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Physicochemical parameters of the western harbor of Alexandria and their effect on the corrosion rate of steel during 2012

Hermine Ramzy Zaki Tadros

Marine Chemistry Lab., Marine Environment Division, National Institute of Oceanography and Fisheries, Alexandria, Egypt

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Abstract

This study focuses on the physicochemical parameters of the Western Harbor of Alexandria and the corrosion rate of steel in seawater by using weight loss technique. Triplicate surface water samples were collected seasonally from fixed 10 stations from winter to autumn 2012. The results indicated that the temperature fluctuated between 16.2ºC to 27.6ºC, with annual average of 22.62ºC. Salinity differed between 22.7 and 37.9, with annual average 34.34. The pH ranged from 7.93 to 8.92. Total alkalinity varied between 1.209 and 4.2meq/l, with an annual average of 3.13meq/l. Dissolved oxygen ranged from 1.136 to 15.445 mg/l, the annual average was 8.324 mg/l. Biochemical oxygen demand fluctuated between 0.12 and 10.45 mg/l; the annual average was 3.62 mg/l. Oxidizable Organic Matter ranged between 0.19 and 7.2mgO_2/l, with annual average 1.551mgO_2/l. While nutrient salts (µmol) displayed wide ranges and annual averages; 0.075- 9.75µmol/l; 2.451µmol/l, 0.476-51.23µmol/l; 13.148µmol/l, 0.005-32.35µmol/l 9.311µmol/l, 0.547-35µmol/l; 9.941µmol/l, 0.702-16.15µmol/l; 3.59µmol/l for phosphate, silicate, nitrite, nitrate, ammonia respectively. N/P ratio showed that phosphorus was the limiting factor. Sulfate fluctuated between 1.015 and 3.25 g/l with annual average of 1.829 g/l. The weight loss was calculated from the differences between the steel panels immersion date in seawater and after 24hrs of immersion in seawater on laboratory scale and the corrosion rate of steel was calculated. The corrosion rates of steel differed between 0.2321 and 0.8998mpy. The annual average was 0.5099mpy. The Water quality index showed that stations 6, 1 and 2 suffered from pollution during summer accompanied by highest silicate, oxidizable organic matter, nitrate and sulfate.

***Corresponding Author:** Hermine Ramzy Zaki Tadros ✉ hermine_rzts@yahoo.com

Introduction

The Western Harbor receives imported and exported materials such as coal, manufactured iron, cement, fertilizers, grains, food, textiles, chemicals, timber, as well as crude and refined oil. Located on the southern and eastern sides of the harbor, the quays for the various maritime activities divide these sides into several small semi-enclosed or open basins. Waste waters of varying quantity and quality are discharged into the harbor, mainly through the Ommum Drain (76.4 m^3s^{-1}) and the Noubaria Canal (1 m^3s^{-1}) through El-Mex Bay (Mohamed *et al.*, 2004).

Eutrophication has become a persistent problem in the Western Harbor of Alexandria and was recorded for the first time in 1985. These problems came about as a result of the continuous enrichment of nutrients from different sources, including maritime activities, several land-based effluents consisting of mixed industrial, domestic and agricultural wastes as well as stored chemical fertilizers. Nutrient loads are directly dependent on human activities, which in turn depend on the growth of the world's human population. Consequently, human-induced eutrophication is in a way related to the increase in human population (De Jonge *et al.*, 2002). In Alexandria City, the human population has just about doubled since the first record of eutrophication in the Western Harbor. This population increase has been associated with the intensive development of human activities, which directly or indirectly have led to the increase in nutrient enrichment in the harbor and the consequent increase in the level of eutrophication during the past two decades. Numerous studies have been conducted on the physical, chemical and biological characteristics of the harbor (Farag, 1982; El-Gindy, 1986; Nessim and Tadros, 1986; Nessim and Zaghloul, 1991; Saad and Hemeda, 1991, 1992a, b; Shriadah and Tayel, 1992; Zaghloul, 1994, 1996; Hassan and Saad, 1996; Saad *et al.*, 2000, 2001, 2002, 2003; Abdel-Aziz, 2002).

Seawater is one of the most corroded and most abundant naturally occurring electrolytes. A great part of metallic constructions exposed in seawater and marine atmospheres are destroyed, due to the corrosion phenomenon (Farro *et al.*, 2009).

Corrosion reaction rate is directly proportional to seawater temperature. Corrosion rate of metals in shallow warm water is higher than in the colder deep seas. Biological activities and dissolved oxygen concentration (DO) are considered in steel corrosion rate of steel in seawater medium (David, 2005). Beside them, also pollution, temperature, salinity and velocity are the major factors which affected the corrosion behavior of materials in the submerged zone (Saleh and Anees, 2005). Previous studies in Lab. scale showed that steel corrosion rate varied between 3.665mpy and 10.462mpy in seawater medium collected from El-Silsila, Stanly, Gleem and El-Montazah (Aida and Hermine, 2009), another one showed that the corrosion rate of steel fluctuated between 4.159mpy and 23.59mpy in Lab. scale for seawater medium extended from Abu-Qir till El-Mex (Hermine and Maged, 2013). With respect to the western part extended from El Dekhela to Marbilla village, the corrosion rate of steel ranged between 2.809mpy and 16.96mpy and it showed inversely proportional relation with sulphate ion concentrations (Aida *et al.*, 2012). Corrosion rate of steel in seawater medium collected from the Eastern harbor of Alexandria (semi-closed area) showed a range between 4.320mpy and 9.813mpy (Aida and Rokaya, 2006).

