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Evaluation of Different Anthropogenic Effluents Impacts on the Water Quality Using Principal Component Analysis: A Case Study of Abu-Qir Bay-Alexandria-Egypt

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Abstract: Background: The growing increase in Egyptian population, as well as urbanization expansion; lead to a corresponding increase in industrial, agriculture, urban effluents that discharged into the aquatic environment of Egypt. Objective: This study was conducted to evaluate the alteration occurred in some water quality characteristics of different water bodies subjected to different types of pollutants. Methods: Different physicochemical parameters, nutrient salts, total dissolved copper, and total dissolved carbohydrate were measured according to advanced experimental methods and analytical techniques. Results: The results of the hydrochemical parameters revealed that the temperature ranges for Abu-Qir drain waste water and Abu-Qir Bay seawater were normal. The values of salinity for waste water and seawater were (0.19-0.43‰) and (30.2-32.2‰), respectively which are much lower than that of the Mediterranean seawater (38.50‰) due to the discharge of huge amounts of fresh waters into Abu-Qir Bay. The pH values varied from one drain to another according to the geographical position and the amount of waste waters discharged into the area. Dissolved oxygen for waste water and seawater are ranged from a complete depletion to 9.42 mg/l and from 4.53 to 4.87mg/l, respectively. On the meantime the range values of oxidizable organic matter for waste water and seawater were 21.6-84.0mg/l and 14.4-42.4mg/l, respectively reflecting the high loads of organic matters added into Abu-Qir drain from different companies. On the other hand, the range values of ammonia varied between 10.20 and 95.6μM for waste water and between 7.50 and 10.10μM for seawater; respectively leading to eutrophication problems in the Bay. The nitrite for waste water and seawater were 2.60-32.40μM and 5.33-6.30μM, respectively, while the range values of nitrate for waste water and seawater were 0.74-36.74μM and 3.51-13.51μM; respectively. The range values of phosphate for waste water were 3.36-21.36μM, while it was 1.30-11.62μM for seawater. It is found that the amount of phosphate in the seawater is small compared to that of waste waters. Generally speaking, the waste and seawaters of the investigated area exhibited high silicate concentrations. Dissolved copper concentrations in Abu-Qir drain and Abu-Qir Bay ranged from 2.80 to 11.58μg/l and from 4.80 to 5.68μg/l; respectively. The range values of TDCHO for wastewater was 0.16-0.92μg/l and for seawater was 0.77-3.15μg/l. Conclusion: It is concluded from factor analysis (FA) that the investigated hydrochemical parameters are the major controlling factors in the distribution patterns of copper and TDCHO in both Abu-Qir drain and Abu-Qir Bay affecting seriously their water quality.

Keywords: Anthropogenic Impacts, Water Quality, Principal Component Analysis, Abu-Qir Bay

1. Introduction

Coastal waters, including estuaries, bays and wetlands represent a resource of enormous economic and environmental value, attracting industry, commerce, and human population to the coastal areas. The resulting environmental pressures, in addition to the direct physical coastline alterations, strongly affect coastal water quality. Local economy suffers from the marine environment degradation and public health is endangered by polluted coastal waters [1-7].

The growing increase in Egyptian population, as well as urbanization expansion; lead to a corresponding increase in industrial, agriculture, urban effluents that discharged into the aquatic environment of Egypt [8-15], leading to water quality deterioration. Poor quality water can lead to water borne diseases as well as death of aquatic life [16-22].

There are many human activities and coastal development actions take place along the coast area of Abu Qir Bay causing many marine problems. These problems stem from a lack of adequate knowledge regarding natural fluxes of, and human intervention on marine ecosystem. Problems are further aggravated by the attitudes of citizens who live in these overcrowded and disturbed environments, mostly unaware of their negative impact on the environment and the fact that, at the same time, they are victims of their own behavior. Because of the dramatic decline in fish stocks and biodiversity and the diminished resilience of the ecosystem to external stressors such as the intrusion of alien species, changes in physicochemical characteristics of water bodies, and the dramatic alteration of the position of the intermixing zone between fresh and saline waters, the hydro ecology of the Bay has become a focus of various studies [23-28].

Since environmental preservation is nowadays a matter of deep concern; the aim of present study was designed to delineate the water quality of Abu Qir Bay by studying the physical and chemical parameters in Abu Qir Bay in an attempt to assess status and to illustrate the influence of the different effluents on the environmental characteristics of Abu Qir Bay.

2. Material and Methods

2.1. Area of Investigation

2.1.1. Abu-Qir Bay

Abu-Qir Bay is located about 36 Km east of Alexandria, lying between longitudes 30°5` and 30°22`E and latitude 31°16`and 31°21`N. The area of the Bay is more than 360 Km^2, with a maximum depth of about 16 m and average of about 10 m. The bay lies on the south Levant basin of the Mediterranean Sea (Figure 1). The Bay was considered one of the most profitable fishing areas before it was assumed polluted by the disposal of sewage and industrial effluents. Now, the bay daily receives continuous effluents mainly agricultural drainage waters; industrial effluents; and sewage waste waters from three land-based sources, namely; El-

