

Impact of Some Physicochemical and Biological Factors on Steel Corrosion in Seawater

Hermine Ramzy Zaki Tadros^{1*}, Mona Fathy El Naggar¹, Khoulood M. I. Barakat², Amaal Eid Abbas Abou-Taleb¹ & Fatma Abd El Rahman Zaghloul³

^{1* & 1} Marine Chemistry Lab, Marine Environment Division, NIOF, Alexandria, EGYPT

² Marine Microbiology Lab, Marine Environment Division, NIOF, Alexandria, EGYPT

³ Marine Hydrobiology Lab., Marine Environment Division, NIOF, Alexandria, EGYPT

Correspondance: E-mail: hermine_rzts@yahoo.com

(Received 10 May, 2015; Accepted 17 May, 2015; Published 21 May, 2015)

ABSTRACT: The present study focuses on steel corrosion rate in seawater by weight loss technique and the impact of some physicochemical and biological marine parameter on it. Surface water samples were collected twice a week over one year; March 2013 -February 2014 at a fixed station in the Eastern Harbor of Alexandria. The results indicated that; water transparency (58.5 - 240.0cm). Temperature (15.5°C - 34.1°C). Salinity (<35.0-37.5). pH (7.80 - 8.92). Dissolved oxygen (2.51 - 7.95ml/l). Total alkalinity (1.3 - 3.6meq/l). While nutrient salts (μmol) displayed wide and rapid changes; 0.77-93.13, 0.03-0.75, 0.03-1.7, 0.01-3.2 and 0.06-38.38 for ammonia, nitrite, nitrate, reactive phosphate and reactive silicate respectively. Parallel to the above mentioned condition, the phytoplankton count (1.02×10^3 - 4.92×10^6 cells/l); while bacterial count (1.3×10^3 - 221.0×10^6 CFU/ml). The corrosion rate ranged between 0.9339-2.3488 mpy. It is directly affected with temperature and nitrite concentrations. The principle component analysis were calculated and discussed.

Keywords: Physicochemical parameters; Biological parameters; Weight loss technique; Corrosion of steel.

INTRODUCTION: The corrosiveness of a marine environment depends on the topography of the shore, wave action, prevailing winds and relative humidity¹. Natural seawater is more aggressive than the artificial seawater. Alloys including stainless steel are used in seawater for various applications. The localized corrosion of these materials is affected by temperature, microbial activity, chlorination and flow rate².

The degree of severity of corrosion in marine environment depends on temperature, salinity, current, dissolved oxygen content, pH, pollution and marine biofouling³.

Rate of corrosion tends to increase with rising temperature. Higher temperatures accelerate the diffusion of oxygen through cathodic layers of protective oxide film⁴.

Algae can modify the local environment of the steel by influencing oxygen concentration, changing the pH and through the production of metabolites which create a more aggressive electrolyte. The presence of an algae fouling might produce a reduction in the local oxygen concentration and studies using steel panels immersed at offshore sites have shown that, initially, corrosion rates were reduced by fouling, with a thin cover of *Enteromorpha* sp.^{5,6&7}.

Relation between bacteria and corrosion can be explained by anyone or more of the following: produc-

ing a corrosive environment, creating electrolytic concentration cells on the metal surface, alternating the surface protecting film, influencing the rate of anodic-cathodic reaction and changing the environment composition⁴.

Microbes can initiate, facilitate, or accelerate electrochemical corrosion reactions⁸. Microbes achieve this through their interactions with the environment surrounding the metal surface. For example, bacteria can generate conditions that enhance corrosion through alteration of some physicochemical properties, excretion of corrosive metabolites, direct or indirect enzymatic reduction or oxidation of corrosion products, formation of biofilms that create corrosive microenvironments⁹.

This work aims to study the corrosion of steel in seawater by weight loss technique and the impact of some physicochemical and biological marine parameters on the weight loss of the steel panels.

MATERIAL AND METHODS:

1. Study area - Eastern Harbor: The Eastern Harbor (EH) is a relatively shallow semi closed basin, sheltered from the sea by break water leaving two openings, El-Boughaz and EL-Selsela, through which the exchange of water between the harbor and the neritic Mediterranean water takes place.

The steel panels' immersion test for the study of corrosion rate of steel was done in seawater of the Eastern harbor in the area located in front of NIOF. Only one marine area was selected (Figure 1).

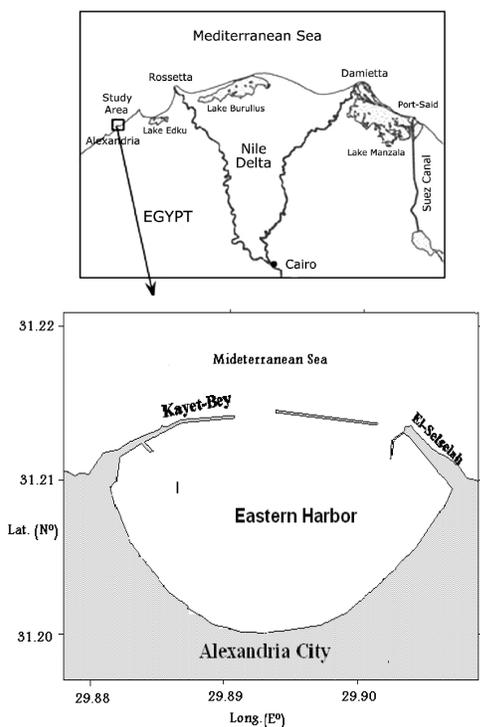


Figure 1: Marine location of panel immersion test in front of NIOF, Eastern Harbour; Alexandria, Egypt.

2. Sample collection: Two liters from surface seawater samples were collected by using Ruttiner sampler twice a week over one year started from March 2013 till February 2014. One liter for physicochemical measurement; transparency, temperature, salinity, dissolved oxygen, total alkalinity and nutrient salts. The other litre of water samples was used for phytoplankton count it preserved in 4% neutral formalin solution, left 48 hours for sedimentation and cells were counted and identified using 2ml settling chambers with a Nikon TS100 inverted microscope at 400 x magnification using Utermöhl (1958)¹⁰ method. The results expressed cells per liter. One hundred ml of water samples were collected in two sterile bottles (100 ml): (1) water sample and (2) steel platelet immersed in water for total variable bacterial count determination, then kept after sampling in an ice box until transferred for laboratory examination according to APHA (1998)¹¹.