This paper aims to study the physico-chemical parameters in this eutrophic harbor such as: Temp., pH, alkalinity, DO, BOD, OOM, SO_4^{-2}, salinity, nutrients (PO_4^{-3}, SiO_3^-, NO_2^-, NO_3^- , NH_3). It aims also to find a relation between these factors and the corrosion rate of steel on Lab. Scale by using weight loss technique.

Materials and methods

Area of study

The Western Harbor of Alexandria is the largest and oldest harbor on the Egyptian Mediterranean coast; it is the main international trade harbor (Mahmoud *et al.*, 1988). It is a shallow, elliptically shaped, semi-enclosed basin with an area of 7.4 km^2 and depth range of 5.5–16 m.

Ten sampling stations were chosen along the Western Harbor (W.H.) of Alexandria as shown in Fig. 1.

Triplicate surface seawater samples, forming totally 120 samples, were collected seasonally from each chosen station from winter 2012 to autumn 2012 according to the standard method published by the American Public Health Association (APHA), 2005.

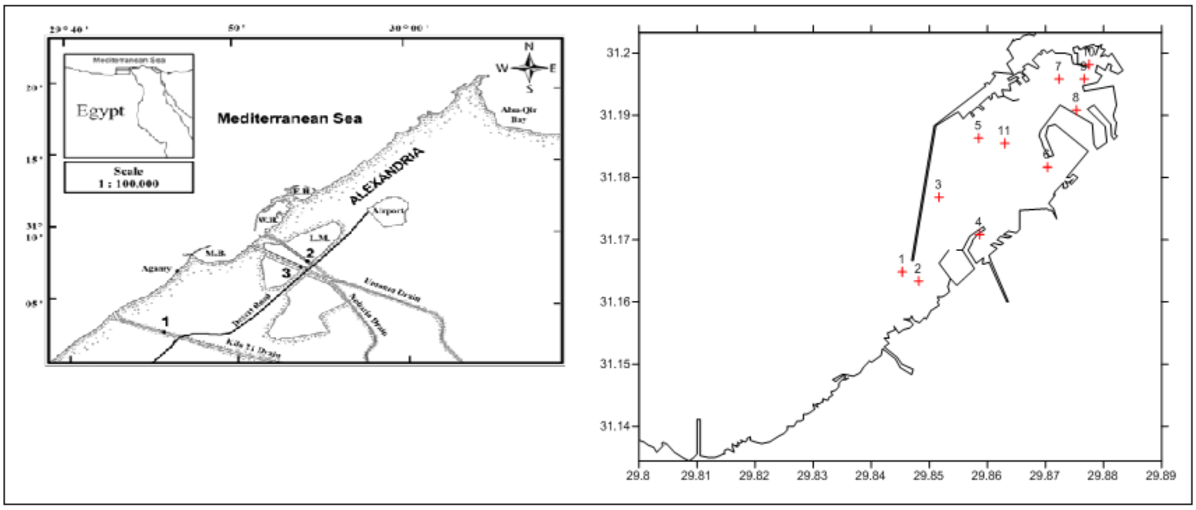

Fig. 1. Sampling locations from the Western harbor (W.H.) of Alexandria during 2012.

Physicochemical parameter measurements of seawater

Temperature

Water temperature was measured using an inductive portable thermometer (range 0-50°C).

Salinity

It was determined by measuring the electrical conductivity using an inductive salinometer (Beckman; model RS-7C). The salinometer was standardized with standard seawater, Copenhagen, Denmark, of chlorinity 19.375 ‰. The conductivity was measured to the nearest 0.0001 and converted to salinity up to the nearest 0.001 ‰ after making temperature correction using the international tables of salinity/conductivity conversion (Wooster *et al.*, 1969).

pH

The pH-value of water samples was measured in the laboratory immediately after collection using bench type (JENWAY, 3410 Electrochemistry Analyzer pH-meter) with reading up to 0.01 pH unit after necessary precautions in the sampling and standardization processes.

Alkalinity

The alkalinity is determined according to standard Methods, Elewa, 1988. Alkalinity is calculated from the following equation:

Total alkalinity = ($\underline{\text{ml of HCl x 1000 x } N_{HCl}}$) / ml of sample

Dissolved oxygen and biochemical oxygen demand

They were determined according to the classical Winkler's method modified by Grasshoff, 1976. The amount of dissolved oxygen in each sample was calculated by applying the following equation:

O_2 ml/l = (N × V × 32000/4)/4(B-2) ×1.43

N= Normality of sodium thiosulphate

V= Volume of sodium thiosulphate

B= Volume of oxygen bottle.

Oxidizable organic matter (OOM)

It was determined using permanganate values test (FAO, 1975), and it is calculated from the following equation:

OOM mgO_2/L = [(V blank – V sample) x 8 x 1000 x N $Na_2S_2O_3$] / V of sample

Nutrient salts

The most important dissolved inorganic forms of nitrogen (ammonia, nitrite & nitrate), phosphate (PO_4^{-3}) and silicate (SiO_3^-) were determined colorimetrically according to the methods described by Parsons, 1984. Their absorbance's were measured by using a Double-Beam spectrophotometer model Shimadzu UV-150-02.The values were expressed as µmol/l.

Sulphate

It is precipitated with Ba^{+2} in acidic medium using glycerol-ethanol solution as a conditional reagent. The sulphate is measured turbidimetric with spectrophotometer at wave length 420nm (Rossum and Villarruz, 1961). Sulphate concentrations are obtained from the standard curve using different known concentrations.

Chemical composition of steel

The used steel had the following chemical composition (wt. %): C, 0.288; Mn, 0.578; P, 0.0698; S, 0.0121; other constituents, 0.1621; Fe, 98.89 (balance Fe).