Tabia pumping station (TPS), the out let of Lake Edku (Boughaz El-Maaddiya) and the Rosetta mouth of Nile River. Along the coast of Abu Qir Bay there exist 22 different factories representing four major categories of industry; namely food processing and canning, paper industry, fertilizers industry and textiles manufacturing. The wastes of these industries pumped to the sea through El-Tabia pumping station (TPS); this station is located in the southern part of Abu Qir Bay, nearly in the mid-way between the city of Abu Qir and Boughaz El-Maaddiya. It pumps out an average amount of 1.5-2×10^{6}m^3/d. In addition, brackish water is drained to the station from a vast cultivated land area of the northeastern part of the Delta. These factors affect the physical, chemical and biological characteristics of the bay waters and consequently on the marine ecosystem biodiversity [23-28].
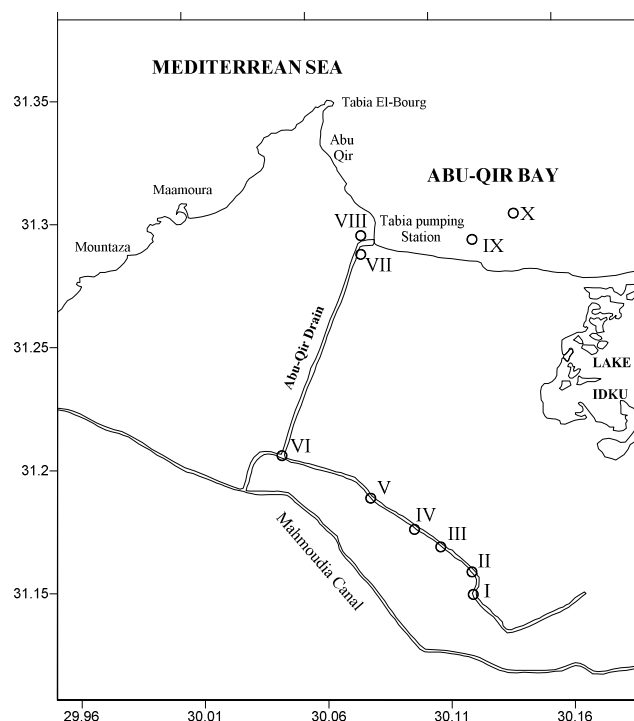

Figure 1. *Locations of sampling sites along Abu-Qir drain and Abu-Qir Bay.*

2.1.2. Abu-Qir Drain

Abu-Qir drain extends and flows through the cultivated areas from Kafer El-Dawar, till Tabia Pumping Station (TPS) which is located on the drain terminal at the south-west corner of Abu-Qir Bay. The drain is about 20 km long some of its parts are wide, and the others are narrow in certain areas. The drain water consists of irrigation drainage, and waste waters from different industries at Kafer El-Dawar and Tabia region [24, 26]. These waters are mixed and combined with agricultural drainage and flow till Tabia Pumping Station through which these waste waters are pumped into the Sea at Abu-Qir Bay (Figure 1). The different varieties of industrial wastes such as textile, pulp and paper, food, dyes, chemicals and fertilizer industries as shown in Table 1.

2.1.3. Sampling

Two major industrial centers were selected along Abu-Qir drain; one is located at Kafer El-Dawar in Behaira Governorate (Site I-VI), and the other one at Tabia region in Alexandria Governorate (Site VII & VIII). The two regions include different varieties of industries such as textile, pulp and paper, food, and fertilizer industries (Table 1). These industries discharge their waste waters into Abu-Qir drain, which in turn dispose its water into the sea at Abu-Qir Bay, via Tabia Pumping Station causing pollution and affecting the aquatic environment of Abu Qir Bay (Figure 1). Waste water samples were collected from eight sites covering Abu-Qir drain and seawater samples were collected from two sites (IX&X) in Abu-Qir Bay. At every site, waste and seawater samples were collected in triplicate from surface water of ten sites during Spring Season of 2012 through one trip using a Hydro-Bios water sampler. Oxygen bottles of capacity 150 ml were used for collecting waste water and seawater samples for the determination of DO. Samples for OOM were collected in brown bottles of capacity 100 ml. Except for ammonia, samples for nutrient salts (nitrite, nitrate, phosphate and silicate) were collected in 0.5L polyethylene bottles from every site and the samples were stored in freezing at -20°C. Brown bottles of capacity 50 ml were used for collecting samples for the determination of ammonia. Waste water and seawater samples for heavy metal (copper) were collected in previously acid-washed polyethylene bottles (2L). Samples for carbohydrates were collected in 0.5L polyethylene bottles from every site and the samples were stored in freezing at-20°C. To minimize the incorrect or inappropriate sample collection and storage procedures, the sample handling and storage recommendations of Batley [29] have been followed in this study.

Table 1. Sample locations and different land-based source.

Site number	Land-based source
Kafer El-Dawar area	
I	Dyestuffs and chemical company waste.
II	Miser Fine Spinning and Weaving company waste.
III	Miser Rayon& polyester fiber company waste (I).
IV	Miser Rayon& polyester fiber company waste (II).
V	El-Beida dyers waste.
VI	Urban area close to Ahmed Maher bridge.
El-Tabia area	
VII	Rakta company waste.
VIII	Tabia pumping station.
Abu-Qir area	
IX	Inside Abu-Qir Bay and subjected to Abu-Qir fertilizers company.
X	Inside Abu-Qir Bay.

2.2. Methods of Analyses

2.2.1. Physicochemical Parameters

The water temperature was measured in the field to the nearest 0.1°C. Salinity was determined by measuring the electrical conductivity using an inductive salinometer (Beckman; model RS-10). The salinometer was standardized with standard seawater, Copenhagen, Denmark, of chlorinity 19.375. The conductivity was measured to the nearest 0.001 and converted to salinity up to the nearest 0.001 after making temperature correction using the international tables of salinity/conductivity. The pH of water samples was measured in the field immediately after sampling by using portable digital pH meter (Model 201/digital). DO was determined according to the method of Grasshoff [30]. Oxidizable organic matter (OOM) was determined by the method described by FAO [31].