These measurements are carried out at the time of the steel panels immersion in seawater and at the time of removal of the frame contains the same panels from seawater to measure the weight loss of the steel panels hanged in the steel frame.

3. Physical parameters: Transparency, temperature and salinity were measured *in situ* using CTD SBE Sea bird electronics.

4. Chemical parameters:

4.1 Dissolved oxygen (DO): It was determined by a modified Winkler's method. Fixation of dissolved oxygen was made *in situ* using manganous sulphate and alkaline potassium iodide solutions¹².

4.2 Alkalinity: Total Alkalinity was measured according to the method described by Strickland and Parsons. Water sample was titrated against diluted HCl using methyl orange as indicator¹³.

4.3 Nutrient salts: nitrite, nitrate, ammonia, Phosphate and silicate were measured according to standard methods¹⁴.

4.4 pH: The pH was measured *in situ* using portable pH meter model (JENWAY, 3410 Electrochemistry Analyzer pH-meter).

5. Bacterial isolation and Enumeration: The isolation process was carried out using Pour Plat technique. One ml of each collected water and steel platelet samples was applied in a sterilized Petri dish. The sterilized nutrient agar medium (45°C)¹⁵ was poured on the inoculated plates, and then incubated at 28°C for 24-48 h. The macroscopic examination of colonies and bacterial count (CFU×10⁶/ml) were observed using a Leica DMLS microscope.

6. Steel panel's composition: 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).

7. Steel panel's preparation: Steel panels were used. Their surfaces were polished and cleaned before immersion in seawater. The steel panels after cleaning were hanged in frame and the frame was immersed in seawater of the Eastern harbor in area front of NIOF.

8. Steel panel's immersion test: The prepared steel panels (two panels immersed each time) were hanged in steel frame and immersed in seawater. The test was repeated two times each week over a period of a year (March 2013-February 2014). Each week the immersion of the frame hanged the panel was tested two times. The immersion time was nearly at the same time of the day.

9. Weight loss method: A simple test for measuring corrosion is the weight loss method. The method involves exposing the clean weighed three panels of the steel to the seawater followed by cleaning to remove corrosion products and weighing each of the panel to determine the loss of weight. The mean of loss in

weight of the three panels each time was calculated^{16&17}.

10. Statistical analysis: Correlation coefficient at a confidence limit 95% ($P \leq 0.05$) were estimated for all data ($n=42$), as well as factor analysis and principle component analysis (PCA) for the average data well done by using SPSS program and discussed.

RESULTS AND DISCUSSION:

1. Physicochemical parameters:

1.1 Transparency: Water transparency of seawater of the studied marine area fluctuated between a minimum of (58.5 and 59 cm) measured at 10/11/2013 and 26/01/2014 and a maximum of 240.5 cm on 12/6/2013; with an annual average of 153 cm. Other low transparency values (78, 85 and 87 cm) were observed during 12 August, 25 December; 18 & 25 August and 1st September, 27 November, 1st, 12 and 25 December. Other high transparency values were observed during 2nd and 5/06/2013 (209.5 & 210 cm). With respect to the monthly average distribution; the transparency of the study marine area ranged between a minimum of 111.67cm during August to highest transparency of 191.69cm during June, 2013, Figure 2.

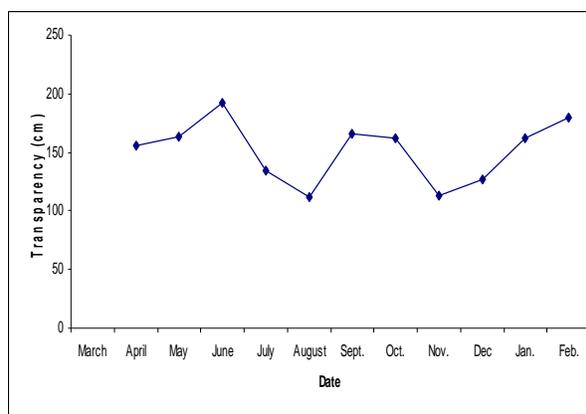


Figure 2: Monthly average distribution of transparency during March 2013- February 2014.

1.2 Temperature: The temperature ranged between a minimum of 15.5 °C, 29/01/2014 to a maximum of 34.1 °C, 2/06/2013 with annual average 23.9 °C. It is noticed that the temperature range and average during 2013-2014 are higher than their corresponding values during 2009¹⁸ and 2011-2012¹⁹ which show temperature ranges (17.1-31.5) °C and (16.5-32.1) °C and averages 24.9 and 22.83 °C, respectively (Table 1).

The highest monthly average of seawater temperature 31.58 °C was found during August and lower values during the cold months (January and February). The lowest monthly seawater temperature average was 16.38 °C during January, Figure 3.

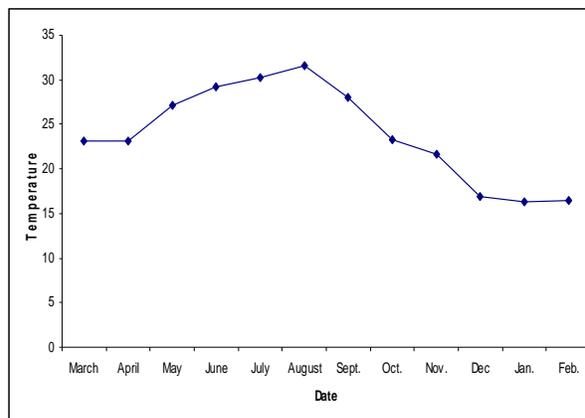


Figure 3: Monthly average distribution of temperature during March 2013- February 2014.

1.3 Salinity: Salinity values differed between 34 on 18/08/2013 and 37.35 on 09/10/2013 followed by another high value 36.8 on 17/04/2013 with an annual average 35.536. These ranges and averages values are lower than their corresponding ones during 2002-2003²⁰, 2009¹⁸ and 2011-2012¹⁹ as their ranges are (34.9-41.3), (35.9-38.9) and (35.5-39.5) respectively, while the averages during 2009¹⁸ and 2011-2012¹⁹ are 37.2 and 37.45 respectively, Table 1.

The monthly averages of salinity value ranged between low of < 35.00 detected during June, July, August and September and the values of (37.00-37.50) measured during October 2013. The monthly average salinity were low values and fluctuated between 34.62 during August to 36.28 during April and October, Figure 4.