Weight loss measurements

30 Sheets of steel with thickness of 0.4 mm were cut to panel dimensions 3.2 × 2.1 × 0.4 cm with a tiny hole at the top. The edges were tabard and their surfaces were polished with a series of emery papers starting with a coarse one (400 grade) and proceeding in steps to finer grades down to 800 grade emery paper, cleaned in acetone rinsed with distilled water, dried, weighed for the original weight and stored in a moisture-free desiccators prior to use. Each panel was immersed in a bottle of 1 L glass containing 1L of seawater collected from the surface seawaters samples of the mentioned stations (Fig. 1) just after measuring the different physical and chemical parameters of the western harbor seawater. After 24 hour the panels were removed and the corrosion products on the specimen surfaces were removed chemically by immersion in a specific solution (500 ml HCl + 500 ml distilled water + 3.5 g hexamethylenetetramine) that was vigorously stirred for 10 min at 25°C, Yuantai *et al.,* 2009 and International standard ISO 9226, 1992. After removal of corrosion products, the specimens were rinsed with distilled water, dried in warm air and then weighed to determine their weight loss. The immersion of steel panels for each station is done three times in each season. After calculating the average weight loss value for each station; corrosion rate of steel is then calculated according to the equation: (Standard Practice, 1990 and Robert, 2005).

Corrosion rate= (K × W) / (A × T × D).

Where K: is a constant, W: is the weight loss (g), A: is the area of steel (cm^2).

T: is the time of exposure (h), D: is the density of steel (g/cm^3).

Statistical analysis

Correlation coefficient at a confidence limit 73.655% ($P \leq 0.05$) were estimated for all data (n=40), as well as factor analysis and principle component analysis (PCA) for the average data well done by using SPSS program version 19 and discussed.

Results and discussion

Temperature

The temperature is an important factor that affects on the corrosion rate in seawater medium as it increases the diffusion rates of the ions and helps in convection mass transfer, both of which promote depolarization (Subir Paul, 2012). In the present work, The temperature ranged between a minimum of 16.2°C at station 6 followed by 16.3°C at station 2 during winter season and a maximum of 27.6°C at station 4 during summer season (Fig. 2), with total annual average of 22.62°C. It is noticed that stations temperature differed widely in both winter and summer seasons (16.2°C; station 6 & 18.1°C at station 1 with total average of 17.16°C during winter and 25.9°C; stations 5, 6, 7 & 27.6°C at station 4 with total summer average of 26.2°C) respectively, while slightly deviations was observed in both autumn and spring seasons 2012 and their seasonal averages were 22.9°C and 24.23°C respectively.

Table 1. Averages of the physicochemical parameters and the corrosion rate of steel in the Western Harbor during different seasons 2012.

Season	Temp °C	Salinity ‰	pH	Total alkalinity meq/l	DO ml/l	BOD	OOM mgO₂/l	PO_4^{-3} µg/l	SiO_3^-	NO_2^-	NO_3^-	NH_3	N/P	SO_4^{-2} g/l	Corrosion rate mpy
winter	17.16	37.19	8.09	3.49	8.154	3.657	0.855	0.989	12.439	0.63	9.453	2.081	7.095	1.608	0.4872
spring	24.23	27.11	8.75	3.76	11.5	4.842	0.534	0.849	4.986	0.239	11.184	2.82	7.084	1.437	0.5285
summer	26.2	35.66	7.93	1.733	5.895	4.751	4.112	6.1	28.959	14.577	15.425	3.919	6.996	2.423	0.4994
autumn	22.9	37.41	8.43	3.535	7.746	1.231	0.704	1.865	5.207	21.799	3.701	5.541	18.79	1.847	0.5246
Average	22.62	34.34		3.129	8.324	3.62	1.551	2.451	13.148	9.311	9.941	3.95		1.829	0.5099

Comparing these results with those obtained by (Mohamed *et al.*, 2004), it is found that the water temperature did not deviate from the seasonal fluctuations and it is normal as found on Egypt's Mediterranean coast (15–29°C).

Table 2. Varimax rotated component matrix for physico-chemical parameters and corrosion rate of steel.
Rotated Component Matrix[a]

	Component PC1	PC2	PC3	PC4
Temp	0.534	-0.319	0.655	-0.194
pH	-0.234	-0.106	0.738	0.273
Alkalinity	*-0.927*	-0.171	-0.005	0.087
DO	-0.437	*-0.71*	0.051	0.238
BOD	0.321	-0.6	-0.057	0.395
OOM	0.855	0.039	0.069	0.234
SO_4^{-2}	0.688	0.104	0.22	0.429
Salinity	0.146	0.907	-0.077	0.138
PO_4^{-3}	0.757	0.15	0.203	0.111
SiO_3^-	0.892	-0.003	-0.244	-0.04
NO_2^-	0.199	0.609	0.636	-0.097
NO_3^-	0.785	0.082	0.083	-0.34
NH_3	0.164	0.166	0.461	-0.411
Corrosion rate	-0.066	0.063	-0.037	*-0.774*
% of Variance	36.091	16.381	11.894	9.29
Cumulative %	36.091	52.472	64.365	73.655

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.[a]
a. Rotation converged in 5 iterations.

Salinity

Salinity is the saltiness or dissolved salt content of a body of water. Salinity is an important factor in determining many aspects of the chemistry of natural waters and of biological processes within it, seawater in the world's oceans has a salinity of about 3.5% (35 g/l). In Western Harbor; salinity differed between 22.7 during spring and 37.9 at station 9 followed by 37.7 at station 7 and 37.6 during autumn (Fig. 3). With respect to seasonal average; it is noticed that spring season showed the lowest salinity for all stations with monthly average of 27.11. This may be due to fresh water discharged during this season through the Ommum Drain and Noubaria Canal

(Dorgham *et al*., 2004). The arrangement of the other monthly average was as follows: summer, winter then autumn 27.11, 37.19 and 37.41 respectively. The total annual salinity average was 34.34. It could be noticed that the fresh water discharged in the harbor in the present work is greater than those obtained by Dorgham *et al*., 2004 as he found that the salinity ranged between 26.3 and 36.8.

