Study on Corrosivity of Karachi Harbour Sea Water and its Impact on Marine Vessels Berthed at Karachi Harbour

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Abstract

This communication reports temporal trends of corrosion inducing attributes of Karachi harbour sea water. Measurements were performed for pH value, chloride ion, sulfate ion and conductivity. Karachi harbour sea water was found to be highly corrosive which may be due to intake of industrial and municipal effluent via lyari drain, sub-tropical warm water coast, and low turbulence due to land lock/gulf with open sea which caused slow diffusion and more residence time period for these corrosive contaminants. Study of sea water corrosivity was followed by statistical evaluation of its effect on some selected marine vessels. As a general trend, high corrosivity of Karachi harbour sea water was found to accelerate marine corrosion. A strong corrosive attack was detected at those locations where vessels preservation methods were weaken.

Keywords: Corrosivity, Karachi harbour, sea water and marine vessels.

Introduction

Sea water covers about 70% of the earth's surface and provides an extended trade network across the globe through shipping. It is a highly complex medium that contains almost every element in the periodic table and a multifarious plethora of living organisms. Hence, it is sometimes described as a 'living' medium and considered to be the most corrosive of the natural environments [1]. Properties of seawater vary considerably by geographical locations, seasons, and water depth. Conventional wisdom is that the corrosivity of sea water is because of its salt (primarily NaCl) content. However, it is not the only but other factors also contributing to the corrosivity of sea water that include high dissolved oxygen, chloride and sulfate contents, low pH, high conductivity, presence of microorganisms, biofouling, and putrefaction [2].

Polluted seawater typically has the lower oxygen content, lower pH, higher sulfide and sulfate-reducing bacteria concentrations and higher ammonia content as compared to unpolluted seawater. Literature survey of corrosion data suggest that at similar temperatures, the effect of lower oxygen content in polluted seawater is offset by the presence of pollutants, especially sulfides. Polluted or putrid seawater containing sulfides may increase the susceptibility to hydrogen embrittlement of stainless steels. Heavy metals, inorganic and organic pollutants from anthropogenic sources of industrial waste can alter the corrosivity of seawater toward certain materials, for example, copper-ion effects on aluminum alloys, sulfides and ammonia on copper alloys, sulfur compounds on steels, and so forth [3-7]. In littoral waters, organic nutrients can reach very high concentrations where river water runoff from land, discharges large amounts of municipal/industrial sewage and fertilizers/decaying organic matter from anthropogenic sources. This nutrient-rich water encourages excessive macro and micro organisms growth which colonizes to form a bio-film on submerged surface of ship hull called fouling. It has been shown that bio-films are more prevalent in warm seawater, compared to cold seawater [8-10].

As corrosivity in sub-tropical marine environment is classified between C_3 and C_5 levels of ISO 9223 while Karachi harbour environment is marine plus industrial due to mixing of untreated industrial effluent via lyari drain [11]. Due to natural gulf or landlock of Karachi harbour water with sea water, conditions are more stagnant and low turbulence which increases residence time period of these contaminates at Karachi harbour sea water. In this communication, we are reporting our findings about corrosivity of Karachi harbour sea water and its fate on ships berthed at Karachi port. Although previously Karachi harbour sea water was studied for environmental concern but there was no study for its corrosivity impact on marine vessels [12-15].

Experimental

Sea water samples were collected in triplicate quarterly from two locations (P_1-Near Fish Harbour and P_2-China Creek) at Karachi harbour. In laboratory, these samples were filtered through Whatman Filter paper to remove suspended particles. pH values were measured at room temperature by Jenco pH meter. Conductivity of sea water samples were recorded by Jenway Conductivity meter.

Sulfate contents of sea water were measured by turbidimetric method [16-18]. Briefly, 100 ml of filtered and diluted sea water sample was measured into a 250 ml Erlenmeyer flask and 5 ml of conditioning reagent was added with stirring. Conditioning reagent was previously prepared by mixing 30 ml Conc. HCl, 100 ml 95% C_2H_5OH, 75 g NaCl and 50 ml glycerol into 300 ml deionised water. Little amount of sample solution was poured into absorption cell cuvette and blank reading was taken by Spectro photometer at 420 nm. Solution was poured back into Erlenmeyer flask and a measuring spoonful of $BaCl_2$ (about

0.1 – 0.2 g) was added. Solution was stirred with magnetic stirrer for one minute. Immediately, some of sample solution was poured again into absorption cell to record the absorbance due to resultant turbidity of $BaSO_4$. Procedure was repeated for various calibration standard solutions to plot concentration versus absorbance curve. Absorbance of sample solution was interpreted into concentration with the help of this plot while giving due consideration to dilution factor.

