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MEASURING AND EVALUATION THE WATER POLLUTION OF SURFACE WATER IN TOBRUK BAY, LIBYA

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ABSTRACT

The aims of the study was to assess the degree of contaminations of the Tobruk gulf by measuring the concentrations of chemical parameters (pH, DO, BOD_5, COD, TN and TP) and heavy metals concentrations (Fe, Zn, Mn, Cu, Ni, Co, Pb, Cd and Cr). Samples collections from seven locations along Tobruk bay. Average concentrations of chemical parameters and heavy metals were compared with the permissible limits of (WHO) 2011 World Health Organization. The results showed that the average concentrations of chemical parameters at all stations were higher than the permissible limits of WHO. However, the heavy metals concentrations fluctuate between some metals were higher than the permissible limits, such as Cr, Fe, Mn, Ni, Co, Pb and Cd and other metals as Zn and Cu exhibit lower contents. The study proved that Tobruk commercial port and Sewage discharge tube as one of the main sources cause polluted in Tobruk bay

قياس وتقييم تلوث المياه السطحية في خليج مدينة طبرق، ليبيا

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الملخص العربي

دل توزيع المعاملات الكيميائية وتركيزالعناصر الثقيلة في خليج طبرق على عدم جودة المياة الحالية وتلوثها من عديد من المصارد المختلفة .تمت مقارنة متوسط تركيزات المعاملات الكيميائية التالية (الاس الهيدروجيني ، مجموع المواد الصلبة العالقة ، مجموع المواد الصلبة الذائبة الكلية، محتوي الاكسجين الذائب، الاكسجين الحيوي، الاكسجين الكيميائي، النيتروجين الكلى و محتوي الفسفور الكلى) وكذلك متوسط تركيزات العناصر الثقيلة مثل الحديد، الزنك، المنجنيز، النحاس، النيكل، الكوبالت، الرصاص، الكادميوم والكروم بمثيلتها في خليج السويس وقناة السويس بمصر وكذلك بالحد المسموح به لمنظمة الصحة العالمية (2011) حيث سجلت اختلافات محلية لهذه المعاملات حيث ظهرت متوسطات تركيزات المعاملات الكيميائية لكل من مجموع المواد الصلبة العالقة والذائبة الكلية، قيم النيتروجين الكلى ومحتوي الفسفور الكلى، الأكسجين الحيوى، الأكسجين الكيميائى والأمونيا جميعها أعلى من الحد المسموح به لمنظمة الصحة العالمية لعام (2011) وعن مثيلتها فى شاطىء وادى السهل وخليج السويس بمصر. كما وجد ان متوسط تركيزات العناصر الثقيلة لكل من الكروم، الحديد، المنجنيز، النيكل، الكوبالت، الرصاص والكادميوم اعلى من الحد المسموح به لمنظمة الصحة العالمية لعام (2011) بينما عكس الزنك والنحاس قيما اقل من الحد المسموح به لمنظمة الصحة العالمية لعام (2011). ايضاسجلت قيم الكوبالت والنيكل أعلى التركيزات في ثلاثة محطات هى ميناء الأتراك لصيد الاسماك ومحطة تحلية المياة والمحطة رقم 6 المقابلة لشركة النفط. و يعتبر كل من المنجنيز، الكوبالت، النيكل، الرصاص، الكادميوم والكروم من العناصر الثقيلة الاساسية في تلوث مياه خليج مدينة طبرق نتيجة للنشاطات البشرية والتلوث النفطى الصارخ فى خليج طبرق.

INTRODUCTION

The coastal zone of Tobruk bay is considered as one of the most used bays by human activities. Remarkable population growth accompanied by intensive urbanization have brought a huge increase in the quantity of discharges and a wide diversification in the type of pollutants, which have undesirable effects on the environment. The coastal communities in the Tobruk bay

discharge their sewage into the sea via pipelines. These pipelines are short or badly sited. In general, Tobruk bay receives different wastewaters from different sources at the border of the bay. These include; untreated industrial wastes, municipal sewages and petrochemical contaminants. Petrochemical pollution from oil transporting process was effective too. Decaying organic matter, nitrates and phosphates in sewage enhances plant growth. Waste products of industrialization and urbanization (generated since the 1970s) have had harmful effects on the ecosystems of the country. The impact of human activity in this bay is becoming a major source of pollutants.