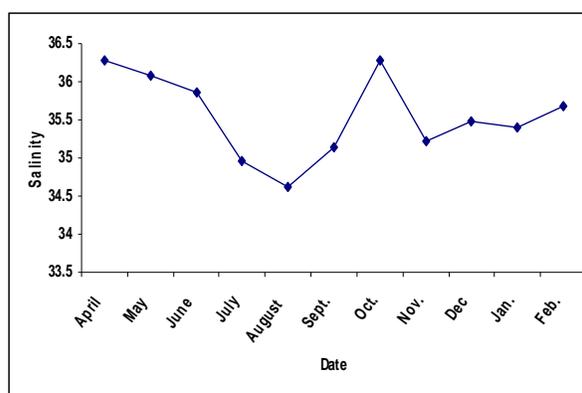
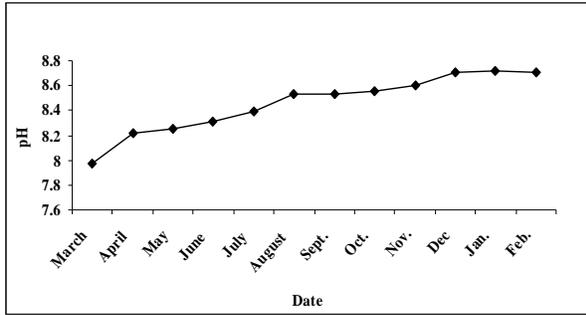


Figure 4: Average variation of total alkalinity of two successive days, E H, (in front of NIOF), during the study period.

1.4 pH: The pH values lie on the alkaline side and their values are fluctuated between 7.8, 24/03/2013 and 8.92, 25/12/2013. These ranges are higher than their corresponding values during 2009¹⁸ and 2011-2012¹⁹ as their ranges are (7.6-8.3 and 7.97-8.45) respectively, Table 1.

With respect to monthly distribution; pH measured high values (8.7) during the winter months and low



values (7.97-8.25) during spring months, Figure 5.

Figure 5: Average variation of DO concentrations of two successive days, E H, (in front of NIOF), during the study period.

1.5 Alkalinity: The total alkalinity measured values showed wide variations over the measured dates of the year. It recorded low value of 1.3meq/l at both 17/04/2013 and 17/07/2013 and the high values of it found during late March (27&30) with value 3.6meq/l and at the beginning of April (3rd), with the value of 3.8meq/l. The total alkalinity annual average value during the studied period was 2.67meq/l. These values are lower than their corresponding ones during 2011-2012¹⁹ as in the previous work the total alkalinity range was 2.65-3.8meq/l and the total average was 3.35meq/l, Table 1.

With respect to the monthly distribution; high total alkalinity averages were found during April, May and June 2013 (3.14, 3.25 & 3.41meq/l respectively) and the averages of low values of total alkalinity detected at August, November, December and February with; 2.04, 2.23, 2.42, 2.15meq/l respectively, Figure 6.

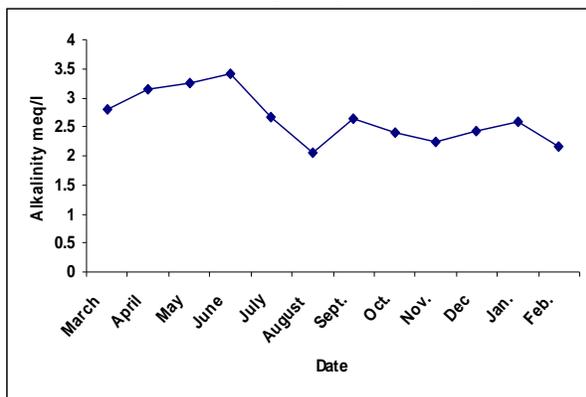


Figure 6: Average variation of nitrite and nitrate concentrations of two successive days, E H, (in front of NIOF), during the study period.

11.6 Dissolved Oxygen (DO): DO show a wide range of variation and lie between a minimum of 2.51ml/l,

11/09/2013 to maximum value of 7.95ml/l at 25/12/2013 with annual average of 5.23ml/l. Also low concentration of DO was detected during the dates of months; 14/09/2013, 2.96ml/l; 22&26/5/2013 and 08/09/2013, 3.87ml/l; 11/07/2013, 3.19 ml/l; 04/08/2013 and 01/09/2013, 3.42 ml/l; 11, 14&18/09/2013, (2.51-3.65ml/l); 28&30/10/2013, (3.43&3.25ml/l) and at 24/11/2013, value recorded low level of 3.86ml/l. The DO range and average are lower than those recorded by Khairy et al 2009¹⁸ (3.5-10.1 ml/l; 6.6 ml/l), but they are higher than their corresponding values recorded by Hermine et al 2014 during 2011-2012¹⁹ (2.01-6.84ml/l; 4.09 ml/l), Table 1.

The maximum monthly average of DO content was recorded during March 2013 (6.91mgO₂/l) and the lowest level 3.715ml/l during September as clear from Figure 7.

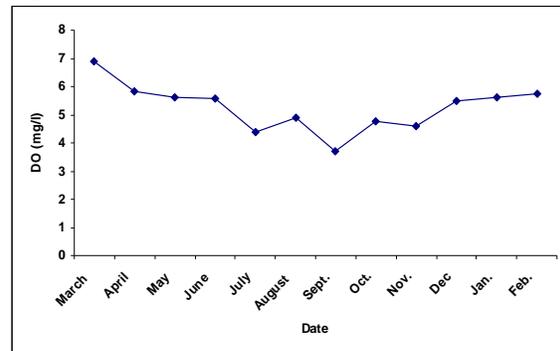
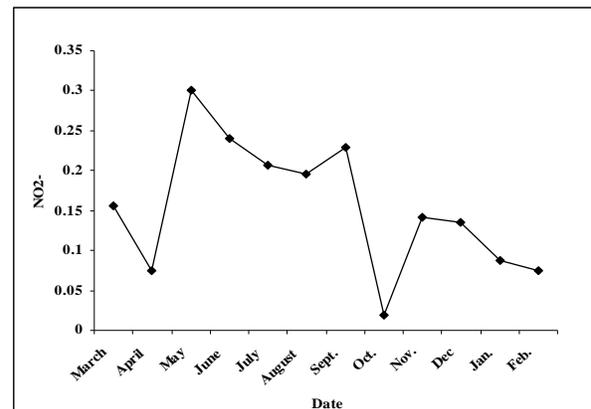


Figure 7: Monthly average distribution of dissolved oxygen during March 2013- February 2014.

