit of the equipment but were used for the calculation of the indexes. In the case of the WQI CCME the admissible ammonium concentration is 0.07 mg/L. However, the detection limit of the equipment is 0.28 mg/L (value used for calculation), which negatively affected the result of the index. On the other hand, even if the ammonium met the objectives, the water quality would still be classified as "Poor". Similarly, phosphates concentrations are lower than 0.46 mg/L (detection limit of the equipment) and the established objective is less than 0.015 mg/L.

In terms of the use of the water most of the parameters consider that the zone has some problems that could affect the environment, except $ICAM_{PFF}$, that obtained an "Adequate" classification in most of their results and the last one said that water has good conditions for aquatic life. The WQI_{HL} ("Very Bad" classification) not recommend direct water contact in this area and insist that is not suitable for the protection of aquatic life. In addition, it only contemplates the use as a port and navigation (Table A5). According to WQI CCME, The "Poor" classification indicates that water quality is almost always threatened or impaired and the "Marginal" classification indicates that the water quality condition is frequently threatened or impaired and for both classifications the conditions usually depart from natural or desirable levels [40].

4. Conclusions

The new marine water quality index ($ICAM_{PFF\text{-}GA}$) can be used to evaluate the water quality of marine waters affected by the discharge of waters with oil and grease and this index helps to take decisions according to the impact that this parameter may have on the marine environment and their effect on the marine biota preservation.

Most of the water quality index applied worldwide do not consider the characteristics of the oil and grease discharges, nevertheless, it is necessary when a wastewater discharged is happening. Based on this, the $ICAM_{PFF\text{-}GA}$ was developed, including oil and grease for the calculations and applying it in an area affected by wastewater dumping (Cartagena's submarine outfall), giving a useful tool to evaluate the water quality of the sea.

$ICAM_{PFF\text{-}GA}$ shows that the water environment in points selected was between "Acceptable" and "Adequate". For points with acceptable result, it is necessary to develop monitoring, bioassay, control actions and supervision on the body of water should be adopted, evaluating physicochemical and toxic parameters and make a contingency plan quarterly to improve the water quality of the study area and ensure that prevention measures taken in the area of the discharge are having a positive effect on the ecosystem studied. For points with adequate result, it is necessary to do monitoring and evaluation: physicochemical and toxic parameters biannual to ensure that prevention measures taken in the area of the discharge are having a positive effect on the ecosystem studied.

For the months studied in 2017, the results for each index were: "Adequate" for $ICAM_{PFF}$, "Poor" for WQI CCME, "Very poor" for WQI_{HL} and "Acceptable" for $ICAM_{PFF\text{-}GA}$. The classification "Poor" for WQI CCME is due to the parameters that present not compliance with the standards of the Asian region: oil and grease, phosphates, nitrates and ammonium; and the classification "Very poor" for WQI_{HL} is due to the oil and grease concentration, which was the parameter that most affected the classification, because it has the highest weight and the values are outside the ranges established.

Rainfall and outfall flow have effect on the new water quality index of the study zone because the water quality index increases when rainfall and flow values increase for the rainy season. The correlation indexes obtained indicate that ICAMPFF-GA simulates the water quality conditions of the studied area.

It is recommended that the entity in charge of managing and managing the resource, conduct bioassays of lethal toxicity (LC50-96) so that the values of the parameters established in article 46 of decree 1594 of 1984 can be adjusted. This, in order to set the parameters to the specific needs of species that inhabit the Caribbean Sea and thus, the calibration curves are constructed from these values. Another recommendation is changing the measurement method for ammonium and phosphates using technical with lower detection limits.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Measurements Methods and Water Quality Indexes Characteristics

Appendix A.1. Measurements Methods

Table A1. Measurements methods.

Parameters	Method	Standard Method
Temperature	Electrometric	SM 2550 B
pH	Electrometric	SM 4500-H^+ B
Dissolved Oxygen	Electrometric	SM 4500-O C
Total Suspended Solids	Gravimetric	SM 2540 D
Turbidity	Nephelometric	SM 2130 B
BOD_5	Winkler. Incubation 5 days	SM 5210 B 4500 OC
Phosphates	Photometric	SM 4500 PE
Total Phosphorus	Photometric	SM 4500 PE
Ammonium	Photometric	Equivalent to EPA 350. 1
Nitrates	Photometric	S.M 4500-NO_3 D
Thermotolerant Coliforms (Fecal)	Multiple tube fermentation	SM 9121 E
Oil and grease	Gravimetric	SM 5520 B
Phenols	Gas chromatographic	SM 6420 B
Hydrocarbons	Gas chromatographic	SM 6440 B

Appendix A.2. WQI CCME

The Water Quality Index proposed by the Canadian Council of Ministers of the Environment (WQI CCME) assess the quality of water depending on the frequency and extent to which the water body in study does not comply with governmental guidelines. The objective is expressed differently: when the substances are contaminants, the value is expressed as the maximum limit allowed in the water body; when they are essential substances (such as dissolved oxygen) the objective is expressed as the minimum value that must be contained [3].

