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FORAMINIFERS AS POLLUTION BIO-INDICATOR AT AL HARIQA OIL HARBOUR OF TOBRUK, LIBYA

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Abstract: *The main objective of this work is to use foraminifera as a pollution bio indicator at Al Hariqa Oil Harbour in Tobruk, northeast Libya. Ten beach sediments samples have been collected and analyzed to define and examine their foraminiferal contents. About ninety-six abnormal foraminiferal tests out of total 1220 picked foraminiferal tests have been encountered in this study. Selected specimens were analyzed and micro-photographed by Scanning Electron Microscope to highlight their morphological variations. The abnormalities in the encountered foraminiferal tests are largely in form of: i) corrosion, smoothing and polishing of test surfaces due to post-morten action which may attribute to water chemistry. ii) coil twisting, deformed chamber size, disturbed suture, dislocated aperture and twinned individuals, which are attributed to high concentration ofheavy metals such as Cadmium and Lead in the studied samples. However, the dirty black or brown colors are also documented on some tests, which may attribute to the reducing conditions as a result of human and industry-related drained wastes respectively.*

Keywords*: bioindicators, heavy metals, pollution, foraminifera, Libya*

INTRODUCTION

The pollution of marine water by anthropological domestic and industrial wastes becomes a major field of researching activity. Several studies on foraminifers were dealt with using benthic foraminifers in detecting the impact of the pollution with heavy metals in marine ecosystem, some of these studies [1, 2, 3, 4, 5, 6]. Morphological deformities of benthic foraminiferal tests in response to pollution by heavy metals proved as well to be useful in studies related to pollution monitoring. [3, 4, 5, 7] were used the "deformation" for abnormalities formed during life of the individual. The foraminiferal test abnormalities can be used to detect high concentration of heavy metals in sea water, this is supported by many studies in world including Libya (e.g., [2, 3, 4, 5, 8]).
The foraminifers have many applications in paleoclimatic and paleo-environmental determination, also it can be used to detect the pollution in marine water by recording the degree of morphological deformities of their tests because of their sensitivity to pollution in different forms and degrees. Test deformities have been linked to a number of environmental factors [2] such as change in temperature, reduced or elevated salinity, lack or overabundance of food, type of substrate, low dissolved oxygen content, insufficient light, and high concentration of heavy metals in area. This is confirmed by many worldwide studies e.g., [8, 9] including Libya e.g. Muftah, [5].
The morphological abnormalities are features occurring among benthic foraminifers, in both cold and warm water [2]. The well-known reasons for abnormalities as proved from experimental studies were salinity [7], acidification [10], food supply [11], and elevated levels of heavy metals [8], low oxygen [12, 13]. The test abnormalities for environmental pollution assessment must be considered in the

instable environments [14].
The presence of abnormal tests is a sign of natural environmental stresses, e.g., changes in ecological parameters [15], extreme environmental conditions [16] or pollution [17], for a long time, it has been difficult to distinguish between abnormalities resulting from natural or anthropogenic stresses. Yanko et al [2] found out that the abnormal (deformed) specimens contain much greater values of Cu and Zn than non-deformed specimens.
Samir and El-Din [18] pointed out those tests with twisted, compressed, and abnormal growth characterized by higher values of heavy metals than forms with protuberances. In order to recognize the probable effects of pollution on Al Hariqa Oil Harbour, ten beach sediments have been collected and analyzed to define and examine their foraminiferal contents. The harbour may receive the pollution from oil tankers by many ways, in particular, oil spill during tanker loading, spillage from the bunker manifold valves or from corrosion of the line and remove water and unwanted sediments, and water balance.

LOCATION

There are six oil exporting harbours in Libya namely; Al Zawia, Al Sidra, Ras Lanuf, Al Breqa, Al Zwitina and Al Hariqa. They may subjected to various levels of oil effects on the components of ecosystem either abiotic such as sea water and beach sediments or biotic components such as micro and macro organisms. At the Al Hariqa harbour, three stations located at coastal part of the Tobruk Gulf, NE Libya (Fig. 1) are subjected to sampling for this study. The Al Hariqa Oil harbour, which is located in Tobruk city is crowded with oil tankers, this problem encourage us to investigate and monitor this active harbour. The coastal water needs close investigation and attention because it is the only marine environments in contact with human activity (swimming, fishing etc.) as well as other biological productivity of marine organisms. This study will draw the attention of the government tooil pollution, and environmental education to people who are not care to this problem.