Chloride concentration was measured by argenometric titration method [19-21]. In brief, about 50 g of filtered sample was taken in 250 ml conical flask by analytical balance of $\pm$0.0001g precision. pH of sample solution was adjusted between 8 to 9 with help of dilute sodium hydroxide solution. Few drops of Potassium chromate indicator solution were added with stirring till yellow color persist throughout the sample. Then resultant solution was titrated against 0.1 N $AgNO_3$ solution under magnetic stirring till a brick red color persists throughout the sample. Chloride ion concentration was measured by following formula

$$\text{Chloride (ppm)} = 3.545 \times V \times N \times 1000 \div S$$

Where:
V = volume (ml) of $AgNO_3$ solution used in titration
N = normality of $AgNO_3$ solution
S = Samples weight in grams

Structural repair data of nine ships, frequently berthed at Karachi port, were collected for last one decade (2001 to 2011). The repair data included the information like year of repair, repair period, type of survey carried out (ultrasonic, hammer test, visual etc.), condition of paint (good / bad), paint scheme, compartment of repairs, strake of repairs, type of corrosion (uniform, pitting etc.) and quantity of plates renewed. This data was analysed through IBM SPSS (a statistical analyses software package). This analysis provided various statistical results for data summaries, trend analyses and inferences.

Results and Discussion

Temporal trends of corrosive contents of Karachi harbour sea water were determined from March 2006 to September 2011. Corrosivity of marine water mainly depends upon pH value, chloride ion, sulfate ion, conductivity, dissolved oxygen and biofouling. Measurements for all above corrosive factors were carried out in this study except for dissolved oxygen and biofouling. Two data collection points were fixed, one more closer to estuary of lyari drain into Karachi harbour (P_1-Near Fish Harbour) and other away from this interception point (P_2-China Creek).

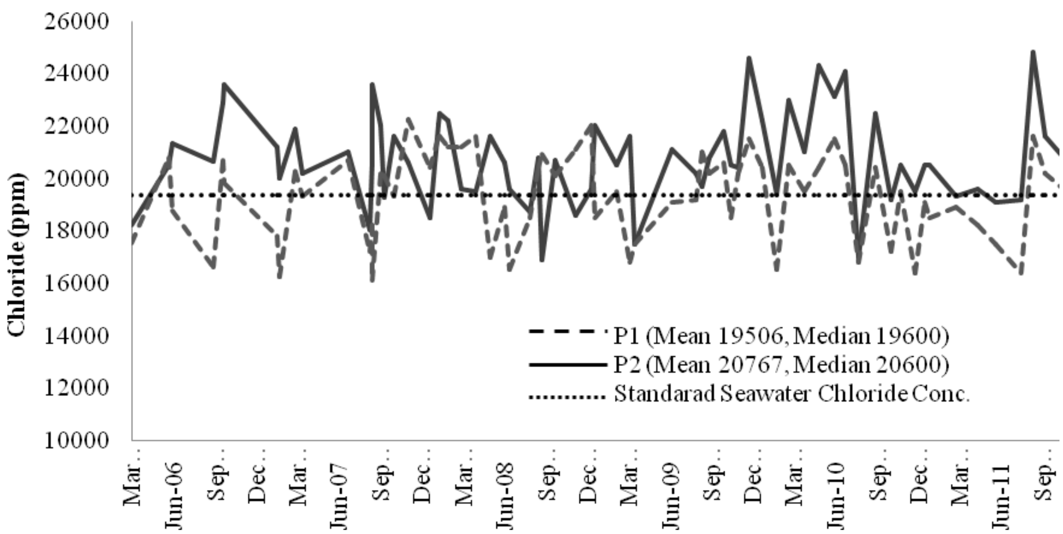


Figure 1: Temporal trends of Cl^- ion concentration at Karachi harbour. (P_1:Near Fish Harbour, P_2:China Creek)