2.2.2. Nutrient Salts

Nutrient salts (ammonia, nitrite, nitrate, phosphate, silicate) were determined spectrophotmetrically (Double-beam JenWay 6405UV/ Vis. Spectrophotometer) according to the methods of Grasshoff [30]. The concentration values are expressed in μM.

2.2.3. Total Dissolved Copper

Total dissolved copper was determined by liquid/liquid extraction method by using (ultrapure) Methyl Isobutyl Ketone (MIBK) and Ammonium Pyroledene Dithiocarbamate (APDC) (ultrapure) according to Grasshoff [30]. Measurements were carried out using flame atomic absorption spectrophotometer (Shimadzu Atomic Absorption Spectrophotometer- AA6800 with auto sampler Shimadzu ASC6100, Japan). Analyses of the samples were carried out in triplicate. The precision was expressed as a coefficient of variation (CV) and the results of precision agreed within 10%. Blanks for copper metal were prepared also in triplicate, using the same reagents and the same standard procedure as that for the samples. Blank values were negligible indicating that contamination was negligible. The limit of detection (expressed in μg/l) was 0.008 for Cu.

2.2.4. Total Dissolved Carbohydrate (TDCHO)

Total dissolved carbohydrate (TDCHO) was determined spectrophotometrically by using double-beam Shimadzu spectrophotometer (visible-UV model 150-02) according to the method described by Strickland and Parsons [32] (1972). Quality control samples represented 10% of the total analytical load. The accuracy of the method for the determination of TDCHO was measured by triplicate analysis of samples with the standard deviation. Blanks for carbohydrate were prepared also in triplicate, using the same reagents and the same standard procedure as that for the samples. The limit of detection (expressed in microgram per liter) was 0.1, depending on the nature of the sugar.

2.3. Data Analysis

The obtained data analyzed statistically lead to understand aspects of the chemical and physical processes prevailing in the present study. Inputs the data include physical and chemical variables; these data were treated by factor analysis using the Principal Components Analysis (PCA). PCA was made by IBM SPSS statistics version 19 computer package. The results are expressed as average values standard

deviation. The statistical analyses were performed by Microsoft Office Excel 2007 and Microsoft Office Word 2007. The map of the location of sampling sites along Abu-Qir drain and Abu-Qir Bay were drawn by Surfer program version10.

3. Results and Discussion

3.1. Water Quality Studies

3.1.1. Physicochemical Parameters

The levels of different hydrographical parameters that influencing aquatic ecosystem either chemically or biologically [6]; i.e. temperature (°C), salinity (S‰), hydrogen ion concentration (pH), dissolved oxygen (DO) and oxidizable organic matter (OOM) are presented in Table 2, and represented graphically in Figure 2. As the drain is subjected to industrial, agricultural and domestic effluents that varies in constitution and quantity from location to another and from time to time, it is not surprising to find such broad variations in physicochemical characteristics of Abu-Qir drain [24, 26]. The range values of water temperature for wastewater (I-VIII) and seawater (IX&X) were (19.5-24.5°C) and (19-19.8°C) respectively. The average values were preceding also normal trend as expected; it is (21.09°C±1.47) for wastewater (I-VIII) and (19.40°C±0.40) for seawater (IX&X) as shown in Table 2. These ranges were comparable to the levels of the southeastern Mediterranean region which is a warm subtropical region and confirming no thermal pollution in this area of study [25, 26].

In the present investigation the range values of salinity for wastewater (I-VIII) and seawater (IX&X) were (0.19-0.43‰) and (30.2-32.2), respectively. The average values were (0.30±0.09‰) for waste water (I-VIII) and (19.40‰±0.40‰) for seawater (IX&X) as shown in Table 2. The lower value of salinity (0.19‰) measured at site III compared to other sites is due to the extreme freshwater discharges at this site and the higher value of salinity (0.43‰) measured at site V compared to other sites is due mainly to the use of sodium hypochloride (NaOCl) in primary finishing process unit. The range of salinity (30.2-32.2‰) for seawater was lower than observed in the Mediterranean seawater (38.50‰) [23], which is attributed to the discharge of huge amounts of fresh waters into Abu-Qir Bay through different land-based sources; especially agriculture discharge of Abu-Qir drain [24, 25].

The pH values of waste water (I-VIII) varied between 7.11 and 8.22; while it varied between 7.65 and 7.66 for seawater (IX&X). The average values were 7.34±0.36 for wastewater (I-VIII) and 7.66±0.005 for seawater (IX&X) as shown in Table 2. It seems that the relative low pH-value (7.11) at site (I) could be attributed to the drop in oxygen concentrations due to the effect of accumulating organic pollutants [8, 23] as well as the discharge of wastewater loaded with domestic, agricultural and industrial wastes [3].