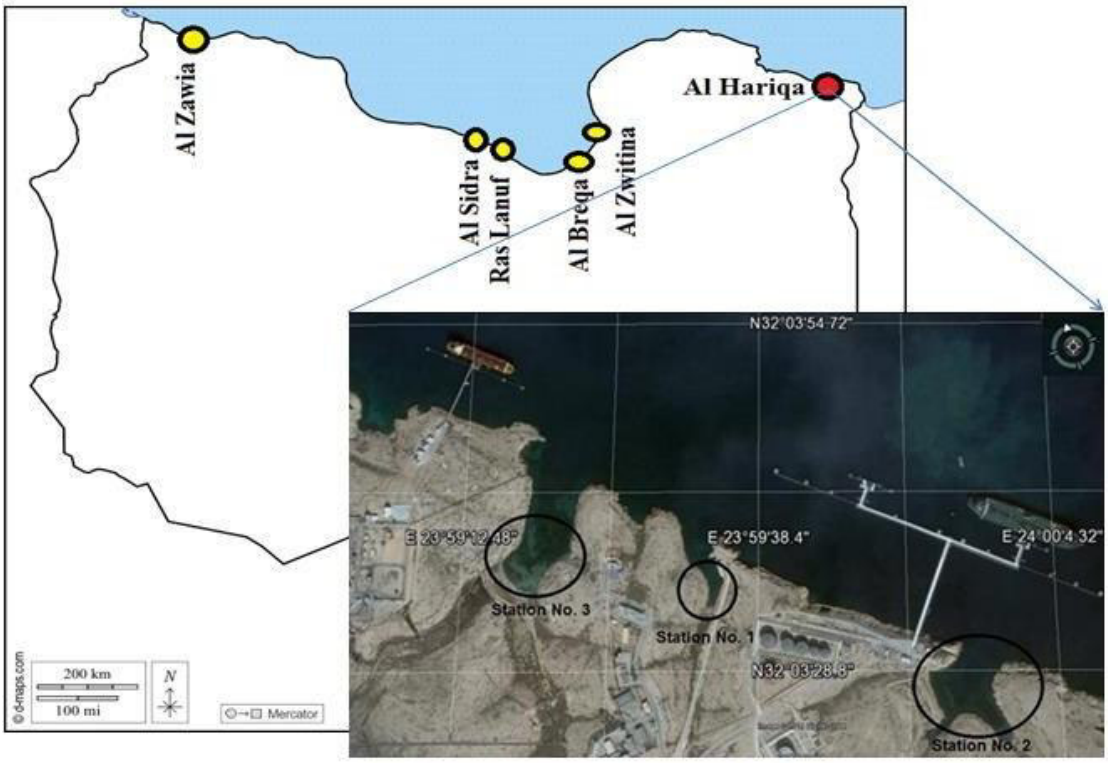


Figure 1. Location map of Libya shows all oil exporting harbors and the Satellite image with studied stations at Al Hariqa harbor in Tubruk.

OBJECTIVES

The objectives of this study are to:
1- Confirm the importance of the benthic foraminifers in detecting the pollution.
2- Sense the coastal environment of Tobruk Oil Harbour by using foraminifers to investigate the pollution from oil tankers.

MATERIALS AND METHODS

Samples were collected from the Al Hariqa harbour, from three stations depending on the nature and topography of the study area (3 to 4 samples of each station). Samples were essentially collected from the coastal nearshore ediments to represent the covered uppermost 30cm of the beach sediments in the sea. Wet samples were washed and sieved through a 63-µm sieve to remove clay and silt.
The residual fraction was dried at 60°C. One thousand two hundred and twenty empty specimens were picked from studied samples. The foraminiferal genera classification is based on [19]. Selected specimens were examined and microphotographed using scanning electron microscopy (SEM). All foraminiferal slides are deposited in the micropaleontology unit of the Department of Earth Sciences, University of Benghazi in Libya.

FORAMINIFERAL STATISTICAL ANALYSIS

The picked foraminifers form the collected samples are mainly representing by empty tests. They are mostly belonging to miliolids "porcelaneous" benthic foraminifers, such as *Peneroplis*, *Quinqueloculina, Triloculina, Spiroloculina, Sorites, Trisegmentina*, and *Adelosina*, with some rotaliids such as *Amphistegina, Lobatula* and *Planopulvinulina*.
Tobruk beach sediments from which the foraminifers are retrieved subjected to geochemical analyzed by Mohamed et al. [20] (Table 1).

Table 1. Chemical analysis data (heavy metals in ppm) of the Al Hariqa beach sediments [20].

Sample No.	As	Cd	Cu	Zn	Co	Ni	Cr	Pb	Hg	Se
6	4.50	1.07	291	334	92.24	326	468	73.45	11.77	0.12
9	5.00	1.10	292	335	93.63	337	479	74.82	11.89	0.14
10	4.77	1.09	291	334	92.35	337	479	73.54	11.83	0.11
12	4.70	1.10	291	334	92.36	336	478	73.50	11.80	0.12
13	3.90	1.05	290	333	91.35	335	477	72.54	11.76	0.14
14	3.67	1.02	290	333	91.26	335	477	72.50	11.72	0.14
25	4.78	1.08	292	335	93.44	337	479	74.63	11.82	0.13
35	5.42	1.10	294	337	95.42	339	481	76.61	11.88	0.12
36	5.09	1.09	293	336	94.35	338	480	75.54	11.85	0.12
37	3.92	1.06	290	333	91.46	335	477	72.65	11.73	0.10