1.7 Nutrients:

1.7.1 Nitrite: The lowest level of nitrite 0.03μmol/l measured at the dates; 27/03, 9/10, 28/10, 30/10, 3/11,



1/12, 15/01, 20/1 and 16/02) and the highest value found to be 0.75 detected at 18/09 & 23/06 and a high

Figure 8: Monthly average distribution of nitrite concentrations during March 2013- February 2014.

concentration of 0.68 $\mu\text{mol/l}$ at 28/08/2013; the annual average 0.155 $\mu\text{mol/l}$. The range and average values of nitrite concentration during this work are lower than their corresponding values during 2011-2012¹⁹ (0.369-2.938 $\mu\text{mol/l}$; 1.658 $\mu\text{mol/l}$), but higher than their corresponding values during 2009¹⁸ (0.02-0.87 $\mu\text{mol/l}$; 0.27 $\mu\text{mol/l}$); Table 1.

The lowest monthly average level of NO_2 was observed during October (0.019 $\mu\text{mol/l}$), while the highest one was observed during May (0.3 $\mu\text{mol/l}$), Figure 8.

1.7.2 Nitrate: Respect to nitrate concentration, the values fluctuated between 0.03 $\mu\text{mol/l}$ measured at 24/03, 1/10, 9/10, 15/01 & 20/01 and the high level of nitrate recorded 1.7 $\mu\text{mol/l}$ at 8/09 and 1.16 $\mu\text{mol/l}$ found at 4/09 and 0.68 $\mu\text{mol/l}$ found at both 21/04 and 25/08/2013, annual average 0.36 $\mu\text{mol/l}$. By comparing these results with those obtained ones during 2002-2003²⁰, 2009¹⁸ and 2011-2012¹⁹; it is noticed that the nitrate concentrations range and average during this work is much lower than the others corresponding values (0.42-72.02 $\mu\text{mol/l}$; 10.48 $\mu\text{mol/l}$, 0.44-11.1 $\mu\text{mol/l}$; 5.33 $\mu\text{mol/l}$ and 1.606-15.633 $\mu\text{mol/l}$; 8.651 $\mu\text{mol/l}$) respectively, Table 1.

The lowest monthly nitrate concentration average was 0.05 $\mu\text{mol/l}$ during January 2014, while the highest one was 1.17 $\mu\text{mol/l}$ in November 2013, Figure 9.

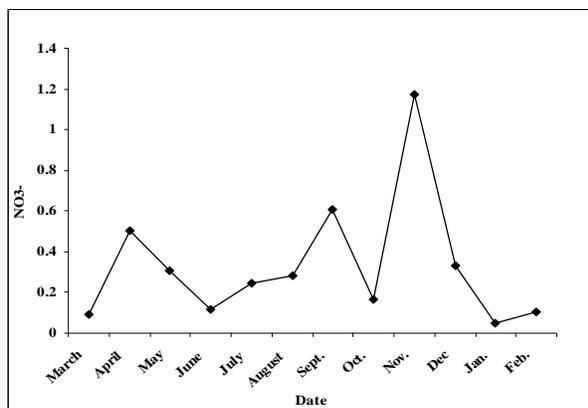


Figure 9: Monthly average distribution of nitrate concentrations during March 2013- February 2014.

1.7.3 Ammonia: Ammonia measured very high level of 93.13 $\mu\text{mol/l}$ at 29/05 and 2/06 and also, 86.5 $\mu\text{mol/l}$ measured at 09/06/2013. The lowest value of ammonia 0.77 $\mu\text{mol/l}$ measured at 9/02/2014, with an annual average of 26.86 $\mu\text{mol/l}$. These values are very high compared to those previous work during 2002-2003²⁰ and 2009¹⁸ that showed ranges and averages as follows: 0.15-43.7 $\mu\text{mol/l}$; 5.33 $\mu\text{mol/l}$ and 0.03-23.49 $\mu\text{mol/l}$; 3.57 $\mu\text{mol/l}$ respectively, Table 1.

The lowest monthly ammonia concentrations average was noticed during February (5.187 $\mu\text{mol/l}$), while the

highest one was observed in May (56.084 $\mu\text{mol/l}$), Figure 10.

It is noticed that; the highest levels of NO_2 and NH_3 are measured during May with average concentrations; 0.30 and 56.084 $\mu\text{mol/l}$ respectively.

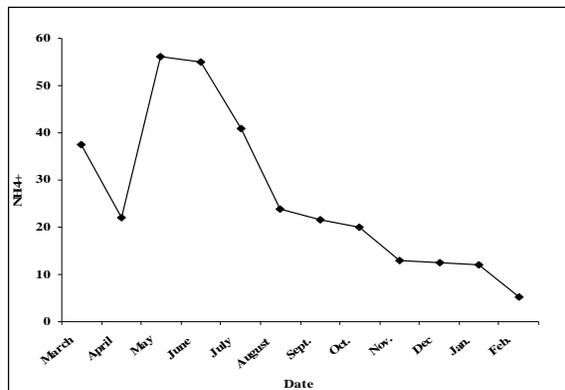


Figure 10: Monthly average distribution of ammonia concentrations during March 2013- February 2014.

1.7.4 Phosphate: Phosphate concentration showed wide variation and ranged between 0.01 $\mu\text{mol/l}$, (27/11 & 8/12/2013) – 3.2 $\mu\text{mol/l}$, 14/04/2013, annual average 1.031 $\mu\text{mol/l}$. Phosphate concentrations range and average is higher than those obtained by Madkour et al 2007 and Kairy et al 2014 for their work done during 2002-2003²⁰ and 2009¹⁸ at the same area of investigation. Their study showed ranges and averages as follows: 0.12-3.78 $\mu\text{mol/l}$; 0.6 $\mu\text{mol/l}$ and 0.02-2.2 $\mu\text{mol/l}$; 0.64 $\mu\text{mol/l}$, but this range and average values are lower than those obtained by Hermine et. al. 2015¹⁹ 0.588-5.538 $\mu\text{mol/l}$; 1.8 $\mu\text{mol/l}$ as shown in Table 1.

The monthly average variations revealed that the lowest value was in July; 0.6 $\mu\text{mol/l}$ while the highest one was in May; 1.79 $\mu\text{mol/l}$, Figure 11.