From a corrosion stand point, chloride ions are considered to be the most aggressive and deleterious species toward passive films in seawater, causing localized corrosion particularly pitting corrosion [22]. Temporal trends of Chloride anion (Cl^-) concentration of Karachi harbour sea water are shown in Figure 1. Chloride anion concentration plot has mean value 20767 ppm & 19506 ppm and median 20600 ppm & 19600 ppm at P_2 and P_1 respectively, which frequently violating standard value (19350 ppm), more at P_2 than at P_1.

Sulfate (SO_4^{2-}) ions play an important role in the activity of sulfate-reducing bacteria (SRB) which proliferate under anaerobic conditions, and can cause serious corrosion problems for certain materials and applications [23]. Sulfate ions concentration was found to be mean 2904 ppm & 2874 ppm and median 2846 ppm & 2580 ppm at P_2 and P_1 respectively (Figure 2). Sulfate ions are significantly exceeding safe limit of 2712 ppm. High Concentration of sulfate anion may be due to industrial effluent and sewerage water.

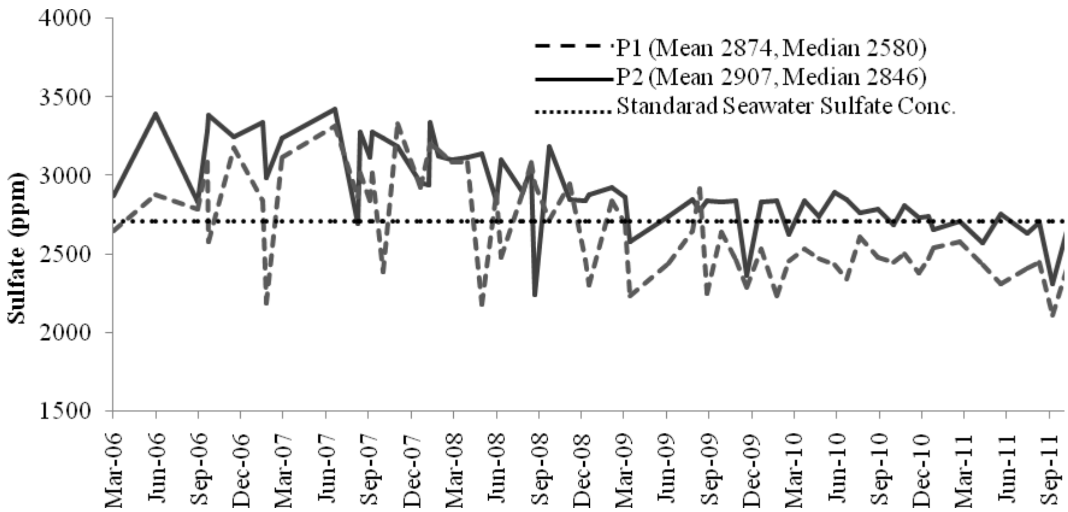


Figure 2: Temporal trends of sulfate ion concentration at Karachi harbour. (P_1:Near Fish Harbour, P_2:China Creek)

Another sea water species, which is important in determining corrosivity, is the hydrogen ion (H^+). As the concentration of this species increases, pH decreases, and the Corrosion Rate (CR) usually rises. Clean surface seawater is typically slightly alkaline. Sea water contains bicarbonate (HCO_3^-) ions, carbonate (CO_3^{2-}) ions, undissociated carbonic acid (H_2CO_3), and dissolved CO_2. These factors interact to maintain the pH in a surprisingly alkaline range (8.1-8.3), and hence, seawater is said to be highly buffered. However, sulfate-reducing bacterial (SRB) activity can generate acidic hydrogen sulfide gas which lowered the pH considerably [1, 24]. pH plot of Karachi harbour water has mean value 7.4 & 7.2 and median value 7.5 & 7.3 at P_2 and P_1 respectively which is surprisingly lower than standard value for sea water i.e. 8.2 (Figure 3). This may be due to sewerage and industrial drain water, enriched with sulfur containing compounds, which is intermingled in Karachi harbour water via lyari river drain.