The result of the analysis showed the average values of Pb, Cr, As, Cd, Zn, Cu, Hg, Ni, Co and Sewere 73.98, 477.5, 4.58, 1.08, 334.4, 291.4, 11.81, 335.5, 92.79 and 0.12 ppm, respectively. These averages were much higher than the elemental composition of typical uncontaminated soil (10, 25, 1, 0.06, 50, 20, 5, 50, 25 and 0.08 ppm, respectively). As shown in http://www.dsa.unipr.it/phytonet/fertilia/partners/tcan4.htm.
Additionally, the Igeo values of the studied Tobruk beach sediments (As, Cd, Cu, Zn, Co, Ni, Cr, Pb, Hg and Sc) are 2.10, 4.97, 1.79, 1.93, 1.48, 1.48, 1.19, 4.27, 3.00 and 1.14, respectively [20].
The samples show very lightly polluted with Cu, Zn, Co, Ni, Cr and Se (grade 2), lightly polluted with As and Hg (grade 3) and highly polluted with Cd and Pb (grade 5). This study focuses on the deformed tests (Figures 2-5) as response to beach sediments pollution by heavy metals especially Cadmium and Lead that recoded by [20, 21].
Mohamed et al [20] suggested that the heavy metals may came from both domestic wastes and leaked

hydrocarbon from ships, boats, adjacent crude oil reservoirs and the refinery. The investigated foraminiferal assemblage displays indication of pollution due to different anthropogenic activities, such as domestic and / or oil tankers seepages, the leaks is during oil-loading process as proved by the oil impregnated foraminiferal tests.

Additionally tests are contaminated and stained with domestic sewage pollutants as detected by tests filled by organic materials. The fragmented tests have been documented in many retrieved specimens from the examined sediments of the investigated localities, although the fragmentation apart from predation, dissolution is more likely a post-morten signatures resulted from surface wave or sea currents action (Plates I_1, $II_{1,3,7}$, $III_{3,4,8}$).

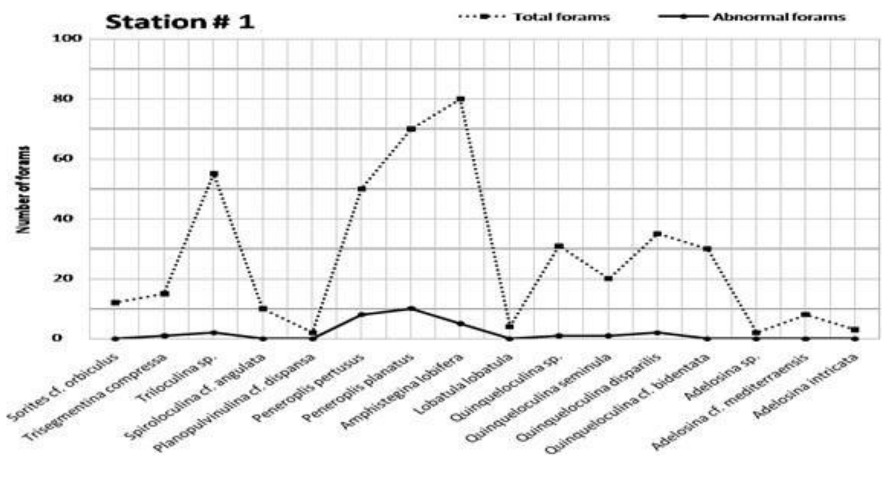


Figure 2. Binary diagram shows number of total versus abnormal foraminifers per 100gm of beach sediments in station No.1 at Al Hariqa oil harbor, NE Libya

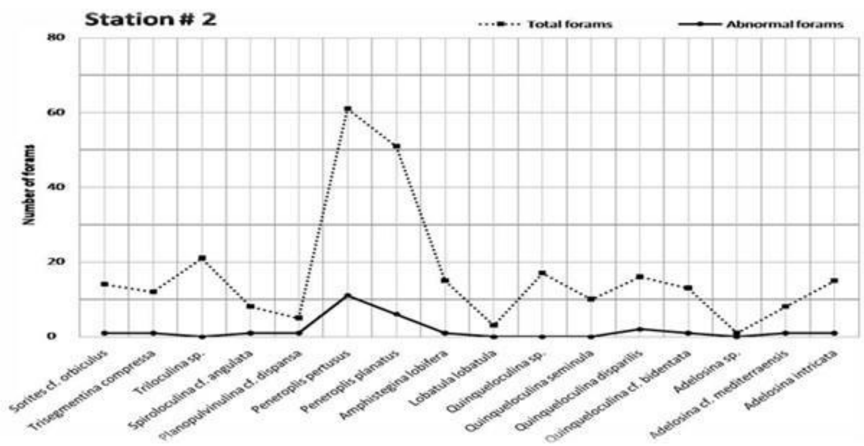


Figure 3. Binary diagram shows number of total versus abnormal foraminifers/100gm of beach sediments in station No. 2 at Al Hariqa oil harbor, NE Libya.