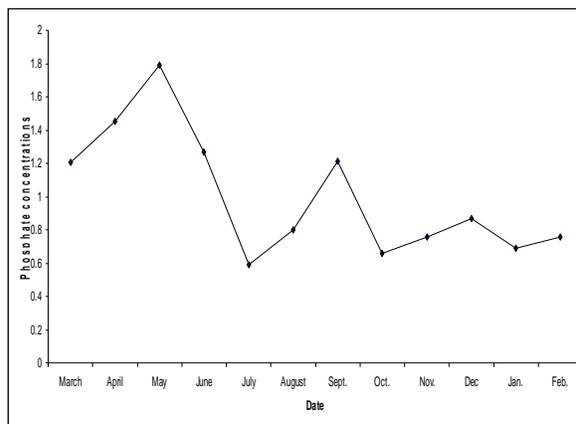


Figure 11: Monthly average distribution of phosphate concentrations during March 2013- February 2014.

1.7.5 Silicate: The highest silicate concentration recorded a value of 38.38 $\mu\text{mol/l}$ 13/03/2013 and the low-

est concentration found to be 0.06µmol/l detected at 20/10/2013, annual average 6.76µmol/l. Ranges and averages obtained during 2002-2003²⁰ and 2009¹⁸ are lower than that obtained in this work; 0.3-12.1µmol/l; 3.36µmol/l and 1.01-27.26µmol/l; 5.85µmol/l, Table 1. This may be attributed with high outfalls water which discharged in the EH.

The lowest monthly average was 3.6µmol/l during July and the highest one was 16.0µmol/l during March, Figure 12.

Generally, the monthly average variations of both phosphate and silicate concentrations showed that they reached their highest average values during March (5.52 and 16.47µg/l). The rest monthly averages of both parameters lie in the range (1.79, May-0.59µg/l, July 2013) and (10.36, August-3.36 µg/l, February, 2013) respectively.

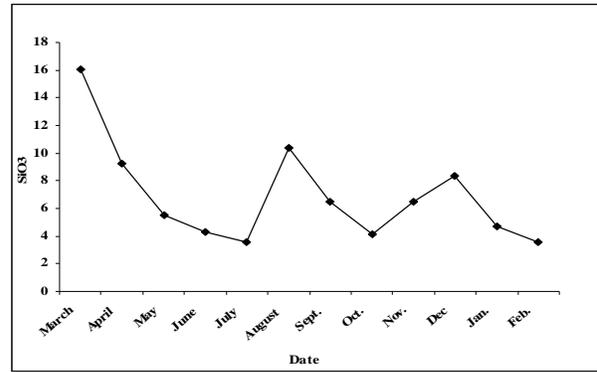


Figure 12: Monthly average distribution of silicate concentration during March 2013- February 2014.

Table 1: Range and average of some physicochemical parameters, phytoplankton, total bacterial counts and corrosion rate during the period 2000-2014.

Year	2002 - 2003		2009		2011 - 2012		2013 - 2014	
reference	Madkour et al 2007		Khairy et al 2014		Hermine et al 2014		Present data	
Parameter	Range	Average	Range	Average	Range	Average	Range	Average
Temperature			17.1-31.5	24.9	16.5-32.1	22.83	15.5-34.1	23.9
Salinity	34.9-41.3		35.9-38.9	37.2	35.5-39.5	37.45	34. -37.35	35.536
pH			7.6-8.3		7.97-8.45		7.8-8.92	
D.O			3.5-10.1	6.6	2.01-6.84	4.09	2.51-7.95	5.23
Alkalinity					2.65-3.8	3.35	1.3-3.6	2.67
Phosphate	0.12-3.78	0.6	0.02 -2.2	0.64	0.588-5.538	1.8	0.01-3.2	1.031
Silicate	0.3-12.1	3.36	1.01-27.26	5.85			0.06-38.38	6.76
Ammonia	.015-43.7	5.33	0.03-23.49	3.57			0.77-93.13	26.86
Nitrite			0.02-0.87	0.27	0.369-2.938	1.658	0.03-0.75	0.15
Nitrate	0.42-72.02	10.48	0.44-11.1	5.33	1.606-15.633	8.651	0.03-1.7	0.36
Phytoplankton	0.12x10 ³ -1.2 x10 ⁶		20.8x10 ³ -2.55x10 ⁶	1.387 x 10 ⁶	3.6x10 ³ -4.59x10 ⁶	1.84x10 ⁶	1.0x10 ³ -4.25x10 ⁶	2.48x10 ⁶
Bacteria						11.5 x10 ⁶	1.3x10 ³ -221 x10 ⁶	44.0 x10 ⁶
Corrosion					3.582-7.5518	4.78303	0.9339-2.3488	1.3866

2. Biological parameters:

2.1 Phytoplankton Structure: The phytoplankton standing crop is represented with three main groups namely; Bacillariophyceae, Dinophyceae and Euglenophyta.

Phytoplankton community changed numerically and species composition. The minimum counts which recorded during May 2013 (19/05), 1.02x10³ cells/l. This met with high water temperature (27°C), pH (8.19), total water alkalinity (3.1meq/l) and DO, 5.24ml/l. The maximum counts of phytoplankton were recorded during December (22/12), 4.92x10⁶ cells/l. This accompanied with low value of water transpar-

ency (87cm), water temperature (17°C), water alkalinity (2.85meq/l) as well as high values of pH (8.77) and DO (7.06ml/l). The increased values are due to increased in counts of Bacillariophyceae (99.09% of total phytoplankton).

It attained to an annual average of 2.48x10⁶cells/l. This value is higher than that recorded during 2009 and 2011/2012 at the same area of investigation (1.387x10⁶ & 1.8x10⁶ cells/l)¹⁹.

Regarding to the monthly averages counts of phytoplankton it fluctuated from a minimum value of 5.31x10³ cells/l during September as a result of minimum concentration of DO (3.72ml/l) to high counts recorded during December and August, 5.72x10⁶ and

7.11×10^6 cells/l respectively. This met with lower average values of water transparency (127.25 & 111.67cm), DO (5.5 & 4.88ml/l), phosphate content (0.87 & 0.8 $\mu\text{mol/l}$) and water salinity (35.48 & 34.62) as shown in Figure 13.