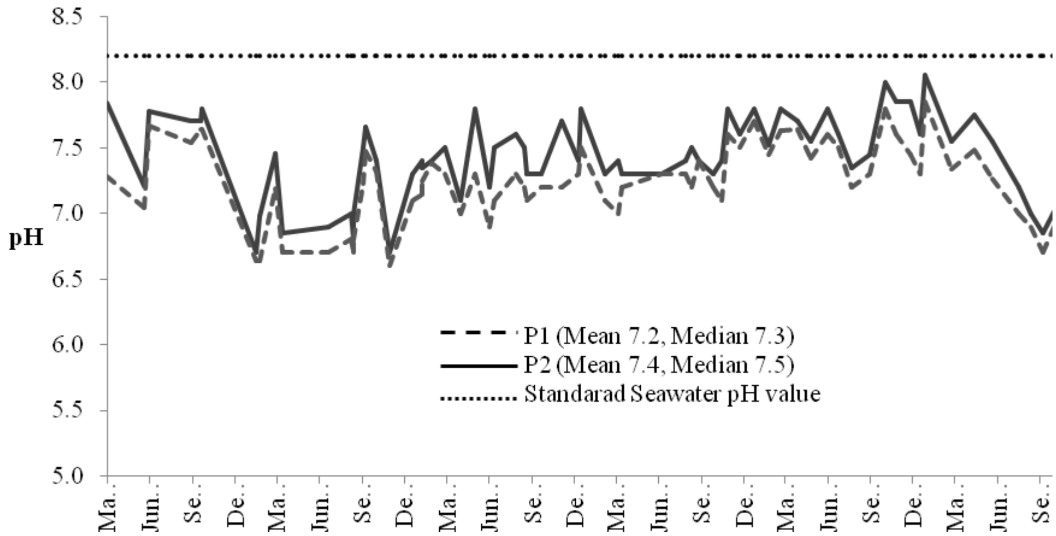


Figure 3: Temporal trends of pH value at Karachi harbour. (P_1:Near Fish Harbour, P_2:China Creek)

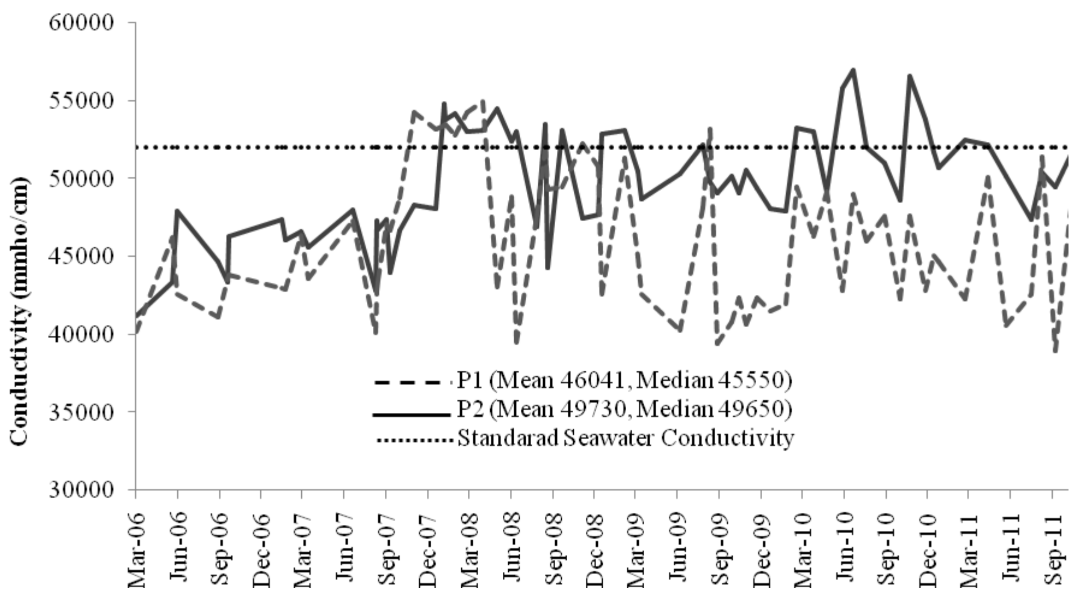


Figure 4: Temporal trends of conductivity at Karachi harbour. (P_1:Near Fish Harbour, P_2:China Creek)