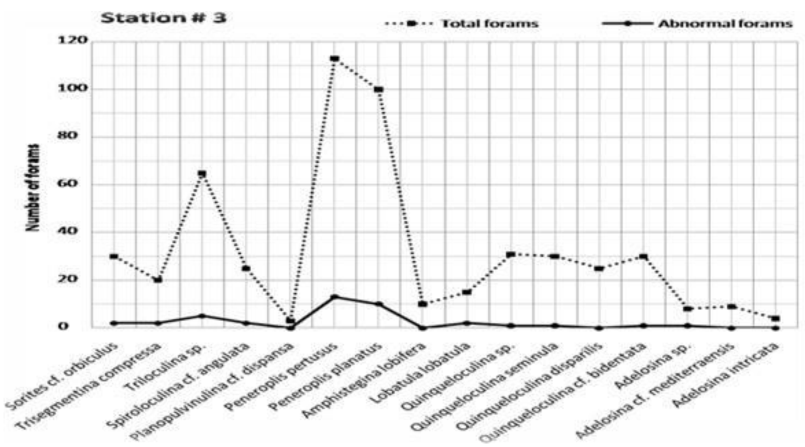


Figure 4. Binary diagram shows number of total versus abnormal foraminifers/100gm of beach sediments in station # 3 at Al Hariqa oil harbor, NE Libya.

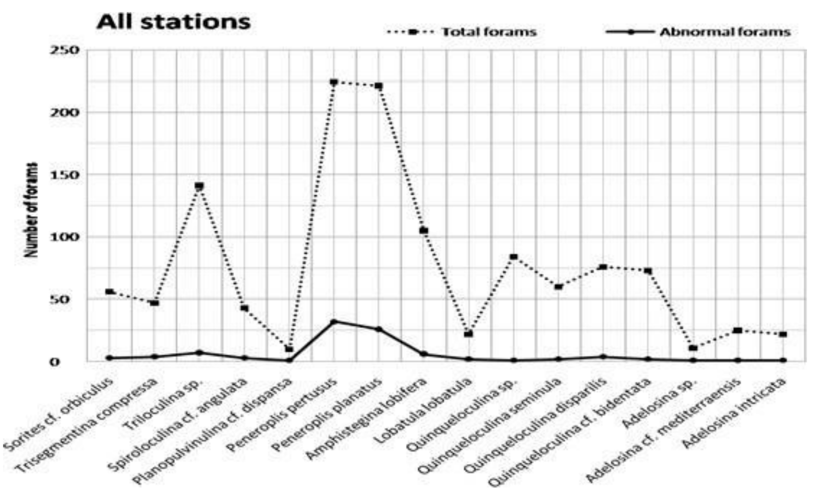


Figure 5. Binary diagram shows number of total versus abnormal foraminefers per 300gm of beach sediments in all stations at Al Hariqa oil harbor, NE Libya

FORAMINIFERAL RESULTS AND DISCUSSIONS

Discoloration of the foraminiferal test: In the investigated area, many post-morten discolored tests (change in normal color from milky to light orange - dark yellow) were observed from all sampled stations and/or partially stained on their surfaces which may attributed to the oil contamination and change in water chemistry. The other possible reason is due to petroleum activities at Al Hariqa harbour, especially in station no. 2. Additionally, the domestic wastes waters reflected as black stainedwithin foraminiferal tests as seen in some collected specimens from the studied station no. 3.

Abundance and Diversity of Foraminifera: The low diversity in living benthic foraminiferal assemblage is highly attributed to the decrease of salinity in brackish water bodies (i.e. the lagoon) El [22, 23] however, in normal marine waters, otherwise is due to increase in heavy metals [18, 24, 25]. Counting of picked foraminiferal tests form 100 grams of each beach sediments sample of studied stations show that the highest diversity and population are recorded at some localities such as station no. 1 (semi isolated water body) and station no. 3 (low current sandy beach). However, the lowest diversity and population are recorded in station no. 2 (open rocky beach), that can be interpreted as result of beach nature and pollution impacts levels at these localities (*see* tables 1-2). For taxonomical details [see 26]. The low diversity in the Manzala lagoon living foraminiferal contents [27] as well in the Burullus Lagoon [23] is more or less agreed with the present study.

P/B Foraminiferal ratio: Nguyen et al, [28]; Boltvoskoy and Totah, [29] confirmed that the decrease in P/B ratio is due to higher rate of dissolution in planktic than benthic assemblages. The foraminiferal tests dissolution lead to decline in foraminiferal diversity, this fact is proved experimentally by [28]. The studied assemblage is predominated by benthic foraminifers with almost lack of planktic foraminifers.