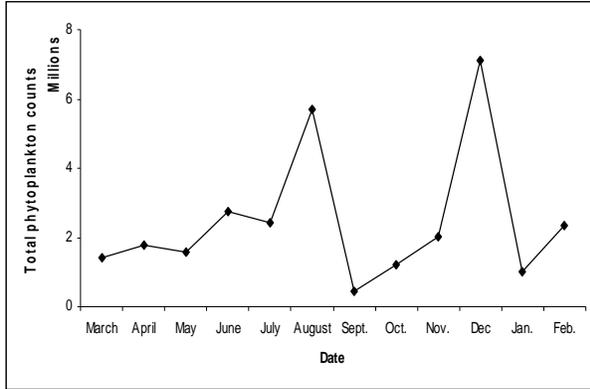


Figure 13: Monthly average distribution of phytoplankton community during March 2013- February 2014.

2.2 Viable bacterial count variations: From the illustrated data in Figure 14, minimum bacterial counts in sea water were recorded during 08/05 and 5/6 at 1×10^5 CFU/ml, also, no count observed during 23 June. This may be related to the lowest counts of phytoplankton community (1.02×10^3 cells/l) during this period. While, the maximum bacterial counts were observed during 7th & 14th July at 64.3×10^6 and 60×10^6 CFU/ml, respectively. This followed by the count records in 5, 9, 20 January ($30, 31.5, 32 \times 10^6$ CFU/ml, respectively), which related to the high pH (8.9), high dissolved oxygen (7.9 ml/l) and maximum phytoplankton count (4.9×10^6 cells/l). In addition, the maximum amount of some nutrients was recorded during the same period: $0.75 \mu\text{mol/l}$ for nitrate and $28.4 \mu\text{mol/l}$ for phosphate; which help in flourishing bacterial community.

Annual bacterial average was 44.7×10^6 CFU/ml. This showed a tendency of increasing bacterial count over that obtained value by Hermine et al. (11.5×10^6 CFU/ml) from the recorded data during 2011/2012¹⁹ at the same area of study.

Monthly averages of bacterial counts were fluctuated from a minimum value of 1.3×10^6 CFU/ml during February as a result of minimum temperature (16.38°C) to high counts recorded during August and December; 221.1 & 145.4×10^6 CFU/ml, respectively. This related to the highest average values of phytoplankton counts (5.72×10^6 and 7.11×10^6 cells/l respectively). Bacterial counts on the steel panels were extremely lower compared with those recorded from sea water samples which ranged from 1 to 28×10^6 CFU/ml.

3. Seasonal average variations of the corrosion rate of the tested steel panels in seawater, EH, (front of NIOF) during 2013-2014: Corrosion rate was measured for the three steel panels immersed in NIOF seawater for 72hrs a time for 42 times during the period March 2013- February 2014.

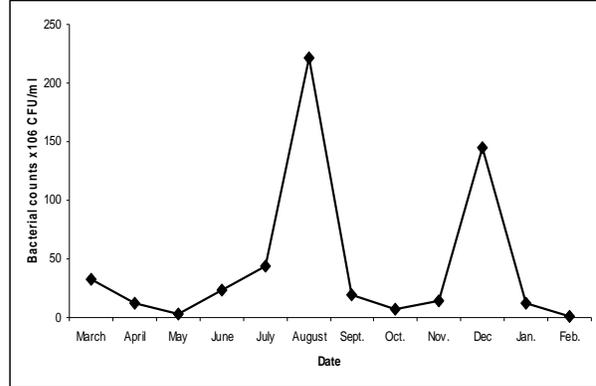


Figure 14: Monthly average distribution of Total Bacteria Count during March 2013- February 2014.

It fluctuated between 0.9339 mpy during winter season and 2.3488 mpy during summer season with an average 1.3866 mpy . These corrosion rate values are lower than their corresponding ones immersed in the same place for 24hrs during 2011-2012¹⁹ which ranged between 3.582 - 7.5518 mpy ; average 4.78303 mpy ¹⁹. This may be explained by the fact that; at first the corrosion rate was very high until the formation of a biofilm on the steel plates within the first couple of days leading to the formation of passive film that affects on decreasing the corrosion rate of the immersed steel panels as presented by Tuthill, 1988²².

The steel corrosion rate range measured on laboratory scale for the same site was between 4.320 mpy and 9.813 mpy ²³. This range is between higher steel corrosion rates values measured in western harbor water (Alexandria, Egypt); $16.24, 16.96$ and 16.30 mpy and 11.476 and 11.934 mpy ²⁴ and lower values measured in the eastern coastal zone of Alexandria ranged between 3.665 - 10.462 mpy ²⁵.

During winter season (December, January and February); the average corrosion rate of steel panels recorded the lowest value (0.9339 mpy) accompanied by the lowest seasonal average of temperature (16.6°C) and lowest seasonal averages of phosphate, nitrite, nitrate and ammonia concentrations ($0.78, 0.104, 0.172$ & $10.818 \mu\text{mol/l}$) respectively; and the highest pH value (8.71). The average monthly counts of phytoplankton during the months of winter season showed the increase in its total counts during December and reach 7.11×10^6 cells/l while during January and February; it reached 1.02×10^6 and 2.34×10^6 cells/l respectively. The phytoplankton counts are mainly due to the numbers of diatoms; *Skletonema costatum* during Decem-

ber and *Chaetoceros* spp. during January and February. The average phytoplankton count during winter was 3.49×10^6 cells/l. The average total counts of bacteria recorded 56.2×10^4 CFU/ml in water.

During spring season (March, April and May 2013); the average corrosion rate of steel panels was (1.4293mpy). This average loss in weight was accompanied by decrease in pH value (8.16) and increase in seasonal average of temperature (24.48°C), dissolved oxygen concentration (6.09 ml/l), highest values of alkalinity (3.07meq/l), phosphate concentration (2.75 μ mol/l), silicate concentration (10.2 μ mol/l) and higher nitrate concentration than winter season (0.32 μ mol/l). Phytoplankton count showed a slight increase during spring months (March, April and May), 1.4×10^6 , 1.77×10^6 and 1.56×10^6 cells/l respectively which are due to increase counts of diatoms particularly *Skletonema costatum* which contribute over 90% by number of the total phytoplankton counts. The average phytoplankton count during spring was 1.58×10^6 cells/l. The highest seasonal average of bacterial counts found during spring season (136.02×10^4 CFU/ml).