There are several hot spots of pollution discharging their untreated effluents directly into the bay. The abundance of decaying plant material falling to the seabed severely reduces the oxygen concentration in bottom waters and most of benthic animals are killed. Domestic wastes and sewage contain a quantity of oil and greases, and depending on the nature of the industry, its wastes may also contain a considerable quantity of hydrocarbons. In coastal areas, these wastes are often discharged into the sea. In addition to the coastal oil refineries on Tobruk bay, the use a steam-cracking process and the water recovered, which is discharged in the effluent contains up to 100 ppm of oil in the water (Clark, 1992). Oil refineries pose a threat to the marine environment in the absence of adequately enforced regulations related to the effluent discharged into the coastal environment. Refineries require a large volume of water which is continuously discharged into the same body of water. In addition, to rain's washed down drains that eventually reaches the Tobruk bay. Shipping channels and ports need regular dredging. The dredging spoil, which is usually dumped into the sea is contaminated with oil. Various kinds of solid municipal and industrial wastes that are dumped into the seawater of the bay may also contain petroleum hydrocarbons. However, the incomplete combustion of petrol or diesel in motor vehicles results in petroleum hydrocarbons being released into atmosphere and washed out directly into the sea.

The limits of heavy metals generally exceeded WHO specifications limits. Thus, the bay water has a negative impact on the quality of drinking water and on the deterioration of the marine ecosystem. Monitoring the presence of large encroachments on the bay water body by human activity is shown in Fig. (1).

Drinking water in Tobruk city depends on desalination of seawater from Tobruk bay. If this water contains any chemical constituents with the concentration higher than the maximum permissible level of WHO (1971 and 1981), it is becoming polluted. The permissible limits given here by WHO (2011) for drinking water quality.