Seawater typically has high electrolytic conductivity due to its significant dissolved salt contents. High conductivity generally corresponds to greater local cell reaction, larger anode-cathode distance interactions, higher galvanic corrosion rates (particularly for active materials such as carbon steel) and higher current output (over potential) from cathodic protection anodes [25, 26]. Study of marine corrosion impact on marine vessels was also carried out by collecting and analyzing a decade's structural repair data for various types of nine ships frequently berthed at Karachi Port. Due to commercial sensitivity, names, roles and hullform details of these vessels are not reproduced in this paper. However, approximate principal particulars of these vessels are summarized in Table 1.

Table 1: Approximate principal particulars of ships for which structural repair data has been collected

Ship Type	LBP (m)	Beam (m)	Draught (m)	Displacement (tons)	Number of Ships
A	150	15	8	4000	02
B	400	35	18	18000	02
C	250	25	12	12000	02
D	60	8	4	1000	03

LBP = Length between perpendiculars

The frequency plots depicting ship type-wise structural repair data points and their chronological distribution (Figure 5) showed that most of the data points pertain to type-D vessels with most repairs carried out in the year 2008. It is pertinent to highlight that on a very few occasions the structural repairs on board ships were attributable to mechanical failure and in most of the cases, it was the marine corrosion that was responsible for the renewal of hull plates.

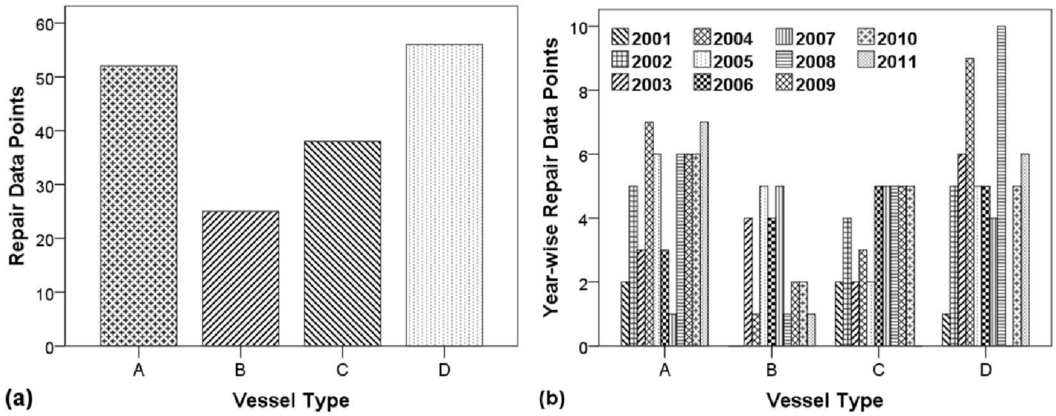


Figure 5: Frequency plots of ship type-wise. (a) repair data points and (b) their chronological distribution

Repair data was also analysed through IBM SPSS (a statistical analyses software package) to obtain the following statistical results:

Type-A Ships' Repair Data Trend Analysis and Inferences

The graphs for compartment and strake-wise frequency of structural repairs and corresponding plate renewals carried out onboard type-A ships , has been shown in Figure 6. Following can be concluded from the Figure 6:

a. The underwater part of the hull was most frequently repaired around machinery spaces.

b. Machinery spaces were the areas where the total frequency of repairs was the highest irrespective of strake (except decks with little repairs).

c. Structural repairs around rudder and shafting areas (underwater) were the second highest followed by sporadic renewal of plating on decks.