Foraminiferal abnormalities: According to Stouff et al, [7] definition, the malformations are abnormalities that take place during individual ontogeny, whereas deformity occurs during the life of the adult foraminifer. But the morphological abnormality is used when the origin of abnormality is not obvious. Herein, morphological abnormalities are detected, where, sixteen abnormal foraminiferal taxa have been documented (see Table 2 and Figures 2-5), with brief description, and these are:-
***Adelosina intricata*:** Only one abnormal specimen out of 22 from all stations (Plate I-1). The abnormal test with missing of the last part of chamber including aperture was collected from station no.2 (Figure 3). However, the other normal tests are from stations no. 1 and 3 (Figures 2-4). The general abnormality represents about 5% of all stations (Table 2 and Figure 5).

Table 2. Normal and abnormal tests of forams from Al Hariqa oil harbor - Tobruk - NE Libya.
(N:Normal -D:Deformed - T:Total - D%: Abnormality percentage)

Species	Station no. 1				Station no. 2				Station no. 3				All stations			
	N	D	T	D%	N	D	T	D%	N	D	T	D%	N	D	T	D%
Adelosina intricata	3	0	3	0	14	1	15	7	4	0	4	0	21	1	22	5
Adelosina cf. mediterraensis	8	0	8	0	7	1	8	13	9	0	9	0	24	1	25	4
Adelosina sp.	2	0	2	0	1	0	1	0	7	1	8	13	10	1	11	9
Quinqueloculina cf. bidentata	30	0	30	0	12	1	13	8	29	1	30	3	71	2	73	3
Quinqueloculina disparilis	33	2	35	6	14	2	16	13	25	0	25	0	72	4	76	5
Quinqueloculina seminula	19	1	20	5	10	0	10	0	29	1	30	3	58	2	60	3
Quinqueloculina sp.	30	1	31	3	17	0	17	0	36	0	36	0	83	1	84	1
Lobatula lobatula	4	0	4	0	3	0	3	0	13	2	15	13	20	2	22	9
Amphistegina lobifera	75	5	80	6	14	1	15	7	10	0	10	0	99	6	105	6
Peneroplis planatus	60	10	70	14	45	6	51	12	90	10	100	10	195	26	221	12
Peneroplis pertusus	42	8	50	16	50	11	61	18	100	13	113	12	192	32	224	14
Planopulvinulina cf. dispansa	2	0	2	0	4	1	5	20	3	0	3	0	9	1	10	10
Spiroloculina cf. angulata	10	0	10	0	7	1	8	13	23	2	25	8	40	3	43	7
Triloculina sp.	53	2	55	4	21	0	21	0	60	5	65	8	134	7	141	5
Trisegmentina compressa	14	1	15	7	11	1	12	8	18	2	20	10	43	4	47	9
Sorites cf. orbiculus	12	0	12	0	13	1	14	7	28	2	30	7	53	3	56	5
Total population of studied species	427 / 100 grams				270 / 100 grams				523 / 100 grams				1220 / 300 grams			
Normal individuals of studied species	397 / 100 grams				243 / 100 grams				484 / 100 grams				1124 / 300 grams			
Abnormal individuals of studied species	30 / 100 grams				27 / 100 grams				39 / 100 grams				96 / 300 grams			
Abnormality % of studied species	7%				10%				7%				8%			

Adelosina* cf. *mediterraensis: Only one abnormal specimen out of 25 from all stations (Plate I-2). The abnormal test with termination of costae at upper half of test (the present of striation only restricted in the lower part of test) was reported only in specimen from station no.2 (Figure 3). However, the other normal tests are from stations no. 1 and 3 (Figures 2-4). The general abnormality represents about 4% of all stations (Table 2 and Figure 5).
Adelosina sp.: Only one abnormal specimen out of 11 from all stations (Plate I-3). Only abnormal test with smoothing of external surface and partial etching was collected only from station no.3 (Figure 4) these post-morten phenomena are more likely related to sea water chemistry. However, the other normal tests are from stations no. 1 and 2 (Figures 2-3). The general abnormality represents about 9%

of all stations (Table 2 and Figure 5). El-Din et al, [22, 27] and Orabi et al, [23] refer the low living benthic foraminiferal content and low number of *Adelosina* sp. in the Egyptian Manzala lagoon and the Burullus Lagoon respectively to the decrease in salinity, which is in agreement with the present study result.

Quinqueloculina* cf. *bidentata: Only two abnormal specimens out of 73 from all stations (Plate I-4). The abnormal specimens with partial dissolution of outer surface were collected from stations no. 2 and 3 (Figures 3-4). However, the other normal tests are from station no. 1 (Figure 2). The general abnormality represents about 3% of all stations (Table 2 and Figure 5).

Quinqueloculina disparilis: Four abnormal specimens out of 76 from all stations (Plate I -5,6). The abnormal tests with eroded aperture, etched or corroded test, as well as lack of ornamentation in earlier chambers of last whorl were collected from stations no.1 and 2 (Figures 2-3). However, the other normal tests are from station no. 3 (Figure 4). The general abnormality represents about 5% of all stations (Table 2 and Figure 5).