Table 3. Principal component factor scores and water quality index, WQI, of water samples in the study area.

Hot spots	PC1	PC2	PC3	PC4	WQI	Parameter
6	2.09	-0.41	0.733	2.04	1.3	According to high PC1 value, the effective parameters are: SiO_3^-, OOM, NO_3^- and SO_4^{-2} beside high value of PC4; corrosion rate
1	2.45	-0.23	-0.36	0.44	1.1	According to high PC1 value, the effective parameters are: SiO_3^-, OOM, NO_3^- and SO_4^{-2}
2	2.17	-0.43	-0.57	0.71	1.0	According to high PC1 value, the effective parameters are: SiO_3^-, OOM, NO_3^- and SO_4^{-2}

pH

The hydrogen ion concentration (pH) plays an important role in many of the life processes. Living organisms are very dependent on and sensitive to pH (Hayat *et al*., 2009). The pH fluctuated between 7.93 at station 10 followed by 8.01 at station 1 during summer and 8.92 at station 5 followed by 8.8 at station 1, then 8.75 at station 10 during spring season (Fig. 4). Generally, as normal the pH values are in the slightly alkaline region.

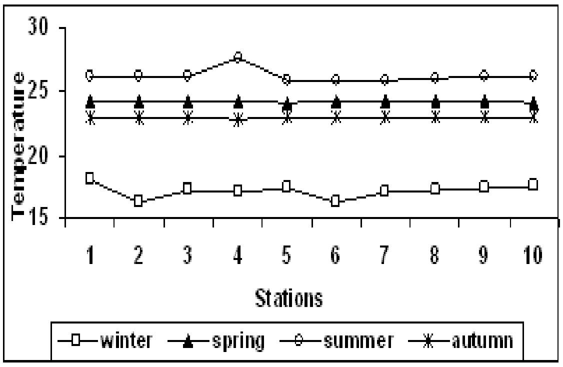

Fig. 2. Relation between the temperature and different stations in the W.H. during 2012.

Total alkalinity

Testing water samples for total alkalinity measures the capacity of the water to neutralize acids. This test is important in determining the estuary's ability to neutralize acidic pollution from rainfall or wastewater (Voluntary Estuary Monitoring Manual, 2006). Total alkalinity varied between 1.209meq/l at stations 5, 9&10 during summer season and 4.2meq/l at station 8 followed by 4.1meq/l at station 9 (Fig. 5), with total annual average of 3.13meq/l. The lowest total alkalinity seasonal values were observed during summer season; with total seasonal average 1.733meq/l, while the highest values were during spring season; with total seasonal average 3.76meq/l.

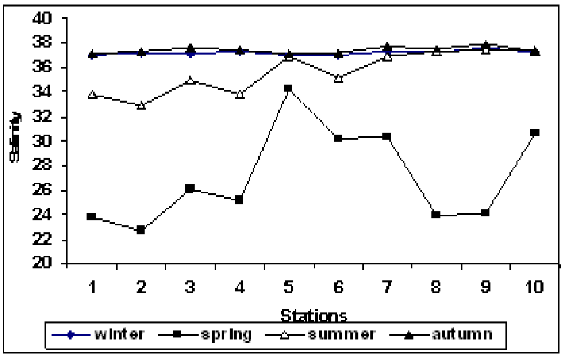

Fig. 3. Relation between salinity and different stations in the W.H. during 2012.

Dissolved oxygen (DO)

Dissolved oxygen is considered as one of the most important and useful parameters for identification of different water masses and for assessing the degree of pollution especially with organic pollutants which affects fish and other marine life through oxygen reduction or depletion (Shaltout and Abd-El-Khalek, 2014). In the present work DO fluctuated a minimum of 1.136 mg/l at station 10 during summer and 15.445 mg/l at station 6 followed by 14.98 mg/l at station 8 during spring (Fig. 6). The highest DO seasonal average was recorded during spring (11.501 mg/l) and the lowest seasonal average was during summer season (5.895 mg/l). The total annual DO average was 8.324 mg/l. From these results, it could be noticed that the harbor in the present work was well oxygenated. This may be attributed to the high levels of DO in El-Mex Bay that discharged in the Western Harbor as discussed by Hamdy *et al*., 2015 who stated that the distribution pattern of DO at El-Mex Bay showed a wide variation and fluctuated between 2.52 to 9.11 mg/l. These values are higher than those observed by Dorgham *et al*., 2004, for the same area, who noticed that the dissolved oxygen at the surface fluctuated between 1.8 and 6 mg/l and for most of the year it was between 3 and 4 mg/l. In this study; it could be noticed that

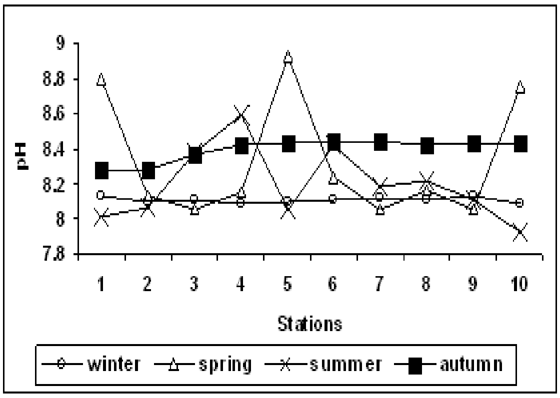

Fig. 4. Relation between the pH and different stations in the W.H. during 2012.