On other hand the high value (8.22) measured at site (V) is mainly due to the alkaline waters from the sodium hydroxide

recovery unit [26]. The pH range of seawater in the present study was always on the slight alkaline side and lower than that of the open sea due to geographical position [33], and waste waters discharges of Abu-Qir Fertilizers Company into the Bay that contributes in decreasing the pH of the seawater [34]. Values of DO for waste water (I-VIII) and seawater (IX&X) ranged from a complete depletion to 9.42 mg/l and from 4.53 to 4.87mg/l, respectively. The average values were 2.07±3.0mg/l for waste water (I-VIII) and 4.70±0.17mg/l for seawater (IX&X) as shown in Table 2. A complete depletion at sites (II&VIII) and an occasional depletion of DO at some other sites are due to the discharge of different effluents loaded with huge amounts of organic materials. These materials may undergo a gradual chemical and/or biological degradations causing a removal of oxygen from the water and resulting in septic conditions characterized by odor, gases, floating solids and a disagreeable appearance. Meanwhile, it reached its maximum of 9.42mg/l at site (V) due to the use of high quantities of sodium hypochloride (NaOCl). It can be observed also that the high DO value was accompanied by an increase in pH-value. Principal component analysis (PCA) revealed a significant positive correlation between DO and pH values (Table 3). Moreover, stepwise regression analysis revealed that 97% of pH variability could be related to DO (pH = 4.55+0.499DO+0.452OOM+0.998T. alkalinity, r = 0.97, p ≤ 0.001) [35]. Moderately oxygenated seawater samples are mainly related to some other environmental factors. The most effective ones are the low water temperature, effect of wind in the aeration of water prevailing during this season. Other important factors include phytoplankton count (less than $12.5×10^3$ unit/l), and decreased rate of oxygen consumption by living marine organisms, especially zooplankton due to the decreased water temperature leading to a pronounced decrease in their activities. PCA revealed an inverse relationship between DO and water temperature (Table 3). It is well known that the rise of water temperature diminishes the solubility of oxygen [36].

In the present investigation the range values of OOM for waste water (I-VIII) and seawater (IX&X) were 21.6-84mg/l and 14.4-42.4mg/l, respectively. The average values were 52.1±23.12 mg/l for waste water (I-VIII) and 28.40±14mg/l for seawater (IX&X) as shown in Table 2. It reached its maximum of 84mg/l at site (VII) which produces large quantities of waste waters loaded with high amounts of organic materials [26]. In contrast a minimum value of 21.6 mg/l was measured at site (II). This refers to low amounts of organic matters introduced into this site. The presence of high concentration of OOM (42.4mg/l) measured at site (IX) is due to the fact that this site produces huge amounts of organic fertilizers resulting in the introduction of an increasing organic supply into such semi-enclosed area characterized by a relative slow rate of self-purification. This leads to the continuous elevation of OOM content at Abu-Qir Bay. In general, oxidizable organic matter in the whole area (average 52.1mg/l) cleared out the high loads of organic matters added into Abu-Qir drain from different companies.

Most companies in the area particularly Rakta, Dyestuffs and chemical company, Miser Fine Spinning and Weaving company use paper industry products, dyes, finishes from the chemical industries. These compounds may be organic or inorganic in nature; either causes a pollution problem which renders water unsuitable for municipal, industrial, agricultural and residential use; or may deposit on stream bottom blanketing aquatic life and even clogging streams [24, 26].

3.1.2. Nutrient Salts

Nutrient dynamics is a key element of the marine ecosystem. The nutrient concentrations are important for marine productivity; therefore, any disturbance in this cycle will adversely affect marine productivity. The most important forms of nutrients in waste and sea-waters are ammonia, nitrite, nitrate, phosphate and silicate [37-39].

The results for investigated nutrient salts are given in Table 2, and Figure 3. In the present study, ammonia varied between 10.20 and 95.6μM for waste water (I-VIII) and between 7.50 and 10.10μM for seawater (IX&X), respectively (Table 2A-Appendix II). The average values were 79.18±26.26μM for waste water (I-VIII) and 8.80±1.30μM for seawater (IX&X). The high concentration of ammonia at waste water stations is attributed to domestic, agricultural, chemical fertilizers and industrial effluents [24, 26]. The high concentration of ammonia may also be due to the depletion of dissolved oxygen that inhibits the rate of chemical oxidation of ammonia [26, 39], and on the same time enhancing the reduction of nitrate to ammonia via a process known as dissimilatory nitrate reduction to ammonium (DNRA) [40]. The absence of phytoplankton that inhibits the uptake of ammonia by phytoplankton can also be an important factor. The amount of ammonia in the seawater is small compared with that of waste waters due to the fact that phytoplankton count was generally low in Abu-Qir Bay leading to the utilization of ammonia by phytoplankton [41]. Increasing concentrations of ammonia in wastewater will definitely lead to eutrophication problems when pumped into Abu-Qir Bay. This problem might result in algal blooms (red tides), enhanced benthic algal growth, and consequent massive growth of submersed and floating macrophysics with cycles of visible bacteria blooms [24, 26]. Concentrations of nitrite for waste water (I-VIII) and seawater (IX&X) were 2.60-32.40μM and 5.33-6.30μM, respectively. The average values were 8.78±9.10μM for waste water (I-VIII) and 5.8±0.49μM for seawater (IX&X) as shown in Table 2. The low value (2.60μM) was measured at site VII could be attributed to the reduction of NO_2 to NH_4 under anaerobic conditions. This can be explained by the fact that the lower nitrite values were accompanied by an increase in NH_4 [37-39], On other hand, the high value (32.40μM) was measured at site IV which produces high amounts of dyes discharged loaded with azodye and NO_2^-. The high values of nitrite for seawater is probably due to the low phytoplankton count in Abu-Qir Bay [41], leading to a decrease in the rate of the uptake of NO_2 by phytoplankton. The high nitrite concentration at site IV may also be due to high amounts of organic fertilizers wastes loaded with NO_2 introduced into the Bay from Abu-Qir Fertilizers Company [34]. The influence of the distribution of nitrite within the surface layers of natural waters may also be a controlling factor [33].