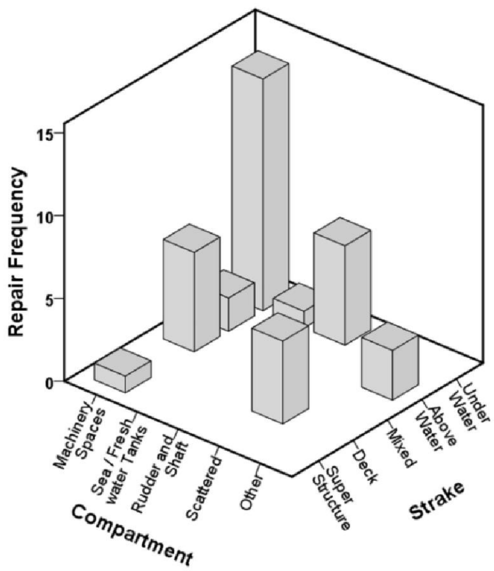
d. In terms of plate renewal quantities, the underwater part of machinery spaces has the highest value.

e. Again, all strakes (except decks) of machinery spaces have the largest plate renewals.

f. Plate renewals on decks at random locations have the second highest values.

g. The quantities of plate renewal on all other locations were relatively small.

It was inferred from the trend analysis of repair data that underwater hull repairs were concentrated around machinery spaces rather than randomly distributed all over the hull. This implies that little can be attributed to preservation coating failure as the same should have led to corrosion issues and hence repair works all over the hull.



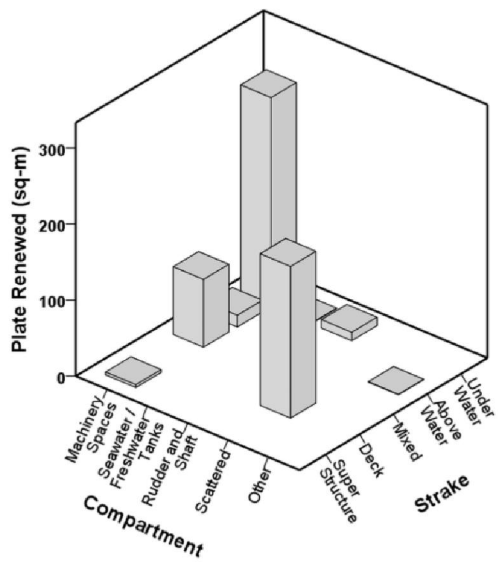


Figure 6: Compartment and strake-wise repair data distribution of type-A vessels (a) frequency of repairs (b) quantity of plate renewed.

Type-B Ships' Repair Data Trend Analysis and Inferences

The graphs depicting repair data trend analysis of type-B vessels (Figure 7) are indicating the following:

a. The highest frequency of structural repairs was sporadically distributed on decks.

b. The second most frequent repairs have been taken place in machinery spaces.

c. In terms of material quantity, the largest amount of plate renewal had been of the decks at random locations, followed by cargo tanks around underwater zone.

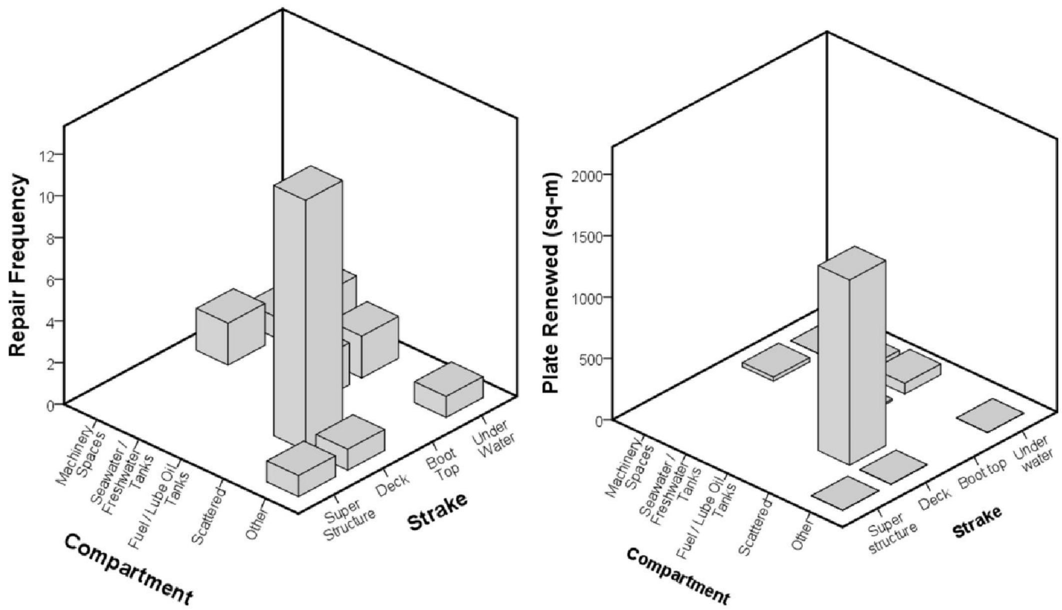


Figure 7: Compartment and strake-wise repair data distribution of type-B vessels (a) frequency of repairs (b) quantity of plate renewed.