Biochemical Chemical Oxygen Demand (BOD)

BOD is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. In present work BOD fluctuated between a minimum of 0.12 mg/l at station 6 followed by 0.23 mg/l at station 8 during spring and a maximum of 10.45 mg/l at station 2 during spring season (Fig. 7). The highest BOD seasonal average was during spring season (4.842 mg/l) as it is consumed by different organisms during this season, while the lowest seasonal average was during autumn season (1.231 mg/l). The total annual average was 3.62 mg/l.

Oxidizable Organic Matter (OOM)

OOM is one of the most criteria to assess sewage pollution and organic loading. It is expressed as a measurement of the oxygen equivalent to the amount of organic matter oxidized by a strong oxidizing agent. The source of OOM in the Harbor water is from biological activities of living organisms, the decomposition products of died organisms (Shaltout and Abd-El-Khalek, 2014). The minimum OOM concentration was 0.19 mgO_2/l at station 1 followed by 0.32 mgO_2/l at station 4 during spring season and station 10 during autumn season. Maximum value of OOM content was recorded in summer 7.2 mgO_2/l at station 8. Most seasonal OOM values and their averages during spring, autumn and winter seasons were in the normal range, their seasonal averages were as follows: 0.534, 0.704 and 0.855 mgO_2/l respectively. The high levels of OOM concentrations was observed during summer season as it ranged between 1.6 to 7.2 mgO_2/l with total summer average of 4.112 mgO_2/l which may indicate the high amount of discharges in the harbor during summer season (Fig. 8). The OOM annual average was 1.551 mgO_2/l. These results confirms the DO concentrations date as most seasons were well oxygenated and the lowest DO values were observed in summer season which showed highest OOM concentrations.

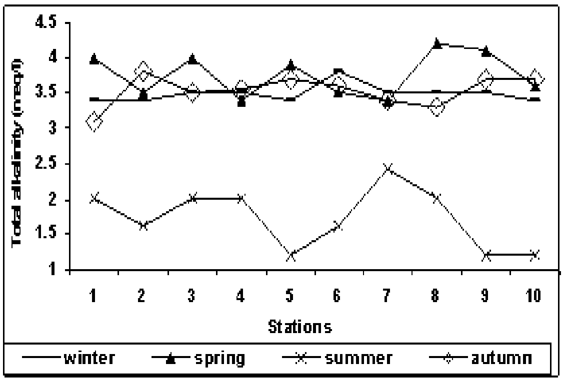

Fig. 5. Relation between the total alkalinity and different stations in the W.H. during 2012.

By comparing the present OOM results with those obtained from Shaltout and Abd-El-Khalek, 2014) who found that the seasonal average was varied from 2.22±0.995 mgO_2/l during and maximum average content 7.27±2.19 mgO_2/l during summer, it could be concluded that as the water discharged in El-Dekhaila Harbor contained high amount of OOM (summer season) so it affected on the Western Harbor Bay and increased its OOM content too. Another study on El-Mex Bay showed that the OOM concentrations ranged between 0.12-10.49 mgO_2/l (Okbah *et al*., 2013).

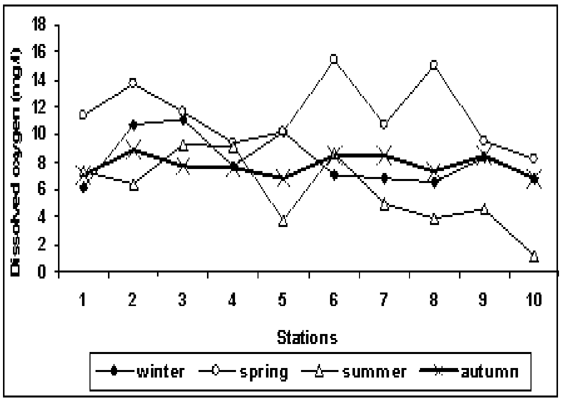

Fig. 6. Relation between dissolved oxygen concentrations and different stations in the W.H. during 2012.

Nutrient salts

Phosphate (PO_4^{-3})

Phosphorus plays a major role in biological metabolism. It is an essential nutrient element, which plays an important role in photosynthesis and other processes in plants. Reactive phosphate fluctuated between minimum values of 0.075, 0.09µmol/l at stations 6&2 respectively during winter and maximum values of 9.75 and 9.65µmol/l at stations 6&1 respectively during summer (Fig. 9). The arrangement of the seasonal averages was as follows: spring, winter, autumn and summer with averages; 0.85, 0.989, 1.865 and 6.1µmol/l respectively. The highest phosphate concentrations 3.69-9.65µmol/l during summer season was accompanied by the highest OOM values too, this may indicate that the Western Harbor received agricultural discharges from Omoum Drain and Noubaria Canal. The total PO_4^{-3} annual average concentration was 2.451µmol/l. Dorgham *et al.*, 2004 found that phosphate ranges were 0.12–5.7µM in the Western Harbor, while Shaltout and Abd-El-Khalek, 2014 found that the annual average of phosphate was 5.77±6.62µM at El-Dekhaila Harbor.