In the present investigation the range values of nitrate for wastewater (I-VIII) and seawater (IX&X) were 0.74-36.74 μM and 3.51-13.51 μM, respectively. The average values were 11.65±12.76 μM for waste water (I-VIII) and 8.5±5.0 μM for seawater (IX&X) as shown in Table 2. The low value (0.74 μM) was measured at site II could be attributed to two factors; the first is the absence of dissolved oxygen that inhibits the rate of chemical oxidation of ammonia and the second is dissimilatory nitrate reduction to ammonium i.e. the reduction of nitrate to ammonia [35, 40, 41]. On other hand the high value of 36.74μM was measured at site VIII could be attributed to high amounts of organic fertilizers, industrial discharges [42, 43], and also may be due to the absence of phytoplankton that inhibits the uptake of NO_3 by phytoplankton. The low value (3.51μM) measured for seawater at site IX which produces high amounts of organic fertilizers wastes loaded with nitrite and nitrate maybe attributed to the reduction of nitrate to ammonia [34, 35, 41]. Obviously, the high value (13.51μM) measured for seawater at site X may be due to the absence of stratification and/or probably due to shallowness of the water column of the area [35, 39].

Phosphorus, which is an essential nutrient element in the marine environment as many organisms utilize both organic and inorganic forms of phosphorous, however inorganic phosphorous seems to be more appreciated by plants than organic phosphorous [35; 41], ranged for wastewater (I-VIII) from 3.36 to 21.36μM, while it was1.30-11.62μM for seawater (IX&X). Furthermore, the average values were14.11± 5.48μM and 1.75± 0.46μM for wastewater (I-VIII) and seawater (IX&X), respectively as shown in Table 2. The low value (3.36μM) was measured at site VII. This low value might be probably resulted from the low amounts of the effluents from companies of Phosphorus and phosphate fertilizers in addition to the discharge from Rakta Company [33] and the decrease in the rate of organic matter decomposition might be an important factor [33-44]. This explanation is strongly supported by high amounts of OOM at this station. High value of 21.36μM measured at site IV is a result of the drainage waters enriched with phosphorous [26, 35], as well as, the impacts of anthropogenic waste waters [34]. The release of large amounts of phosphate during decaying and oxidation of organic materials is also considered [44]. It is found that the amount of phosphate in the seawater is small compared with that of waste waters. This is probably due to the deposition and migration of phosphorus from overlying water to the sediment [16, 45], the high rate of consumption at the surface layer by organisms [33], the slow rate of regeneration of phosphate from underlying sediment [33, 35], and the influence of the distribution of phosphate within the surface layers of natural waters [44].

The range values of silicate, which is an important factor as a major nutrient for the construction of the cell wall of diatoms, for waste water (I-VIII) was 50.58-135.00μM, while it was34.20-34.62μM for seawater (IX&X). The average

values were 72.26±25.80μM and 34.41± 0.21μM for waste water (I-VIII) and seawater (IX&X), respectively (Table 2). It is interesting to observe that the higher silicate values were observed at all stations of wastewater. The relatively high concentrations are due mainly to the huge amounts of industrial, domestic, agricultural and drainage effluents enriched with silicate, the decrease or complete depletion of DO at most sites of Abu-Qir drain resulting in an anaerobic condition causing an increase in the rate of decomposition and oxidation of organic matter [24, 26]. The release of large amounts of silicate during decaying and oxidation of organic matter was more pronounced at station VIII (135.00μM) where oxygen was completely depleted [26, 46]. It is noticed also that the seawater has in general quite high silicate contents (Table 2). This owing to high effect land-based sources (i.e. sewage, agriculture, and/or industrial effluents) [16, 26], the increase of regeneration rate of silicate from underlying sediments, the decomposition and death of diatom [35], and the low rate of the uptake of silicate by microorganisms especially diatoms. This is strongly supported by the low count of diatoms in Abu-Qir Bay [26, 45]. These conditions could be principally controlled by the circulation pattern of seawater in the area of study. Generally speaking, the waste and seawaters of the investigated area exhibited high silicate concentrations reflecting an eutrophication condition [26, 34, 41].

Based on the results of nutrient salts, it is strongly recommended to have in-plant control for the different industries as well as combining treatment for the final wastes of industries in El-Tabia complex [24, 26, 34]. It is clear from the present study that the concentrations of nutrient salts are more controlled by the inputs from El-Tabia pump station (TPS) which discharge about 730 x10^6 m^3 y^{-1} of untreated sewage, agricultural and industrial waste waters into the Bay [46-48]. Therefore, it became necessary to know the flow of each industry for determination of the pollutional parameters as the discharged volume is included in the calculation of the organic load, which determines the actual pollutional level of each industry [23, 24, 26].

3.1.3. Trace Metals

The increase in the levels of trace metals in aquatic ecosystems is a worldwide problem and the discharge of trace metal wastes has many obvious impacts on the marine environment such as the increase in residue levels in water, sediments, and biota, decreased productivity and increase in exposure of humans to harmful substance [3, 26, 49-54].

Copper was selected in the present study because it is an essential micronutrient for organisms, involved in several metabolic processes. It may also become highly toxic when concentrations exceed levels that are physiologically required, it has become the major biocide added in anti-fouling paints as a consequence of the prohibition of paints based on tributyl tin (TBT), it is used in small amounts as fertilizers in some soils deficient in this element. Cu is also used as an algaecide and fungicides [54, 55], its concentrations are often elevated in harbors, which usually

are located at estuaries, and the sources of copper to the aquatic environment are both natural, such as weathering of rock, minerals, anthropogenic, waste water discharges as a consequence of agricultural and industrial activity [3, 15, 56].