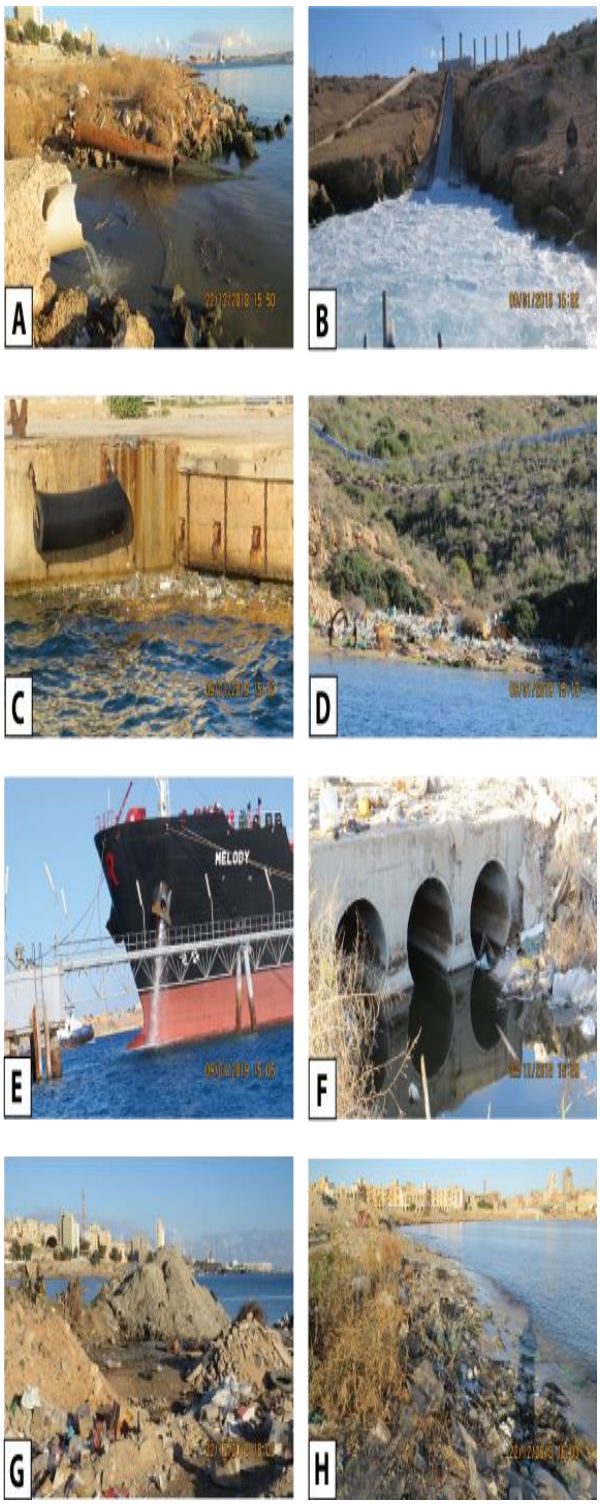

Fig. (1): Reconnaissance of pollution sites along the Tobruk bay.

- **(A) Waste water effluent at Tobruk corniche.**
- **(B) Desalination plant.**
- **(C) Garbage accumulation in commercial port.**
- **(D) Garbage accumulation in gulf shores.**
- **(E) Dumping waste water from ships.**
- **(F) Opening for dumping municipal sewage.**
- **(G) Construction piles on the shore.**
- **(H) Accumulation of waste water on the beach.**

Location map showing station sites of collecting water samples along the shore of Tobruk bay showing in Fig. (2)

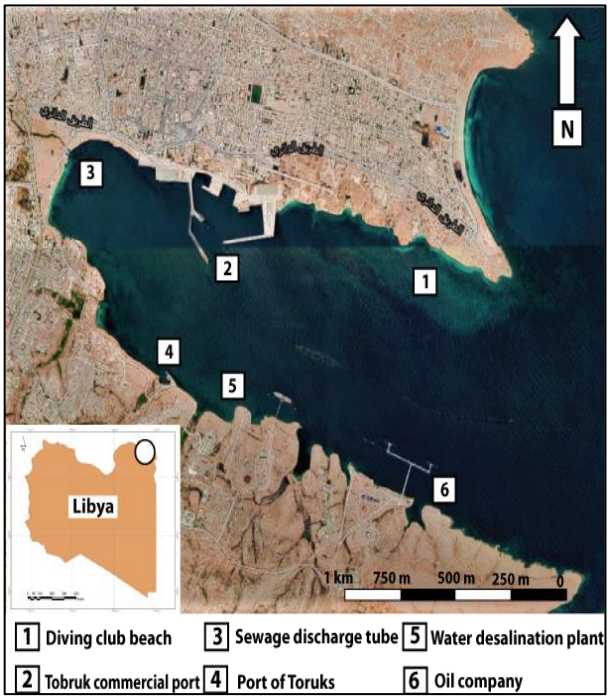

Fig. (2): Location map showing station sites of collecting water samples along the shore of Tobruk bay.

MATERIALS AND METHODS:

The study area

Tobruk bay occurs east of the city of Tobruk (Fig.3) with length extends to about 5 km and width varies between 2 km at the entrance and 0.6 km at the end. The depth of water in the bay ranges from 5 to 16 meters. Effect of urban and industrial pollution was the main target of the present part.

Collection of Samples

Seven water samples were collected by Nelson tube at 1m depth from the surface. Six samples represent 6 locations along Tobruk bay, these includes; Diving Club beach, Tobruk commercial port, Corniche beach (Sewage discharge tube), Port of Toruks, water desalination plants. In addition to one sample from an Oil Company and one sample from seawater in front of Wadi Elsahal (18 km away from Tobruk bay) for comparison. All water samples were kept in black bottles and transferred to the laboratory for analyses. The current state of water quality in Tobruk bay can be studied by determination of the hydrochemical parameters (pH, DO, BOD_5, COD, TN and TP) and heavy metal concentrations (Fe, Zn, Mn, Cu, Ni, Co, Pb, Cd and Cr). Location sites of collecting water samples from Tobruk bay as well as the pH of the samples are summarized in Table (1) and shown in Fig. (3). The collected water samples were mixed with addition of 2 ml concentrated HNO_3 to preserve the different metals in the bottles. Concentrations of heavy metals; Fe, Zn, Mn, Cu, Ni, Co, Pb, Cd and Cr were measured by Atomic Absorption Spectrophotometer in the laboratory of Chemistry Department, Faculty of Science, Mansoura University.