Taking the preservation of marine biota as water use, seven objectives were selected (Table A2) considering the Article 46 of the Decree 1594 of 1984 of the Colombian standard and the marine water criteria for the protection of aquatic life proposed by the Association of Southeast Asian Nations (ASEAN). The objectives for pH and DO where established according to Colombian standard. However, the admissible values for the other substances are defined in terms of lethal concentrations (LC50-96 hour) that depend on bioassays, to date has not been conducted on Colombia's Caribbean Sea. For this reason, the objectives for oils and grease, phenols, NH_4, NO_3 and PO_4 were concentrations determined for the ASEAN.

Table A2. Water quality criteria for the preservation of marine biota [41,42].

Parameters	Units	Value
pH	UpH	Between 6.5–8.5
DO	mg/L	Greater than 4
NH_4	mg/L	Less than 0.07
NO_3	mg/L	Less than 0.06
PO_4	mg/L	Less than 0.015
Oil and Grease	mg/L	Less than 0.14
Phenols	mg/L	Less than 0.12

CCME WQI integrates three variables: Scope (F_1), the number of variables whose objectives are not met; Frequency (F_2) represents the percentage of individual tests that do not meet objectives and Amplitude (F_3) represents the amount by which failed test values do not meet their objectives [43]. The index incorporates an unweighted harmonic mean function (Equation (A1)) [3].

$$\text{WQI CCME} = 100 - \left(\frac{\sqrt{{F_1}^2 + {F_2}^2 + {F_3}^2}}{1.732} \right) \tag{A1}$$

The index produces a number between 0 (worst water quality) and 100 (best water quality). These numbers are divided into five descriptive categories to simplify presentation (Table A3) [43].

Table A3. WQI CCME classification [40].

Water Quality	Value	WQI CCME Description
Excellent	95–100	The water quality condition is protected with a virtual absence of threat or impairment; conditions are very close to natural levels.
Good	80–94	The water quality condition is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels.
Acceptable	65–79	The water quality condition is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels.
Marginal	45–64	The water quality condition is frequently threatened or impaired; conditions often depart from natural or desirable levels.
Poor	0–44	The water quality condition is almost always threatened or impaired; conditions usually depart from natural or desirable levels.

Appendix A.3. WQI-HL

In a study conducted in the coastal area of Ha-Long Bay, Vietnam, a water quality index (ICA_{HL}) was developed and applied in order to establish if the coastal water was adequate for the preservation of aquatic life. The parameters used for the determination of WQI_{HL} were: oil and grease, total suspended solids (TSS), NH_4, total phosphorus (TP), BOD_5, FC and DO. A weighting factor was given to each parameter taking into account its importance in the aquatic system and the characterization of Ha-Long Bay, Vietnam (Table A4) [32].

Table A4. The selected parameters for the WQI in the coastal zone and their weights [32].

No.	Parameters	Units	Importance	Temporary Weight	Final Weight (w_i)
1	OG TSS	mg/L mg/L	1	2.5	0.17
2	NH_4 TP	mg/L mg/L	1.5	1.7	0.11
3	BOD_5	mg/L	2	1.3	0.08
4	FC DO	MPN/100mL %sat	2.5	1	0.07

The calculation of the index is based on a weighted geometric mean function that considers the weight (w) that is given to each parameter and a sub-index (q) that unifies them on the same dimensionless scale (Equation (A2))

$$WQI_{HL} = \left(\prod_{1}^{n} {q_i}^{w_i} \right)^{\frac{1}{\sum_1^n w_i}} \tag{A2}$$

The development of the sub-index of each selected parameter in the study is based on the following information: (1) National technical regulation on coastal water quality — QCVN 10:2008/BTNMT, (2) Marine and coastal water quality standards and criteria of ASEAN (Thailand, Indonesia, Japan, Australia), and (3) Requirements of water quality for coral reef and seabed grass [32]. The classification proposed goes from 1 to 100 which represents the poorest and the highest water quality respectively (Table A5). Table A6 shows the ranges given for each parameter and its sub-index value.