The highest average corrosion rate of steel panels was observed during summer season (June, July and August) and was found to be 2.3488mpy. This highest average corrosion rate was accompanied with highest temperature (30.2°C), highest nitrite concentration (0.0.216 μ mol/l), highest ammonia concentration (41.404 μ mol/l) and lowest salinity value 35.19. The phytoplankton counts during summer months (June, July and August) showed increase and their counts; 2.73×10^6 , 2.42×10^6 and 5.72×10^6 cells/l respectively. This is due to increase of diatoms *Skletonema costatum* and *Cyclotella* during both June and July, while the increase in phytoplankton community during August is mainly due to increase in dinoflagellate particularly *Alexandrium minutum*. The highest average phytoplankton count was observed during summer; 3.62×10^6 cells/l. The average total counts of bacteria during this season recorded 69.03×10^4 CFU/ml in water.

The average corrosion rate of steel panels found during autumn season (September, October and November) was 1.3514mpy. The average corrosion rate of steel was accompanied by highest seasonal average of transparency (149.8 cm) and nitrate concentration (0.648 μ mol/l) and lowest dissolved oxygen concentration (4.35 ml/l), silicate concentration (5.62 μ mol/l) and ammonia concentration (18.575 μ mol/l). Phytoplankton standing crop during the same autumn months, (September, October and November) found to be 0.42×10^6 , 1.21×10^6 and 2.0×10^6 cells/l respectively. The increase number during October is mainly due to increase of both diatoms (*Skletonema costatum*)

and dinoflagellate (*Protoperidinium*), while the increase in November is mainly due to increase in counts of diatoms (*Skletonema costatum*). The average phytoplankton count during autumn was 1.22×10^6 cells/l. The lowest seasonal average of bacterial counts in water was recorded during autumn (18.34×10^4 CFU/ml).

Generally, it is noticed that the lowest corrosion rate (0.9339mpy) was accompanied by the lowest seasonal average of temperature (16.6°C) and lowest seasonal averages of phosphate, nitrite, nitrate and ammonia concentrations (0.78, 0.104, 0.172 & 10.818 μ mol/l) respectively and the highest pH value (8.71); while the highest corrosion rate (2.3488mpy) was accompanied by the highest temperature (30.2°C), nitrite concentration (0.0.216 μ mol/l), ammonia concentration (41.404 μ mol/l), total phytoplankton count and lowest salinity value 35.19.

4. Principal Component Analysis (PCA): Principal component analysis is derived from the water parameters analysis of the weekly average data in Eastern harbor. The output data reveals five factors (PC1-PC5) affect Eastern harbor water, association and sources, with cumulative covariance of 90.58%. Varimax rotated components matrix is presented in Table (2) to give an overview of the nature of loading among the parameters. PC1, PC2, PC3, PC4 and PC5 have covariance of 31.54%, 23.74%, 16.53%, 10.10% and 8.68%, respectively. PC1 represented high loading of ammonia, alkalinity, nitrite, phosphate, temperature, and; (0.933, 0.813, 0.800, 0.767 & 0.726 respectively) associated with negative loading of pH (0.887) which can demonstrate that autochthonous sources of outfalls. PC2 had loading of total count of Bacteria (0.946), Dinophyceae (0.943), total phytoplankton (0.701) and silicate (0.712) with negative loading of transparency (0.615). This illustrate that high count of phytoplankton reduce water transparency. PC3 represented loading of dissolved oxygen (0.674), salinity (0.611) with high negative loading of corrosion rate (0.895), this relation can be explained as follows: with respect to salinity; Melchers (2003) stated in that for "at-sea" conditions, salinity is of little practical importance to marine corrosion. Also, the effect of small changes in salinity appears to be marginal for steels in quiescent conditions. Melchers stated also that salinity reduction doesn't necessarily mean a reduction of corrosion^{26&27}. With respect to dissolved oxygen, it may be considered that the concentration of oxygen dissolved in the water, thickness, porosity, density, adhesion and iron permeability of corrosion products and temperature are the main factors governing the corrosion rate of steel immersed in seawater in the diffusion controlled stage²⁸. PC4 represented high loading of

Bacillariophyceae (0.980) and total phytoplankton (0.694). PC5 represented negative loading of nitrate (0.972) where phytoplankton consumed nitrite salts.

Table 2: Varimax rotated component matrix for physico-chemical, biological and corrosion rate.

	Component				
	PC1	PC2	PC3	PC4	PC5
Transparency	0.203	-0.615	0.286	-0.202	0.556
Temp	0.726	0.387	-0.352	-0.386	-0.018
pH	-0.887	0.091	-0.154	0.168	0.027
Alk	0.813	-0.429	0.235	0.062	0.144
DO	0.024	-0.12	0.674	0.407	0.43
PO ₄ ³⁻	0.767	-0.171	0.541	-0.019	-0.153
SiO ₃ ⁻	0.072	0.712	0.43	0.116	-0.469
NO ₂ ⁻	0.8	0.184	-0.272	0.042	-0.097
NO ₃ ⁻	-0.01	-0.041	-0.07	-0.043	-0.972
NH ₃	0.933	-0.065	-0.153	-0.016	0.234
S	0.169	-0.615	0.611	0.05	0.188
diat	-0.103	0.039	0.05	0.98	-0.025
dino	0.024	0.943	-0.046	-0.273	0.112
Total phyto	-0.077	0.701	0.013	0.694	0.057
Bacterial count x10 ⁶	-0.056	0.946	-0.055	0.292	0.007
Corr.rate	0.133	-0.087	-0.895	0.055	0.016
% of Variance	31.535	23.741	16.528	10.103	8.677
Cumulative %	31.535	55.276	71.804	81.906	90.583

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.^a (a=Rotation converged in 7 iterations)

CONCLUSION:

Corrosion rate was measured for the three steel panels immersed in NIOF seawater for 72hrs a time for 42 times during the period March 2013- February 2014. The monthly corrosion rate of steel located between 0.9339-2.3488 mpy with an annual average 1.3866 mpy. The change of corrosion rate of steel is directly affected with temperature and nitrite concentrations. The lowest monthly average corrosion rate of steel (0.9339mpy) was accompanied by the lowest seasonal average of temperature (16.6°C) and lowest seasonal averages of phosphate, nitrite, nitrate and ammonia concentrations (0.78, 0.104, 0.172 & 10.818µmol/l) respectively and the highest pH value (8.71). The highest monthly average corrosion rate of steel (2.3488mpy) was accompanied by the highest temperature (30.2°C), nitrite concentration (0.0.216µmol/l), ammonia concentration (41.404µmol/l), total phytoplankton count (3.62x10⁶ cells/l) and the lowest salinity value 35.19.