Chemical analysis

Hydrochemical parameters which include: (pH) was determined in water samples using pH meter. TSS (Total Suspended Solid), TDS (Total Dissolved Solids), TN (Total Nitrogen) was measured by using Kjeldahl method (Jackson, 1973). , TP (Total Phosphorus) was determined by using ascorbic acid molybdate method (Murphy and Riley, 1962). , DO (Dissolved Oxygen) concentration was measured by using the modified Winkler method according to Standard Method 4500 (APHA, 1992)., BOD_5 (Biochemical Oxygen Demand) was measured by using the 5 days method (ABHA1980) , NH_3 (Ammonia), and COD (Chemical Oxygen Demand) was determined by using the potassium dichromate (APHA, 1976). were measured at Dakahlia Water and Sewage Company Laboratories and Laboratory of Soil fertility test and fertilizers quality control at Faculty of Agriculture, Mansoura University.

Table (1): Locations and pH of water samples in Tobruk bay (1m depth).

Site No.	Locations	pH	Latitude	Linguae
1	Diving Club beach	8.5	32º 04' 19" N	**24º 00' 15" E**
2	Tobruk commercial port	8.4	32º 04' 33" N	**2º3 58' 42" E**
3	Sewage discharge tube (Corniche beach)	8.3	32º 04' 41" N	**23º 58' 09" E**
4	Port of Toruks (Fishing port)	8.4	32º 03' 56" N	**2º3 58' 34" E**
5	Water Desalination plant	8.5	32º 03' 47" E	**23º 58' 55" E**
6	Oil Company	8.5	32º 03' 25" E	**23º 59' 59" E**
7	Wadi Elsahal beach	9.7	32º 08' 14" E	**23º 49' 52" E**

Heavy metals analysis

The collected water samples were mixed with addition of 2 ml concentrated HNO_3 to preserve the different metals in the bottles. Concentrations of heavy metals; Fe, Zn, Mn, Cu, Ni, Co, Pb, Cd and Cr were measured by Atomic Absorption and were determined by the extracting method (APHA, 1992). Spectrophotometer in the laboratory of Chemistry Department, Faculty of Science, Mansoura University.

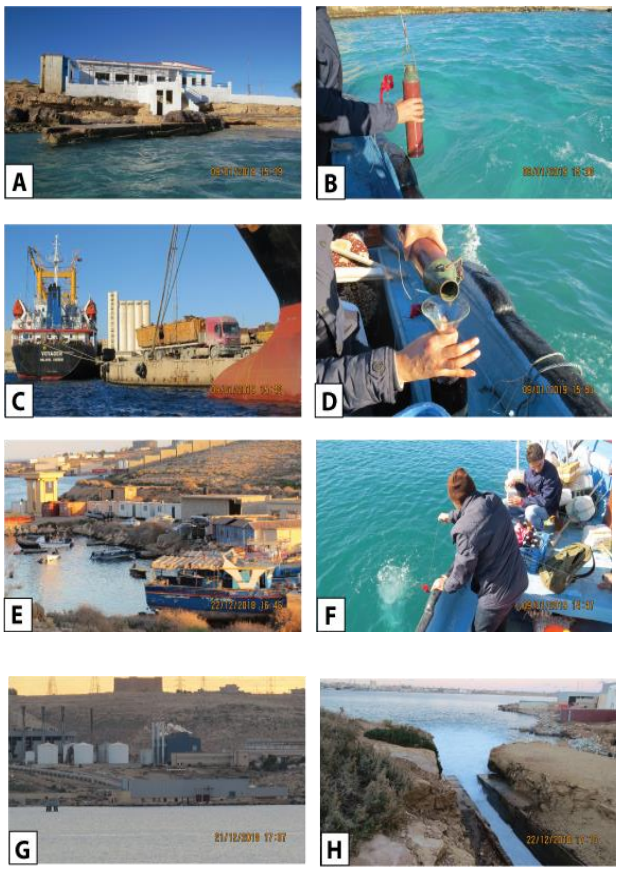

Fig (3): Locations of collecting water samples in Tobruk bay.