Table A5. Water quality classification and usages [32].

Water Quality	WQI_{HL} Value	Water Use Ability
Excellent	97–100	Can be used for any purpose.
Good	92–96	Can be used for any purpose, except protection of aquatic life or special aquaculture.
Medium	70–91	Tourism, recreation without direct water contract, ports and navigation, industrial water supply.
Bad	35–69	Ports and navigation, industrial water supply or other purposes which do not need high water quality.
Very bad	1–34	Ports and navigation only.

Table A6. Sub-index values [32].

I	q	Oils and Greases (mg/L)	TSS (mg/L)	NH_4 (mg/L)	TP (mg/L)	BOD_5 (mg/L)	FC (MPN/ 100 mL)	OD % Sat
1	100	0	<=20	<=0.1	<=0.02	<=1.2	<=100	100
2	67	0.1	50	0.3	0.05	1.6	-	65 or 140
3	34	0.2	-	0.5	0.5	10	500	40
4	1	>0.3	>100	>1	>1	>20	1000	20

Appendix A.4. ICAM-PFF

The Quality Index of Marine and Coastal Waters for the preservation of Marine biota ($ICAM_{PFF}$) developed by INVEMAR considers the following parameters for its calculation: DO, FC, pH, BOD_5, NO_3, PO_4, and dissolved and dispersed hydrocarbons (DDH) [28].

This index gives each parameter a weighting factor (W_i) and a sub-index (Xi) to transform the variables into a dimensionless scale that allows its aggregation. The parameters used by the $ICAM_{PFF}$ and its weight are summarized in Table A7.

Table A7. Parameters for the $ICAM_{PFF}$ and their weights [28].

Parameters	Units	Weight
OD	mg/L	0.16
FC	MPN/100 mL	0.14
pH	UpH	0.12
BOD_5	mg/L	0.13
NO_3	µm/L	0.09
PO_4	µm/L	0.13
DDH	µm/L	0.10
TSS	mg/L	0.13

The index uses a weight geometric mean function (Equation (A3)). The variables represent, according to their values of acceptance or rejection, a quality or condition of the water based on the reference values of national or international standards considered suitable to protect the habitat of species or a community in coastal ecosystems [28].

$$ICAM_{PFF} = \left(\prod_{i=1}^{n} X_i^{W_i}\right)^{\frac{1}{\sum i\, w_i}} \tag{A3}$$

The indicator enables the interpretation of the quality of the marine environment, the evaluation of the impact of anthropogenic activities and the design and implementation of measures to preserve and recover the marine water quality, that is, their capacity to withstand marine life and the biological processes [28]. Table A8 shows the sub-index ranges with which the quality of marine and coastal waters is classified, focused on the preservation of marine biota.

Table A8. ICAMPFF classification [28].

		$ICAM_{PFF}$
Water Quality	**Value**	**Description**
Optimum	90–100	Excellent water quality.
Adequate	70–90	Water with good conditions for aquatic life.
Acceptable	50–70	Water that keeps good conditions and few restrictions on use.
Inadequate	26–50	Water that presents many restrictions of use.
Poor	0–25	Waters with many restrictions that do not allow proper use.

References

1. Cude, C. Oregon Water Quality Index: A Tool for Evaluating Water Quality Management Effectiveness. *JAWRA J. Am. Water Resour. Assoc.* **2001**, *37*, 125–137. [CrossRef]
2. Ramírez, A.; Restrepo, R.; Viña, G. Cuatro índices de contaminación para caracterización de aguas continentales. formulaciones y aplicación. *CT&F-Ciencia, Tecnología y Futuro* **1997**, *1*, 135–153.
3. Caho-rodríguez, C.A.; López-barrera, E.A. Determinación del Índice de Calidad de Agua para el sector occidental del humedal Torca-Guaymaral empleando las metodologías UWQI y CWQI 1. *Producción+ Limpia* **2017**, *12*, 3. [CrossRef]
4. Science Direct Report of Oil and Grease searchs. Available online: https://www.sciencedirect.com/ (accessed on 28 March 2019).
5. Brown, R.; Mcclelland, N.; Deininger, R.; Tozer, R. A water quality index: Do we dare? *Water Sewege Works* **1970**, *117*, 339–343.