Type-C Ships' Repair Data Trend Analysis and Inferences

The graphs illustrating repair data trend analysis of type-C vessels (Figure 8) have given the following results:

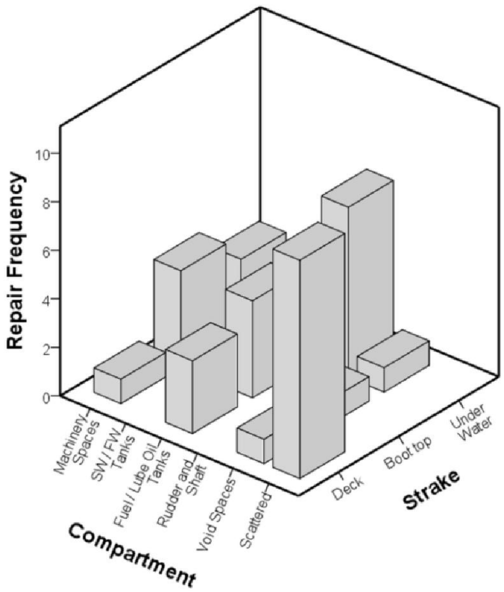
a. Structural repairs were most frequent on decks all over the vessels.

b. The second most frequent category of repair zone was the rudder and shafting (underwater) followed by the machinery spaces (boot top and water strakes).

c. Defects in boot top zone were spread over all compartments.

d. In terms of plate quantities, the largest repairs have been carried out on decks.

e. The second largest plate renewal had been in the void spaces around underwater zone, which was typical of such ships due to limited access for cleaning and maintenance of these areas.



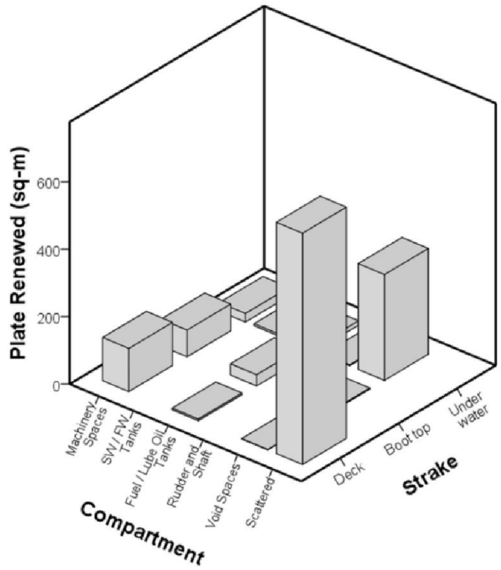


Figure 8: Compartment and strake-wise repair data distribution of type-C vessels (a) frequency of repairs (b) quantity of plate renewed.

It has been inferred from the trend analysis of repair data that the most frequent and largest repairs (in terms of plate renewal) on deck were indicating preservation issues. Due to intended role of the type-C vessels, relatively frequent repairs around boot top area were observed. They frequently came alongside other vessels / jetties, which led to accelerated mechanical erosion of boot top paint by the available fendering arrangements e.g. cylindrical mild steel catamarans with tires attached to them.

Type-D Ships' Repair Data Trend Analysis and inferences

The graphs exhibiting repair data trend analysis of type-D vessels (Figure 9) have furnished the following conclusions:

a. The frequencies of repairs were randomly distributed all over the compartments and strakes of the vessels.

b. Nevertheless, underwater repairs (all areas) followed by the sporadic repairs were most frequent.

c. In terms of renewal plate quantities, random (sporadic) repairs on virtually all strakes were the highest.