Silicate (SiO_3^-)

Silicate is one of the important constituents in the sea water. It is a good indicator of fresh water dispersion and of the potential for diatom (Fahmy *et al.*, 1999). SiO_3^- concentrations ranged between minimum values of 0.476&0.774µmol/l at stations 5& 7 respectively during autumn and 51.23µmol/l at station 2 during summer 2012 (Fig. 10). The arrangement of the seasonal averages was as follows: spring, autumn, winter then summer; 7.986, 5.207, 12.439 and 29.959µmol/l respectively. The highest seasonal averages of silicate were accompanied by the increase of both phosphate and OOM concentrations during summer season; this indicates that the Western Harbor received agricultural discharges from Ommum Drain and Noubaria Canal (Dorgham *et al.*, 2004). The total annual SiO_3^- average was 13.148µmol/l. The low levels of SiO_3^- during spring and autumn seasons may be attributed to the plankton's consumption of SiO_3^- during these warm seasons. Dorgham *et al.*, 2004 found that silicate levels ranged between 0.3 and 36.3µM. Most SiO_3^- concentrations in the present work were within Dorgham's *et al* range except some higher values found during summer due to high amount of agricultural discharges in the Harbor.

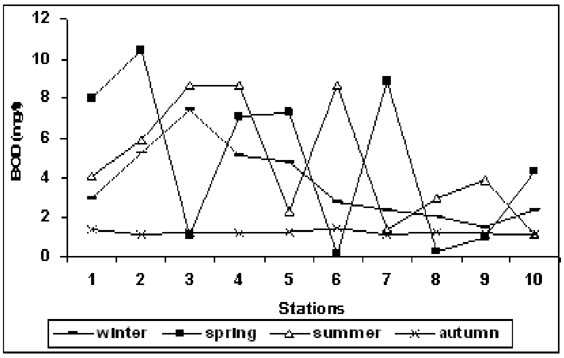

Fig. 7. Relation between the Biochemical oxygen demand and different stations in the W.H. during 2012.

Nitrite (NO_2^-)

Nitrite is the result of bio-chemical oxidation of ammonia (nitrification) or the reduction of nitrate (denitrification). NO_2^- concentrations fluctuated between a minimum value of 0.005µmol/l at station 7 during spring and a maximum value of 32.35µmol/l at station 6 during autumn 2012 (Fig. 11). The seasonal averages of nitrite were as follows: spring, winter, summer and autumn; 0.239, 0.63, 14.577&21.799µmol/l respectively. The total annual

NO_2^- concentration average was 9.311µmol/l. Dorgham *et al.*, 2004 found that nitrite levels ranged between 0.21 and 20.46µM. These data represent that nutrient salts discharged in the Western Harbor in this work are much greater than previous work.

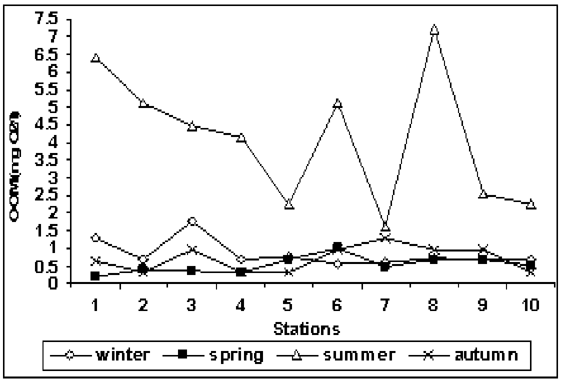

Fig. 8. Relation between Oxidizable organic matter concentrations and different stations in the W.H. during 2012.

Nitrate (NO_3^-)

The most stable form of inorganic nitrogen in oxygenated water is nitrate and it is the end product of nitrification process in natural water. NO_3^- differed between 0.547µmol/l at station 8 during winter and 35µmol/l at station 3 followed by 34.35µmol/l at station 1 during summer (Fig. 12). The total annual nitrate concentrations average was 9.941µmol/l. Nitrate seasonal average was arranged as follows: autumn, winter, spring then summer; 3.701, 9.453, 11.184 & 15.425µmol/l respectively. It is noticed that the highest nitrate concentrations were observed during summer accompanied with highest temperature, OOM, phosphate and silicate concentrations. Previous results reported by Dorgham *et al.*, 2004 stated that NO_3^- ranged between 0.29 and 3.3µM. These results agree with the assumption that through the present work the Western Harbor received agricultural discharges from Ommum Drain and Noubaria Canal.

Ammonia (NH_3)

Ammonia is the major nitrogenous product of the bacterial decomposition of organic matter containing nitrogen, and is an important excretory product of invertebrates and vertebrates. As for the utilization of nitrogenous materials, ammonia is the preferred inorganic source because of its ease of uptake and incorporation into amino acids (N-assimilation). In the present work NH_3 fluctuated between 0.702µmol/l at both stations 5&9 during winter and autumn respectively and 16.15µmol/l at station 1 followed by 9.065µmol/l at station 2 during autumn (Fig. 13). Both stations 1&2 are in the opening of the Western Harbor; this may indicate high amount of drainage discharged in Ommum Drain and Noubaria Canal and affected on the water quality of both stations (1&2) during autumn. Seasonal ammonia averages were arranged as follows: winter, spring, summer and autumn; 2.081, 2.82, 3.919 and 5.541µmol/l. The annual average of ammonia was 3.59µmol/l. Comparing these results with those obtained by Dorgham *et al.*, 2004 who found that ammonia differed between 0.56 and 57.46µM; it could be concluded that the water quality in the Western Harbor during the present work is much better than the previous one.

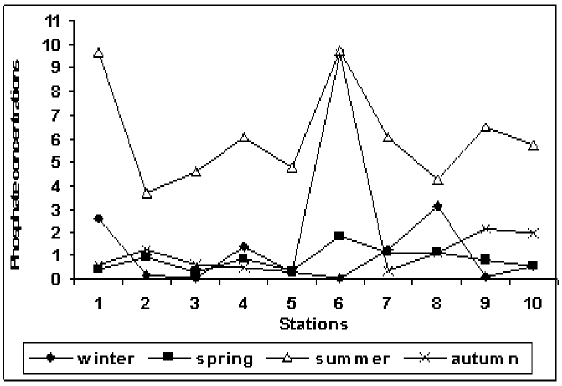

Fig. 9. Relation between phosphate concentrations and different stations in the W.H. during 2012.