6. Noori, R.; Berndtsson, R.; Hosseinzadeh, M.; Franklin, J.; Rabiee, M. A critical review on the application of the National Sanitation Foundation Water Quality Index. *Environ. Pollut.* **2019**, *244*, 575–587. [CrossRef] [PubMed]
7. Triaji, M.; Risjani, Y.; Mahmudi, M. Analysis of Water Quality Status in Porong River, Sidoarjo by Using NSF-WQI Index (Nasional Sanitation Foundation—Water Quality Index). *Indones. J. Environ. Sustain. Dev.* **2017**, *8*, 117–119. [CrossRef]
8. INVEMAR. *Informe del Estado de los Ambientes y Recursos Marinos y Costeros de Colombia*; Serie de Publicaciones Periódicas No. 3.; INVEMAR: Santa Marta, Colombia, 2017.
9. Torres Bejarano, F.; González Márquez, L.C.; Díaz Solano, B.; Espinosa Torregroza, A.C.; Cantero Rodelo, R. Effects of beach tourists on bathing water and sand quality at Puerto Velero, Colombia. *Environ. Dev. Sustain.* **2016**, *20*, 255–269. [CrossRef]
10. AWE International Oil in Water Analysis. Available online: https://www.aweimagazine.com/article/oil-in-water-analysis-1260 (accessed on 23 March 2019).
11. Schulz, T.J.; Marczan, P.J.; Fane, A.G. Behavior of sewage effluent oil and grease in the ocean. *Water Environ. Res.* **1994**, *66*, 800–804. [CrossRef]
12. Blanco Campo, R.; Sierra Salcedo, J. Calidad de las aguas de las playas del sector turístico de Cartagena de Indias, Norte de Colombia. Undergraduated thesis, Universidad Tecnológica de Bolívar, Cartagena, Colombia, 2016.
13. Tchobanoglous, G.; Burton, F.L.; Metcalf & Eddy. *Wastewater Engineering*; McGraw-Hill: New York, NY, USA, 2002; ISBN 0070416907.
14. Michigan Department of Environmental Quality. Oil and Grease. Available online: https://www.michigan.gov/documents/deq/wrd-ot-oil-and-grease_445275_7.ppt (accessed on 23 March 2019).
15. United States Environmental Protection Agency. Vegetable Oils and Animal Fats. Available online: https://www.epa.gov/emergency-response/vegetable-oils-and-animal-fats (accessed on 20 March 2019).
16. United States. Environmental Protection Agency. Office of Water Regulations and Standards. *Quality Criteria for Water Reuse*; U.S. Environmental Protection Agency, Office of Water Regulations and Standards: Washington, DC, USA, 1986; ISBN 0160175739.
17. Alade, A.O.; Jameel, A.T.; Muyubi, S.A.; Abdul, M.; Alam, Z. Removal of Oil and Grease as Emerging Pollutants of Concern (EPC) in wastewatee stream. *IIUM Eng. J.* **2011**, *12*. [CrossRef]
18. Pintor, A.M.A.; Vilar, V.J.P.; Botelho, C.M.S.; Boaventura, R.A.R. Oil and grease removal from wastewaters: Sorption treatment as an alternative to state-of-the-art technologies. A critical review. *Chem. Eng. J.* **2016**, *297*, 229–255. [CrossRef]
19. Fondriest Environmental Inc. Dissolved Oxygen. Available online: ameters/water-quality/dissolved-oxygen/#2 (accessed on 10 January 2019).
20. Banco Mundial. *Restauración del Ambiente Costero de Cartagena, Colombia*; Banco Mundial: Washington, DC, USA, 2014.
21. DANE Colombia se Acerca a los 50 Millones de Habitantes 2017. Available online: https://www.eltiempo.com/colombia/otras-ciudades/colombia-llegara-en-el-2018-a-los-50-millones-de-habitantes-segun-el-dane-143190. (accessed on 10 January 2019).
22. Arango, L.; Godoy, R. Análisis multi-temporal de la calidad del agua en la zona de vertimiento de los emisarios submarinos. caso de estudio: Punta Canoa, Cartagena de Indias. Undergraduated Thesis, Universidad de Cartagena, Cartagena, Colombia, 2018.
23. Vaughan, M.R. *Marine Water Quality Annual Report 2016*; Auckland City Council: Auckland, New Zealand, 2017; ISBN 9781988529844.
24. Knutzen, J. Effects of Decreased pH on Marine Organisms. *Mar. Pollut. Bull.* **1981**, *12*, 25–29. [CrossRef]
25. Sawyer, C.; Parkin, G.; McCarty, P. *Chemistry for Environmental Engineering*; Mc Graw-Hill Book Company: New York, NY, USA, 2003.
26. Mocuba, J.J. Dissolved Oxygen and Biochemical Oxygen Demand in the Waters Close to the Quelimane Sewage Discharge. Master Thesis, The University of Bergen, Bergen, Norway, 2010.
27. Tayeb, A.; Chellali, M.R.; Hamou, A.; Debbah, S. Impact of urban and industrial effluents on the coastal marine environment in Oran, Algeria. *Mar. Pollut. Bull.* **2015**, *98*, 281–288. [CrossRef] [PubMed]
28. INVEMAR. *Protocolo Indicador Caliad Ambiental de Agua ICAMPFF*; INVEMAR: Santa Marta, Colombia, 2014; ISBN 9789588448664.