Initially it was inferred that preservation of the underwater hull is a reason for structural defects on type-D ships. However, a closer look at the grillage and focused interview with structural repairing staff indicated that these defects may be attributed to relatively low thickness of the hull. The small thickness of hull plating may help in structural weight savings but leaves very little corrosion margin.

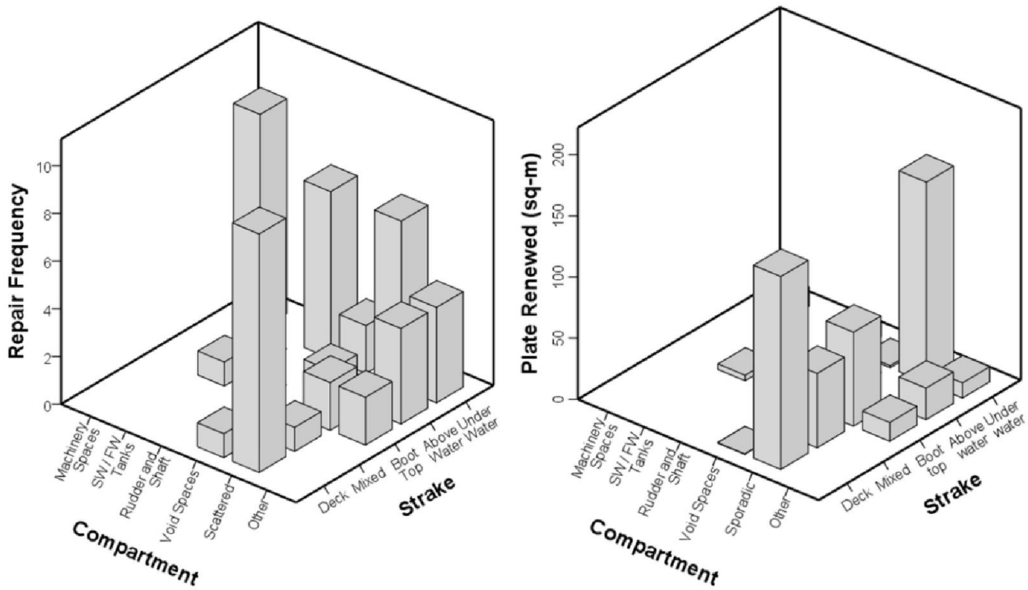


Figure 9: Compartment and strake-wise repair data distribution of type-D ships (a) frequency of repairs (b) quantity of plate renewed.

All above measured attributes of Karachi harbour sea water have indicated its high corrosion inducing tendency for bare metal surfaces, a little more at P_2 (China Creek) than at P_1 (Near Fish Harbour) which have indicated that although lyari river drain is main cause of corrosivity enhancement but conditions are more sever at China Creek, probably due to relatively stagnant conditions. Whereas, analysis of repair data of various marine vessels frequently berthed at Karachi harbour revealed random corrosion damages at ship structure, not only limited to hull but extends to super structure of ships. These corrosive attacks were intensified where vessels preservation methods were failed either due to poor application or improper maintenance. Therefore, corrosion control measurements like paint defensive line, incorporation of corrosion resistivity in base materials, sacrificial anode and Impressed Current Cathodic Protection (ICCP) etc. needs to be more strengthen in the order to preserve marine vessels, frequently berthed in highly corrosive Karachi harbour sea water.

Conclusion

All above measured attributes of Karachi harbour sea water have indicated its high corrosion inducing tendency for bare metal surfaces, a little more at P_2 (China Creek) than at P_1 (Near Fish Harbour) which have indicated that although lyari river drain is main cause of corrosivity enhancement but conditions are more sever at China Creek, probably due to relatively stagnant conditions. Whereas, analysis of repair data of various marine vessels frequently berthed at Karachi harbour revealed random corrosion damages at ship structure, not only limited to hull but extends to super structure of ships. These corrosive attacks were intensified where vessels preservation methods were failed either due to poor application or improper maintenance. Therefore, corrosion control measurements like paint defensive line, incorporation of corrosion resistivity in base materials, sacrificial anode and Impressed Current Cathodic Protection (ICCP) etc. needs to be more strengthen in the order to preserve marine vessels, frequently berthed in highly corrosive Karachi harbour sea water.

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