Table 2 and Figure 3, show concentrations of total dissolved copper in Abu-Qir drain waste water and Abu-Qir Bay seawater. It is observed that the dissolved copper concentrations in Abu-Qir drain (I-VIII) and Abu-Qir Bay (IX&X) ranged from (2.80-11.58μg/l) and from (4.80-5.68μg/l), respectively. Moreover; the average values for wastewater (I-VIII) and for seawater (IX&X) were 5.42± 3.02μg/l and 5.24±0.44μg/l, respectively. The low value of 2.80μg/l (measured at site VI) is mainly due to the low concentration of copper in the drainage effluents of this station VI [24, 26], low pH value [23]. The low dissolved copper value was always accompanied by a decrease in pH-value. This is strongly supported by principal component analysis. Significant positive correlation between dissolved copper concentrations and pH values were found (Table 3). Diffusion and deposition of copper from the bulk water into sediment, the adsorption of copper by humic materials, the chelation of copper by other artificial compounds deposited on the bottom sediment [15, 52, 53, 56], and low DO (0.16 mg/l) are additional important factors. A significant positive correlation between dissolved copper concentrations and DO values were observed (Table 3). On the meantime, the high value (11.58μg/l) measured at site V was due to the high chemical industrial wastes from El-Beida Dyers company such as dyes and high quantities of copper which used in printing unit of this company and the high pH value [24, 26]. PCA revealed a significant positive correlation between the pH and dissolved copper concentrations (Table 3).The release of copper from sediments to overlying water [3, 15, 56], as well as the high DO (9.42 mg/l) are important factors. Concentrations of copper found to increase by increasing the DO which is strongly supported by PCA (Table 3 & Figure 4). It can be pointed out from the data that high concentrations of copper at seawater stations are attributed to domestic, agricultural, chemical fertilizers and industrial effluents discharged into the bay [23, 24, 26], desorption and diffusion of copper from bottom sediments into the surface layer of the Bay, the leaching of copper from paints on the hulls of ships, the low biological consumption by phytoplankton in Abu-Qir Bay which is supported by the low phytoplankton count, as well as the higher values of pH (7.56 & 7.66), and DO (4.54 & 4.87 mg/l) in the bay which is supported by the PCA (Table 3) are controlling factors. The low rate of copper uptake by aquatic organisms (such as the fish) at Abu-Qir Bay should also be considered [3, 15, 56].

It has been anticipated that the change in physicochemical characteristics of the drain and the Bay waters such as the change from oxic to anoxic conditions, the presence of high amounts of organic matter, ammonia, silicate, phosphate and depletion of DO will definitely control the concentration levels and the distribution of copper. Obviously, the low concentrations of dissolved copper in waters of both the drain and the Bay does not definitely mean it is safe and does not

accumulated either in sediments and/or marine organisms. The presence of relatively high concentrations of copper in sediments of the drain and the Bay has been reported by many researchers [3, 24, 26, 52, 53]. Several processes such as the diffusion, the adsorption and the precipitation of copper into sediments are important factors in the distribution of a dissolved element in an aquatic system [57-60].

3.1.4. Total Dissolved Carbohydrate (TDCHO)

The results of TDCHO in waste water of Abu-Qir drain and seawater of Abu-Qir Bay cleared out that the range values of TDCHO of the present study for waste water (I-VIII) was 0.16-0.92 μg/l and for seawater (IX&X) was 0.77-3.15 μg/l. The average values were 0.52±0.32 μg/l and 1.96±1.19 μg/l for waste water (I-VIII) and seawater (IX&X) respectively (Table 2 & Figure 5). In general; it can be noticed from the results that TDCHO occur at low concentrations in Abu-Qir drain waste water. This is probably due to deposition in drain sediments as a result of the biological liability of carbohydrates [62], and low salinity [63] confirmed by PCA as a good significant positive relationships between salinity and TDCHO was observed (Table 3). The decrease in concentrations of MCHO and PCHO [32] the low of bacterial cell numbers and its activity leading to a decrease in the biological processes by bacteria resulting in a decrease in the production of TDCHO was

decreased [63], and the low concentrations of TDCHO in industrial, agriculture, aquaculture and domestic waste of Abu-Qir drain waste water [64] should be considered. It can be pointed out that TDCHO exhibited the lowest value of 0.77 μg/l in seawater of Abu-Qir Bay at site X located inside the Bay (Table 2). This is can be explained as a result of several factors among which the location of site (X) which is far from the land based sources, deposition of TDCHO into sediments of the Bay [61], the biological processes resulting in low production TDCHO by bacteria [32], high rate of bacterial uptake [65], the low production of TDCHO by phytoplankton as their count were low in Abu-Qir Bay [61], and the high degradation rate of bioactive dissolved carbohydrates [66]. On contrast, the high value (3.15 μg/l) of TDCHO was measured in Abu-Qir Bay seawater at site (IX) which is subjected to the discharge of Abu-Qir Fertilizers Company, in addition to the rapid development of industry, agriculture and aquaculture in this region, the input of industrial and domestic wastes, which enriched with TDCHO into the Bay [67], leakage of TDCHO from senescent algal cells as an extracellular product [64], excretion of TDCHO by the macrophytes and the periphyton or by heterotrophic microorganisms, bacterial lysis of algal cells [64], the high salinity [62], which accompanied by high TDCHO, and viral lysis of phytoplankton cells [64].

Table 2. Hydrographical parameters, nutrient salts, total dissolved copper, and total dissolved carbohydrates of Abu-Qir drain and Abu-Qir Bay*.