ACKNOWLEDGEMENT:

The authors are great thankful to the Late Prof. Dr. Aida Botros Tadros for her idea of this work as it is a

part of her project titled with: "Statistical Study on Some Physical, Chemical and Biological Factors affect Steel Corrosion in Seawater and its Protection using some Marine Natural Extracts". The authors are also thankful to the NIOF as it is through of the strategic plan of Marine Chemistry Lab., Environment Division, NIOF, Alexandria, Egypt, that funded this work.

REFERENCES:

- Vashi R. H. and Kadiya H. K. (2009) Corrosion study of Metals in Marine Environment, *E-Journal of chemistry*, 6 (4), 1240-1246.
- Sridhar N., Brossia C. S., Dunn D. S. and Anderko A. (2004) Predicting Localize Corrosion in Seawater, *Corrosion*, 60 (10), 915-936.
- Soares C. G., Garbatov Y. and Zayed A. (2011) Effect of environmental factors on steel plate corrosion under marine immersion conditions, *Corrosion Engineering, Science and Technology*, 46 (4), 524-541.
- Chang T. and Lansing F. (1982) Review of Corrosion Causes and Corrosion Control in a Technical Facility, TDA Progress Report, 42 -69.
- Bartlett A. (1977) Marine corrosion, Dock and Harbor Authority, 58, 154-157.
- Ridler K. (1977) Protecting offshore structures. *Civil Engineering*, 31-35.
- Hodgkeiss, T. (1978) The effects of seawater on the integrity of offshore structures, Proceedings of the Royal Society of Edinburgh, 76 (B), 95-114.
- Mand J., Park H. S., Jack T. R., Voordouw G. (2014) The role of acetogens in microbially influenced corrosion of steel, *Front Microbiol*, 5- 268.
- Little B. J. and Lee. J. S. (2007) Microbiologically influenced corrosion, Wiley-Interscience, Hoboken, NJ.
- Utermöhl, H. (1958) Zur Vervollkommnung der quantitativen phytoplankton Methodik, *Mitt. Int. Ver. Theor. Angew. Limnol.*, 9 (1), 1-38.
- American Public Health Association (APHA) (1998) American Water Works Association, and Water Pollution Control Federation, Standard methods for the analysis of water and wastewater (20th ed.): Washington, D.C., American Public Health Association.
- Grasshoff K., Kremling and Ehrhardt M. (1999) Methods of seawater analysis. 3rd completely revised and extended edition, Willey-VCH Verlag GmbH, Germany, 634.
- Strickland J. D. and Parsons T. R. (1972) A Practical Handbook of Sea Water Analysis. Canada Ottawa, 311.
- American Publication Health Associations (APHA) (1989) Standard Methods for the Exami-

- nation of Water and Wastewater, 17th ed., APHA Washington, D.C.
15. Zobell (1946) Marine Microbiology, Waltham, MA: Chronica Botanica, 240.
 16. Standard Practice, for Preparing, Cleaning and Evaluating Corrosion Test Specimens 1990.
 17. Robert B. (2005) Corrosion Tests and Standards Manual: Environmental effects on corrosion, Chapter 48- steels, 559, Chapter 53- steels, 604. Copyright © 2005 by ASTM International. www.astm.org.
 18. Khairy H. M., Hussein N. R., Faragallah H. M. and Dorgham M. M. (2014) The phytoplankton communities in two eutrophic areas on the Alexandria coast, Egypt. *Revista de Biologia Marina y Oceanografia*, 49 (2), 267-277.
 19. Hermine R. Z. T., Mona F. El N., Fatma A. Z., Aida B. T. and Gehan M.A. El. (2015) Study on Steel Corrosion Rate in Semi Closed Seawater Area by Weight Loss Technique, *Asian J. Adv. Basic Sci.*, 3 (2), 45-53. ISSN (online): 2374-4114. www.ajabs.org
 20. Madkour F., Dorgham M. M. and Fahmy M. (2007) Short term scale observations on phytoplankton in the Eastern Harbor of Alexandria, Egypt. *Egyptian Journal of Aquatic Research* 33 (1), 193-209.
 21. Pugnetti A., Del Negro P., Giani M., Acri F., Aubry F.B., Bianchi F., Berto D., Valeri A. (2010) Phytoplankton-bacterioplankton interactions and carbon fluxes through microbial communities in a microtidal lagoon. *FEMS Microbiol Ecol.*, 72 (2), 153-164.
 22. Tuthill A. (1988) Guidelines for the Use of Copper Alloys in Seawater, NIDI Publication 12003.
 23. Tadros A. B. and Goma R. H. (2006) Effect of physicochemical and biological parameters of seawater on steel corrosion on laboratory scale. *4th Conference on scientific Outlook & Technology Development in the Arab World, Syria Arab Republic*, Extended Abstract, 1054-1056.
 24. Tadros A. B., Rokaya H. G., Hermine R. Z. T., Manal G. M., Ebtessam El-Sayed M. and Ahmad R. (2012) Change of the Corrosion Rate of Steel with the Sulphate Ions in Seawater, *Journal of the Arab Institute of Navigation*, 28, 7-18.
 25. Aida B. T. and Hermine R. Z. T. (2009) Environmental Parameters and steel corrosion studies of Eastern Coastal Area, Alexandria, Egypt. *Pakistan Journal of Oceanography*, 5(1&2), 29-44.
 26. Robert E. M. (2003) Probabilistic Models for Corrosion in Structural Reliability Assessment—Part 2: Models Based on Mechanics, *Journal of Off-shore Mechanics and Arctic Engineering-transactions of The Asme - J OFFSHORE MECH ARCTIC ENG*, 125(4). Journal: DOI: 10.1115/1.1600468.
 27. Guedes Soares C. (2010a), Safety and Reliability of Industrial Products. Systems and Structures – Guedes Soares (ed) © 2010 Taylor & Francis Group, London, ISBN 978-0-415-66392-2. Chapter 29: Corrosion of Steels in marine environment, monitoring and standards, 376.
 28. Guedes Soares C. (2010b), Safety and Reliability of Industrial Products. Systems and Structures – Guedes Soares (ed) © 2010 Taylor & Francis Group, London, ISBN 978-0-415-66392-2. Chapter 29: Corrosion of Steels in marine environment, monitoring and standards, 379.