N/P ratio

Regarding to the dissolved inorganic nitrogen (DIN) and PO_4-P (which are the main forms of N and P that are readily bioavailable for the growth of phytoplankton); it is noticed that the N/P ratio in the present study is lower than the assimilatory optimal N/P=15/1 and the Redfield's ratio N/P=16/1 except in autumn season (18.8/1). According to the previous works, extremely variability of N/P ratio is common along the Mediterranean Sea coast of Egypt, particularly in areas exposed to land based runoff

(Dorgham *et al*., 2004). Marine algae are P-limited at N: P ratio > 6 and N – limited at ratio < 4.5; in range of 4.5 – 6, the two nutrients are near their optimal assimilative proportion; Chraudani and Vighi, 1978. In the present study, N/P ratio ranged between ≈ 7 in winter, spring and summer seasons and high value 18.788 during autumn season (Table 5). This consideration showed that phosphorus was the limiting factor in the Western Harbor.

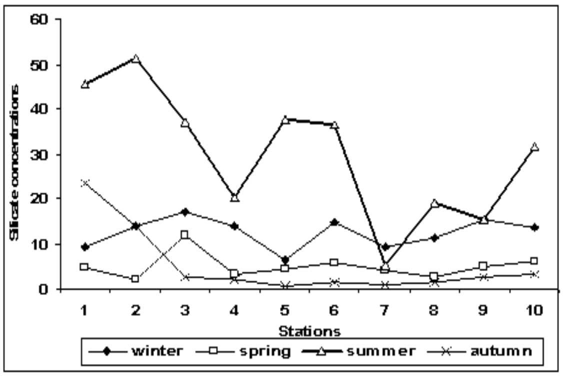

Fig. 10. Relation between silicate concentrations and different stations in the W.H. during 2012.

Sulphate (SO_4^{-2})

Sulphate is one of the major constituents of seawater which make a significant contribution to salinity. Sulphate concentration fluctuated between a minimum value of 1.015 g/l at station 10 during winter followed by 1.054 g/l at station 2 during spring and a maximum value of 3.25 g/l at station 6 during summer season (Fig. 14). The seasonal SO_4^{-2} concentration averages were as follows: 1.437, 1.608, 1.847 and 2.423 g/l for spring, winter, autumn and summer respectively. The total annual SO_4^{-2} average was 1.829 g/l.

Corrosion rate of steel

Corrosion rate of steel is an important factor to be studied specially in harbors as it gives indication about the effect of corrosion on ships, pipes as well as the maritime activities in harbors. Corrosion rate of steel was calculated by using weigh loss technique and its experiments were done three times for each station on laboratory scale then the averages were calculated for each station during the different seasons. It was noticed that the lowest corrosion rates of steel were 0.2321mpy followed by 0.2396mpy at both stations 7&6 respectively during summer season, also low values of 0.2459&0.2867mpy were observed at both stations 4&8 during spring season (Figure 15). The highest corrosion rate of steel was 0.8998mpy at station 10 during summer. The seasonal average corrosion rate of steel was as follows: winter, summer, autumn then spring; 0.4872, 0.4994, 0.5246 and 0.5289 respectively. The total annual average was 0.5099mpy. Generally, the corrosion rate of steel in the Western Harbor on laboratory scale is lower than its corresponding values in the Eastern Harbor (4.320-9.813) mpy (Aida and Rokaya, 2006) as well as in the eastern coastal zone of Alexandria that ranged between 3.665 – 10.462mpy (Aida and Hermine, 2009) and in the western area water (Alexandria, Egypt); 16.24, 16.96 and 16.30mpy and 11.476 and 11.934mpy (Aida *et al*., 2012).

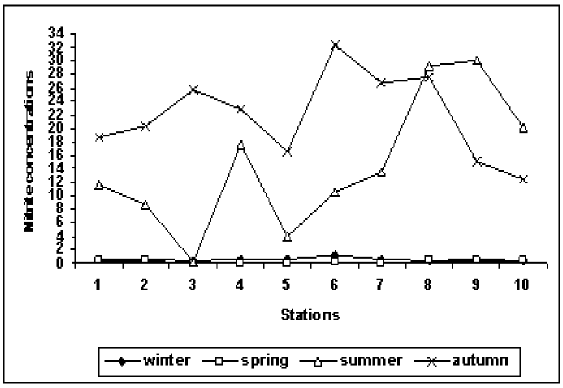

Fig. 11. Relation between nitrite concentrations and different stations in the W.H. during 2012.

As shown from Table 1, it is noticed that the lowest seasonal average corrosion rate 0.4872 mpy during winter was accompanied by lowest temperature, pH and NH_3 concentration and highest DO. The highest seasonal average corrosion rate of steel 0.5285mpy during spring was accompanied by lowest salinity, OOM, PO_4^{-3}, SiO_3^{-}, NO_2^{-}, N/P ratio& SO_4^{-2} and highest pH, total alkalinity& DO.