Parameters Stations	Temperature °C	Salinity	pH	DO mg/l	OOM mg/l	Ammonia μM	Nitrite μM
I	20	0.22	7.11	2.27	68	10.20	7.53
II	22	0.36	7.18	0.00	21.6	89.75	6.43
III	21	0.19	7.21	0.16	28	87.65	5.65
IV	19.5	0.22	7.18	1.30	58.4	95.6	32.40
V	20.2	0.43	8.22	9.42	48.8	88.10	7.33
VI	21	0.35	7.28	0.16	80.8	88.40	5.65
VII	24.5	0.26	7.33	3.25	84	83.40	2.60
VIII	20.5	0.41	7.20	0.00	27.2	90.30	2.63
Average±SD	21.091.47	0.300.09		2.073.00	52.1023.12	79.1826.26	8.789.10
IX	19.8	32.2	7.65	4.87	42.4	7.50	5.33
X	19	30.2	7.66	4.53	14.4	10.10	6.30
Average±SD	19.400.40	31.201.00		4.700.17	28.4014.00	8.801.30	5.810.49

Table 2. Continued.

Parameters Stations	Nitrate μM	Phosphate μM	Silicate μM	Cu μg/l	Carbohydrates μg/l
I	1.59	20.69	61.08	5.41	0.88
II	0.74	15.70	50.58	3.49	0.92
III	5.52	16.90	51.00	4.56	0.84
IV	4.66	21.36	80.40	3.32	0.70
V	8.87	11.81	56.04	11.58	0.24
VI	5.52	11.47	74.52	2.80	0.23
VII	29.54	3.36	69.48	9.16	0.16
VIII	36.74	11.62	135.00	3.07	0.17
Average±SD	11.6512.76	14.115.48	72.2625.80	5.423.02	0.520.32
IX	3.51	1.30	34.20	4.80	3.15
X	13.51	2.21	34.62	5.68	0.77
Average±SD	8.515.00	1.750.46	34.410.21	5.240.44	1.961.19

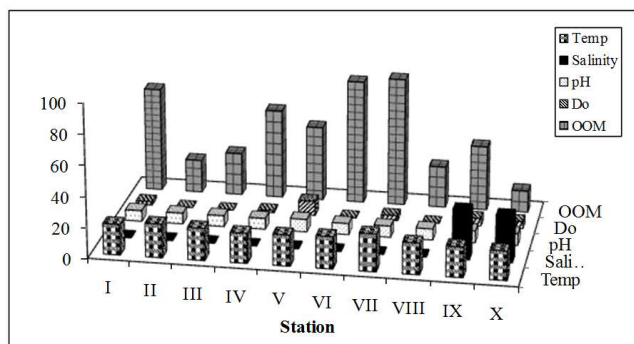* Average values of triplicate determinations.

Figure 2. The physicochemical parameters for Abu-Qir drain and Abu-Qir Bay.
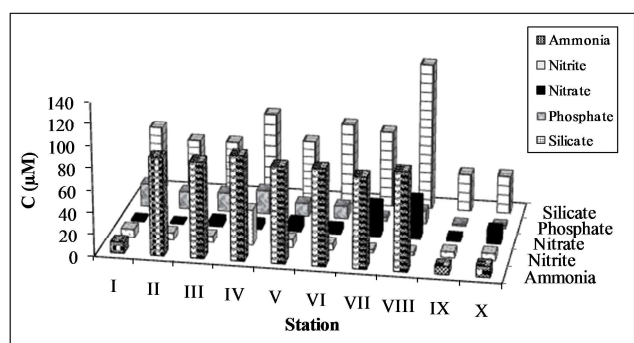

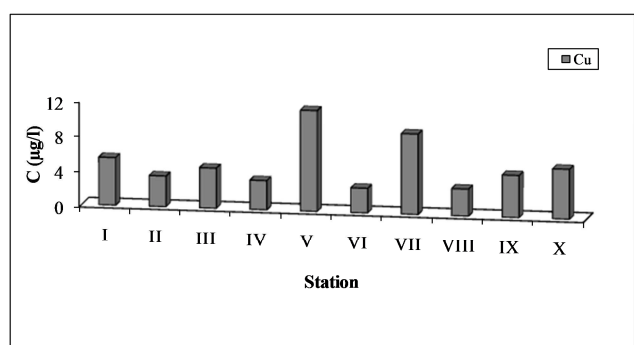*Figure 3. Nutrient salts for Abu-Qir drain and Abu-Qir Bay.*

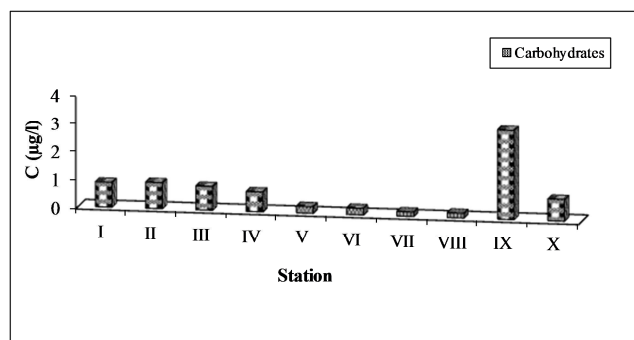*Figure 4. Total dissolved copper for Abu-Qir drain and Abu-Qir Bay.*

Figure 5. Total dissolved carbohydrates for Abu-Qir drain and Abu-Qir Bay.