29. Tahir, N.M. *Asean Marine Water Quality Criteria For Oil And Grease*; Marine Environment Division, Water quality management Bureau, Pollution Control Department: Jakarta, Indonesia, 2014.
30. Sun, H.; Liu, H.; Wang, S.; Liu, Y. Remediation of oil spill-contaminated sands by chemical-free microbubbles generated in tap and saline water. *J. Hazard. Mater.* **2019**, *366*, 124–129. [CrossRef] [PubMed]
31. Enviromental Pollution Centers Oil Spill Pollution Causes. Available online: https://www.environmentalpollutioncenters.org/oil-spill/causes/ (accessed on 22 March 2019).
32. Loan, Đ.; Nguyên, N.T.; Hồi, N. Development of Water Quality Index for Coastal Zone and Application in the H ạ Long Bay. *VNU J. Sci. Earth Environ. Sci.* **2013**, *29*, 43–52.
33. National Research Council. *Oil in the Sea: Inputs, Fates, and Effects*; The National Academies Press: Washington, DC, USA, 1985; ISBN 978-0-309-07835-1.
34. Barbee, G.; Miles, S.; Umejuru, O.; Hall, S.G. Acute Toxicity (LC50) of South Louisiana Crude Oil, Mineral Oil and Peanut Oil to the Red Swamp Crayfish Procambarus clarkii. *Freshw. Crayfish* **2010**, *17*, 227–233.
35. Coletti, C.; Testezlaf, R.; Ribeiro, T.A.P.; de Souza, R.T.G.; Pereira, D.D.A. Water quality index using multivariate factorial analysis. *Rev. Bras. Eng. Agrícola e Ambient.* **2010**, *14*, 517–522. [CrossRef]
36. Shyue, S.; Lee, C.; Chen, H. An approach to a coastal water quality index for Taiwan An Approach to A Coastal Water Quality Index for Taiwan. In Proceedings of the OCEANS 96 MTS/IEEE Conference, Fort Lauderdale, FL, USA, 23–26 September 1996.
37. Naratanan, R.; Sharmila, K.; Ramalingam, M. Development of Integrated Marine Water Quality Index—A GIS Approach Development of Integrated Marine Water Quality Index—A GIS Approach. 2016.
38. Abbasi, T.; Abbasi, S. *Water Quality Indices*; Elsevier: Amsterdam, The Netherlands, 2012; ISBN 9780444543042.
39. Garcés, O.; Espinosa, L. *Diagnóstico y Evaluación de la Calidad de las Aguas Marinas y Costeras en el Caribe y Pacífico Colombianos*; Informe técnico 2016. Serie de Publicaciones Periódicas No. 4 (2017) del; INVEMAR: Santa Marta, Colombia, 2017; 260p.
40. Cash, K.; Saffran, K.; Wright, R.; Shaw, J.; Kerr, A. *Canadian Water Quality Guidelines for the Protection of Aquatic Life CCME WATER QUALITY INDEX 1. 0 Technical Report*; Canadian Council of Ministers of the Environment: Winnipeg, MB, Canada, 2001.
41. *Decreto 1594 de 1984*; Ministerio de Agricultura y Ministerio de Salud: Bogotá, Colombia, 1984; pp. 1–52.
42. ASEAN. *ASEAN Marine Water Quality: Management Guidelines and Monitoring Manual*, 1st ed.; ASEAN: Jakarta, Indonesia, 2008; ISBN 9780980413915.
43. Canadian Council of Ministers of the Environment. Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0, User's Manual. In *Canadian Environmental Quality Guidelines 1999*; Canadian Council of Ministers of the Environment: Winnipeg, MB, Canada, 2001.