Principal Component Analysis (PCA)

Principal component analysis is derived from the water parameters analysis of the seasonally average data in Western Harbor. The output data reveals four factors (PC1-PC4) affect Western Harbor water, association and sources, with cumulative covariance of 73.655%.Varimax rotated components matrix is presented in Table 2 to give an overview of the nature of loading among the parameters.PC1, PC2, PC3 and PC4 have covariance of 36.091%, 16.381%, 11.894% and 9.29% respectively. PC1 represented high loading of silicate, oxidizable organic matter, nitrate, phosphate and sulphate (0.892, 0.855, 0.785, 0.757&0.688 respectively) associated with negative loading of alkalinity (0.927) which can demonstrate autochthonous sources of alkalinity outfalls. PC2 had loading of salinity (0.907) with negative loading of DO (0.71). This illustrates the relation between salinity and dissolved oxygen. PC3 represented loading of pH (0.738) and nitrite (0.636). PC4 represented high negative loading of corrosion rate (0.774) with covariance % of 9.29.

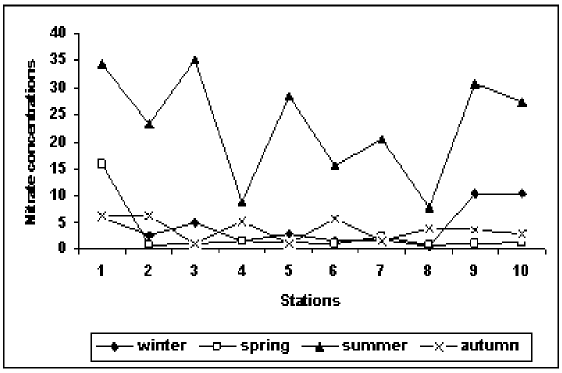

Fig. 12. Relation between nitrate concentrations and different stations in the W.H. during 2012.

Water Quality Index (WQI)

Water Quality Index (WQI) is calculated according to the following formula (Davis, 1986):

$WQI=\Sigma^{n}_{n=1} (\lambda n / \Sigma\lambda) \times PCn.$

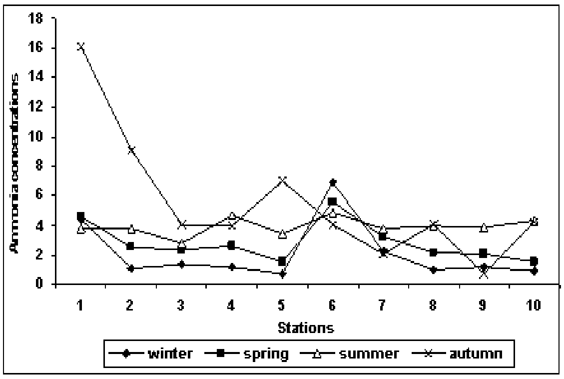

Fig. 13. Relation between ammonia concentrations and different stations in the W.H. during 2012.

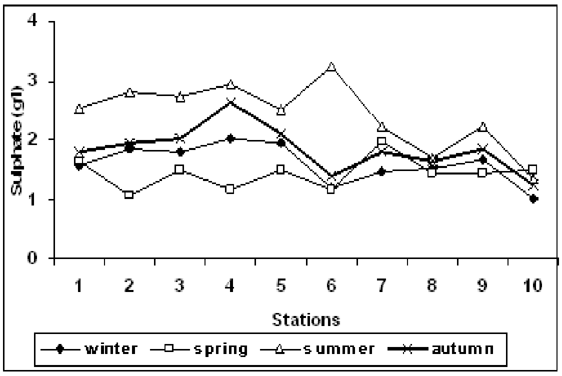

Fig. 14. Relation between sulphate concentrations and different stations in the W.H. during 2012.

For PC Assessment model where n: The number of effective components; they are the Eigen values of the effective components, Σ λ sum of the Eigen values and PCn are the n critical principal component scores (El-Iskandarani *et al.*, 2004). According to calculation of water quality index, station 6 (WQI =1.3), station 1 (WQI =1.1) and station 2 (WQI =1.2) suffered from pollution during summer season.

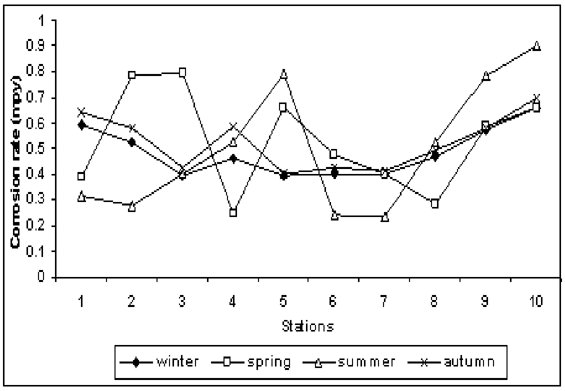

Fig. 15. Relation between the corrosion rate of steel and different stations in the W.H. during 2012.

These stations are highly affected by discharged water of El-Ommum Drain where silicate, oxidizable organic matter, nitrate and sulphate are the effective parameters (Table 3).

Conclusion

Spring season showed the highest alkalinity, DO, BOD and corrosion rate and lowest OOM, sulphate, salinity, phosphate, silicate and nitrite concentrations as these nutrients are consumed by different planktons during this season.

Summer season showed the highest temperature, OOM, sulphate, phosphate, silicate and nitrate concentrations and the lowest alkalinity, DO and N/P ratio.

The minimum corrosion rate of steel was 0.4872mpy during winter; accompanied by lowest temperature and ammonia concentration.

The maximum corrosion rate of steel was 0.5285mpy during spring; accompanied by the highest alkalinity, DO and BOD lowest OOM, sulphate, salinity, phosphate, silicate and nitrite concentrations.

N/P ratio in the Western Harbor during 2012 showed that phosphorus was the limiting factor.

Stations 6, 1 and 2 suffered from pollution during summer season accompanied by highest silicate, oxidizable organic matter, nitrate and sulphate concentrations.

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