3.2. Data Analysis

The data of the hydrographical parameters (such as, temperature, salinity, pH, DO and OOM), copper and

TDCHO in Abu-Qir drain and Abu-Qir Bay were treated by factor analysis (FA) using the Principal Components Analysis (PCA). The factor analysis (FA) is a more adequate multivariable technique when the goal is not only to reduce the number of variables (called factor) but also to detect structures in the relationships between variables [3].

Using factor analysis, linear correlation between the hydrographical parameters such as temperature, salinity, pH, DO and OOM, total dissolved copper and TDCHO in waste and seawaters of both Abu-Qir drain and Abu-Qir Bay was determined (Table 3 & Figure 6). This helped much in interpretation of correlation between hydrographical parameters, copper and TDCHO in the study area. Based on eigen values and varimax rotation two factors explained (74.02%) of the variability. Factor (1) exhibited (39.18%) of the total variance of (74.02%) with heavily positive loading on pH (0.930), DO (0.979) and copper (0.917). This factor indicated that copper showed highly positive relationships with pH and DO, (i.e. copper increases by increasing pH and DO) [69], and these two hydrographic parameters are major factors involved in controlling distribution of copper in the area. The increase in pH values; i.e. decrease in the acidity of solution (i.e. H^+ low) and consequently a decrease in the solubility of copper free ions leading to a decrease in the uptake of copper free ions by aquatic organisms causing an increase in the concentrations of copper free ions. Moreover; an increase of dissolved copper occurred by increasing oxygen concentrations resulting from re-dissolution processes which occur in an oxygenated aquatic system [68].

Factor (2) exhibited (34.84%) of the total variance of (74.02%) with high positive loading on salinity (0.843) and TDCHO (0.760). This factor indicated that TDCHO showed highly positive correlation with salinity revealing the increase of TDCHO concentration by increasing the salinity value, suggesting that salinity was among the factors that influenced TDCHO distribution in the Abu-Qir drain and Abu-Qir Bay [63]. It is well known that salinity affects the photosynthesis process and its rate, and consequently TDCHO concentration as products of photosynthesis can be affected by salinity [69].

Table 3. Varimax rotated component matrix for hydrographical parameters, Cu and TDCHO in Abu-Qir drain and Abu-Qir Bay.

Parameters	F1	F2
Temperature	-0.036	-0.737
Salinity	0.259	0.843
pH	0.930	0.236
DO	0.979	0.162
OOM	0.101	-0.650
Cu	0.917	-0.320
TDCHO	0.025	0.760
Variance	39.18	34.84
CV (%)	39.18	74.02

Factor (2) also was characterized by high negative loading on temperature (-0.737) and moderate negative loading on OOM (-0.650) leading to existence of negative relation between the temperature and OOM. This factor indicated that

temperature showed highly effect on OOM, this can be attributed to the biodegradation of organic matter increases by increasing temperature [3].

Rotation Method: Varimax with Kaiser Normalization,

CV: cumulative variance, Bold number indicates positive correlation, and Negative italic number indicates negative correlation.
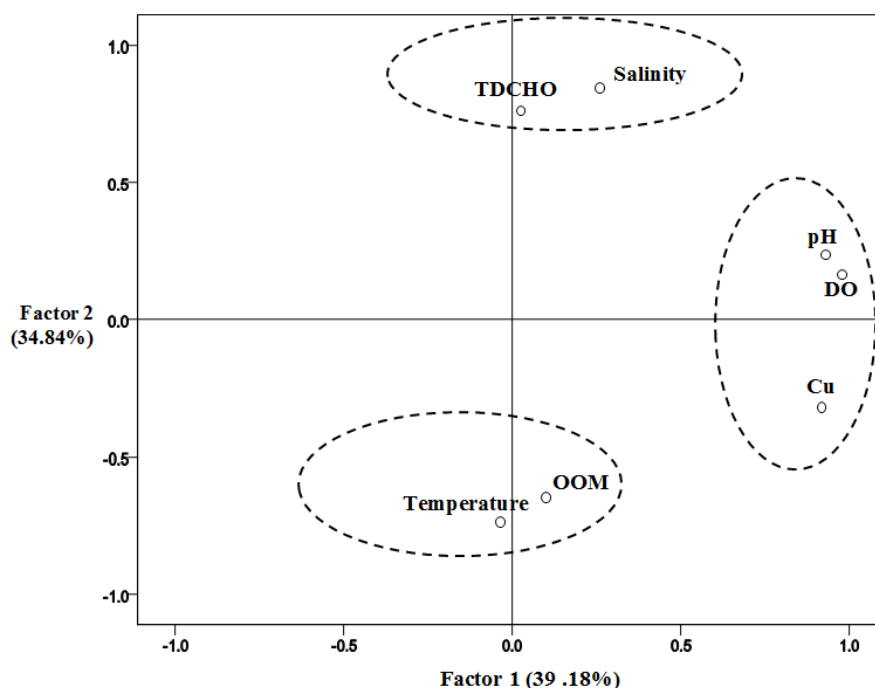

Figure 6. Graphical representation of the application of PCA method for the data of hydrographical parameters (temperature, salinity, pH, DO and OOM), Cu and TDCHO for Abu-Qir drain and Abu-Qir Bay.

4. Conclusion

It is concluded from factor analysis (FA) that the hydrographical parameters are the major controlling factors in the distribution patterns of copper and TDCHO in the Abu-Qir drain and Bay of the present study. Indeed, (FA) could be useful in the interpretation or explanation of the data. In addition, the use of (FA) could be compiled the comprehensive monitoring data of the present study into two factors which responsible for data structure explaining (74.02%) of total variance in Abu-Qir drain and Abu-Qir Bay.

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