Quinqueloculina seminula: Only two abnormal specimens out of 60 from all stations (Plate I-7). The abnormal tests with slightly disturbed sutures were collected from stations no.1 and 3 (Figures 2-4). However, the other normal tests are from station no. 2 (Figure 3). The general abnormality represents about 3% of all stations (Table 2 and Figure 5).

***Quinqueloculina sp.*:** Only one abnormal specimen out of 92 from all stations. This rare twinned test has been detected on this species, five chambers and two apertures in the visible side of tests. The abnormal specimen was collected from station no. 1 (Figure 2). However, the other normal tests are from stations no. 2 and 3 (Figure. 3-4). The general abnormality represents about 1% of all stations (Table 2 and Figure 5).

***Lobatula lobatula*:** Only two abnormal specimens out of 22 from all stations (Plate II-1, 2, 3). The abnormal tests with corroded chambers and abnormal test surface were collected from station no. 3 (Figure 4). However, the other normal tests are from stations no. 1 and 2 (Figures 2-3). The general abnormality represents about 9% of all stations (Table 2 and Figure 5).

Amphistegina lobifera: Six abnormal specimens out of 105 from all stations. **(**Plate II- 4, 5**).** The abnormal tests with corroded chambers were collected from stations no. 1 and 2 (Figures 2-3). However, the other normal tests are from station no. 3 (Figure 4). The general abnormality represents about 6% of all stations (Table 2 and Figure 5).

Peneroplis planatus: Twenty-six abnormal specimens out of 221 from all stations **(**Plate II- 6, 7**).** The abnormal tests with slightly twisted last portion of test, corroded chamber with coiling and chamber size problem were collected from all stations (Figures 2-4). The general abnormality represents about 12% of all stations (Table 2 and Figure 5).

Peneroplis pertusus: Thirty-two abnormal specimens out of 224 from all stations (Plate III- 1, 2, 3, 4, 5, 6)**.** The abnormal specimens represented by one or more of the following:

1) Coil problem in last chambers (twisted) of the last formed whorls of the test.
2) Destruction of test due to dissolution.
3) Chamber size problem.
4) Partially serrated suture.

The abnormal specimens were collected from all stations (Figure. 2-4). The general abnormality represents about 14% of all stations (Table 2 and Figure 5).

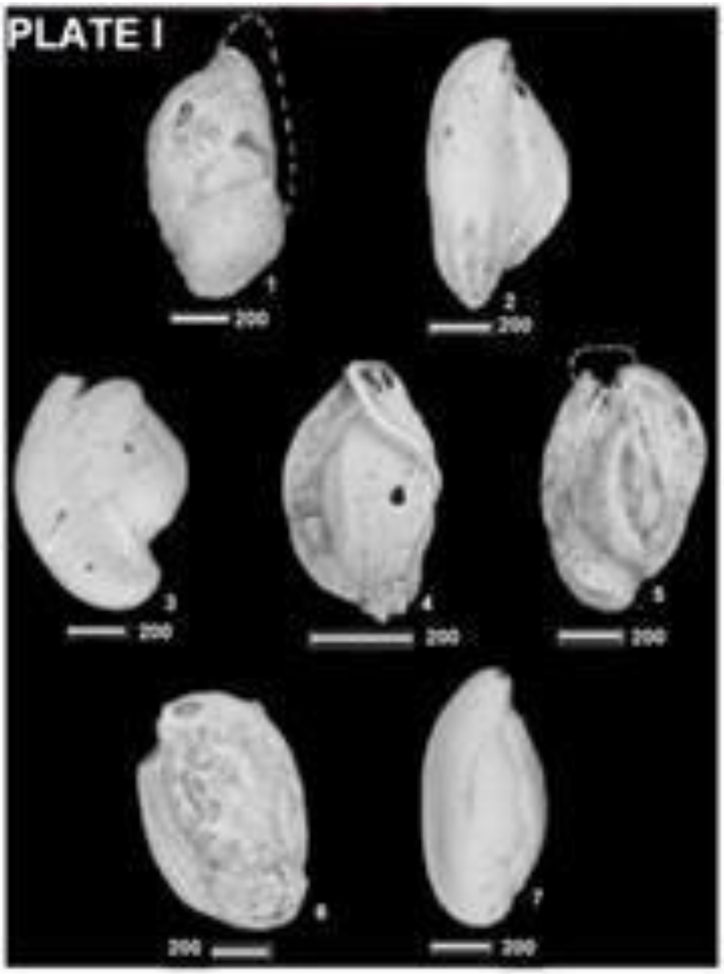
Planopulvinulina* cf. *dispansa: Only one abnormal specimen out of 10 from all stations (Pate III- 7). The abnormal specimens represented by incomplete test (i.e. the last part of the test is partially corroded) was collected from station no. 2 (Figure 3). However, the other normal tests are from stations no. 1 and 3 (Figures 2-4). The general abnormality represents about 10% of all stations (Table 2 and Figure 5).

Spiroloculina* cf. *angulata: Three abnormal specimens out of 43 from all stations (Plate III -8). The abnormal specimens with margin's etching were collected from stations no. 2 and 3 (Figures 3-4). However, the other normal tests are from station no. 1 (Figure 1). The general abnormality represents about 7% of all stations (Table 2 and Figure 5).

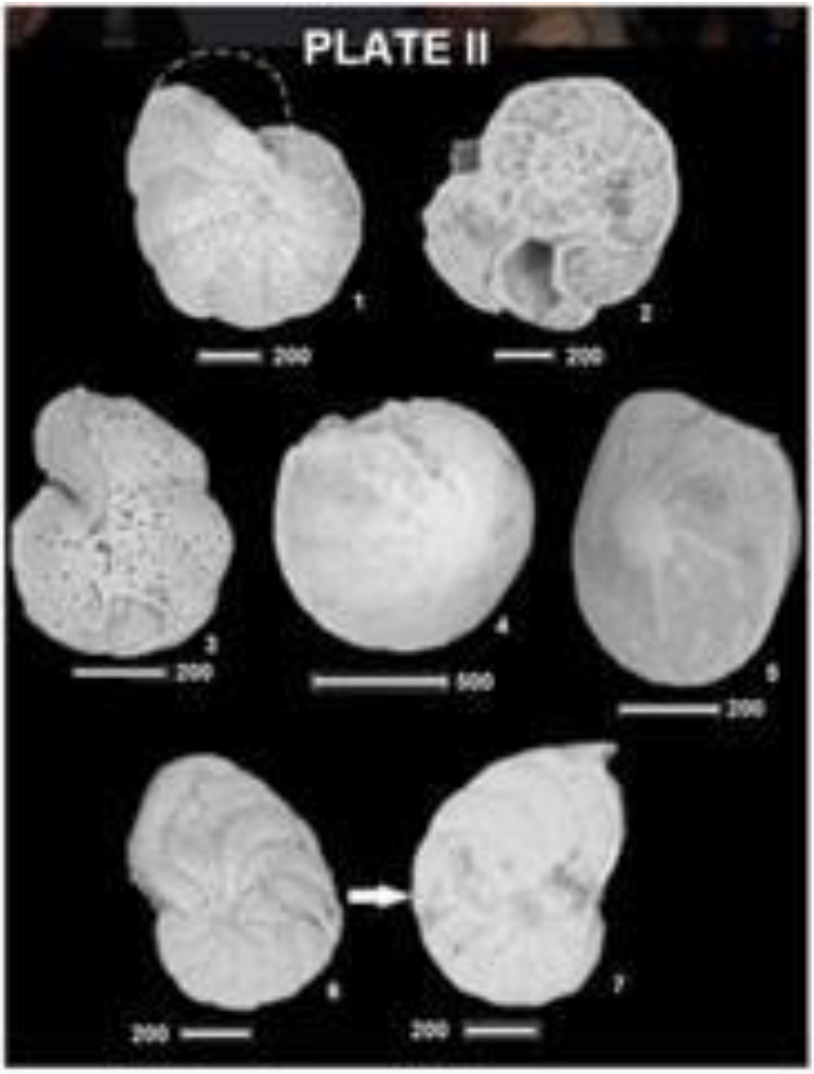
Triloculina sp.: Seven abnormal specimens out of 141 from all stations. The abnormal specimens with dislocated and slightly twisted aperture were collected from stations no. 1 and 3 (Figures 2-4). However, the other normal tests are from station no. 2 (Figure 3). The general abnormality represents about 5% of all stations (Table 2 and Figure 5).

Trisegmentina compressa: Four abnormal specimens out of 47 from all stations. The abnormal test with deformed last chamber was collected from all stations (Figures 2-4). The general abnormality represents about 9% of all stations (Table 2 and Figure 5).

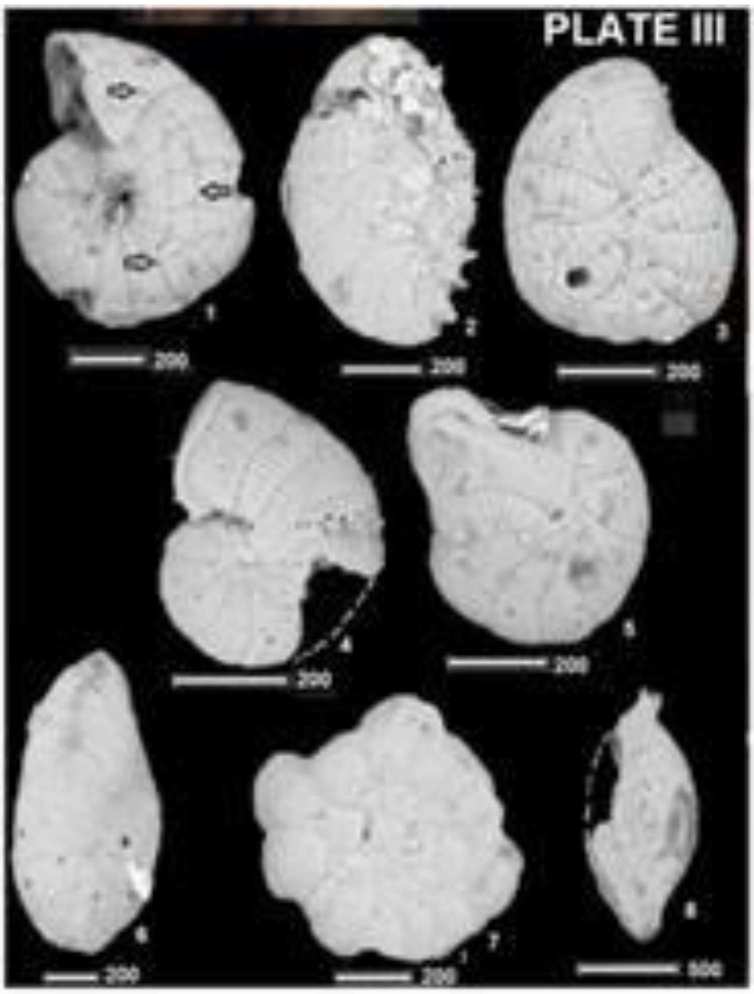
***Sorites* cf. *orbiculus*:** Three abnormal specimens out of 56 from all stations. The abnormal twisted tests were collected from stations no. 2 and 3 (Figures 3-4). However, the other normal tests are from station no. 1 (Figure 2). The general abnormality represents about 5% of all stations (Table 2 and Figure 5).



EXPLANATION OF PLATE I (Bar scale is in µm): Example of SEM photographs for deformed forams collected from studied stations at Al Hariqa crude oil exporting harbor, Tobruk - NE Libya. (1): Fragmented *Adelosina intricata* shows missing part of the last formed chamber including aperture, Station no.2. (2): *Adelosina* cf. *mediterraensis* abnormal test shows termination of costae at upper half of test, station no.2. (3): *Adelosina* sp. abnormal test shows smoothing of external surface and partial pitting, station no. 3. (4): *Quinqueloculina* cf. *bidentata* shows corroded test, Station no.3. (5-6): *Quinqueloculina disparilis*. 5 shows eroded aperture, Station no.2. 6 shows ornamentation missed in earlier chambers of last whorl, fragmentation is also featured, Station no.1. (7): *Quinqueloculina seminula* shows slightly disturbed suture, Station no.3.



EXPLANATION OF PLATE II (Bar scale is in µm): Example of SEM photographs for deformed foraminifers collected from studied stations at Al Hariqa crude oil exporting harbor, Tobruk - NE Libya. (1-3): *Lobatula lobatula*. 1 Ventral view shows collapsed chambers, 2 Dorsal view shows corroded chamber. 3 Ventral view shows abnormal test surface, Station no.3. (4-5): *Amphistegina lobifera* ventral and dorsal view shows corroded last chambers, Station no.2. (6-7): *Peneroplis planatus*. 6 Shows slightly twisted last portion of test. 7 Shows corroded chamber with coiling and chamber size problem (arrowed), Station no.1.



EXPLANATION OF PLATE III (Bar scale is in µm): Example of SEM photographs for deformed forams collected from studied stations at Al Hariqa crude oil exporting harbor, Tobruk - NE Libya. (1-6): *Peneroplis pertusus*.
1 Shows coil problem in early portion of the last formed whorl of the test and microboring activities (arrowed).
2 Half of the last whorl eroded.
3 Chamber size problem and some etching signs.
4 Corroded chamber, microzigzaged and highly serrated suture.
5 Deformed last part of test including aperture.
6 Reduced size of last chamber, Station no.1 and 3.
(7): *Planopulvinulina* cf. *dispansa* shows partially eroded last part of test, Station no.2.
(8): *Spiroloculina* cf. *angulata* shows peripheral etching, Station no. 2.

CONCLUSIONS

Ninety-six abnormal foraminiferal tests out of 1220 have been encountered in this study. The abnormalities of foraminiferal tests in the studied area include: coil twisting, deformed chamber size, disturbed suture, smoothing and polishing of some test surfaces, dislocated aperture and twinned individuals as well as dissolution or corroded tests. In addition to a dirty black or brown color are also noticed on some tests. This is attributed to the reducing conditions due to human and industry-related drained wastes. The diversity was low in some localities which may attribute to pollution by oil; this is slightly applied to station no. 2. Absence of agglutinated foraminifers is also attributed to polluted water [30]. However, the documented foraminiferal abnormalities in the studied area are more likely linked to some degree of pollution such as the high concentration of some heavy metals, which have been recorded in the geochemical analyzed of the coastal sea water, molluskan shells and beach sediments samples from the same studied localities [21]. Accordingly, the heavy metals which drained from both domestic wastes and leaked hydrocarbon from ships, boats and the refinery may be considered as the possible sources. On the other hand, the examined foraminiferal assemblage shows that a high percentage of the tests display post morten test corrosion (dissolution) along their periphery, or on the surface, due to change in water chemistry or wave and current transportation.

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