(A) and (B) Diving club beach. (C) Tobruk commercial port. (D) Corniche beach.(E) and (F) Port of Toruks. (G) and (H) Water Desalination plant. (I) and (J) Oil Company.(K) and (L) Wadi Elsahal beach.

RESULT AND DISCUSSIONS

Chemical parameters characteristic of seawater in Tobruk bay

The chemical parameters determined in water samples include; pH, total suspended solids (TSS), total dissolved solid (TDS), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH_3), total nitrogen (TN), and total phosphorous (TP). Results are summarized in Table (2) and are illustrated graphically in bar graphs shown in Figs. (2 -9). Average concentrations of these parameters are compared with those determined in the Gulf of Suez of Egypt.

Table (2): Data of chemical parameters in Tobruk bay water (Data given in ppm).

Site No.	Locations		TSS	TDS	TN	TP	DO	BOD_5	COD	NH_3
1	**Diving Club Beach**		35	40200	8.5	0.074	5	1150	583	1.77
2			30	39600	15.2	0.095	2.8	3500	1208	0.59
3	**Sewage discharge tube (Corniche beach)**		45	40080	10.0	0.065	2.9	1700	740	2.06
4	**Port of Toruks**		25	40020	9.58	0.039	3.4	1000	498	1.18
5	**Water Desalination Plant**		21	40560	12.5	0.074	1.3	1300	564	1.19
6	**Oil Company**		25	38880	19.3	0.034	3.8	900	462	0.59
Average			**30.16**	**39890**	**12.51**	**0.063**	**3.2**	**1591**	**675.8**	**1.23**
Average Gulf of Suez (Emara et al.,2013)		**S**	-	**35644**	-	**0.034**	**2.87**	**250**	**131.7**	**2.15***
		W	-	**35525**	-	**0.020**	**1.94**	**151**	**190.7**	**1.54****
7	**Wadi Elsahal Beach**		40	33480	3.5	0.026	6	1100	584	0.0

- **The pH values:**

The pH values were raged between 8.3 and 9.7, The maximum **pH** values was recorded at Wadi Elsahal beach, while the lees values recorded at Sewage discharge tube (Corniche beach).

- **Total Suspended Solids (TSS)**

Jalgaif et al. (2018) found high contamination of seawater in Tobruk bay. The absence of treatment and the long-term exposure to these discharges will lead to dangerous levels that affecting the marine life. While Aghow et al. (2018) dealt with the heavy metal pollution of the Tobruk water bay and the extent of the impact of this pollution on drinking water in the Tobruk city. It was reported that

concentrations of heavy metals were high in the bay waters; hence the drinking water is affected resulting from the desalination of the bay water

Total suspended solids (TSS) in water either consist of inorganic or organic particles. Inorganic solids include soil constituents that are transported from land to the sea, while organic materials such as biological and fibers solids as bacteria and algal cells are the common constituents of surface water. Suspended solids are aesthetically displeasing and provide adsorption sites for chemical and biological agents. Suspended organic solids degrade biologically resulting in objection able by-products of foul odours (Vanloon and Duffy, 2000). Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated waste water is discharged in the aquatic environment. TSS concentrations in Tobruk bay are listed in Table (2) and shown in Fig. (4). It was found that TSS values vary between 21 and 45 ppm with an average of 30.16 ppm. The maximum TSS content was recorded at sewage discharge tube station. However, TSS value in the unpolluted sample of Wadi Elsahal beach equal 40 ppm which is generally higher than the average concentration of TSS in Tobruk bay, this is probably related to the supplied materials transported to the sea during flash flooding in the wadis

- **Total Dissolved Solids (TDS)**

TDS concentrations are given in Table (2) and illustrated in Fig. (5). Their values range from 38880 to 40560 ppm with an average of 39890 ppm, which is generally higher than the contents in Wadi Elsahal beach and Gulf of Suez (33480 and 35644 ppm, respectively). No sharp variation in TDS concentrations was noticed in the study area. The average concentration of total dissolved solids in Tobruk bay water was higher than the permissible limits of WHO (2011) for drinking water (1000 and 500 mg/l).

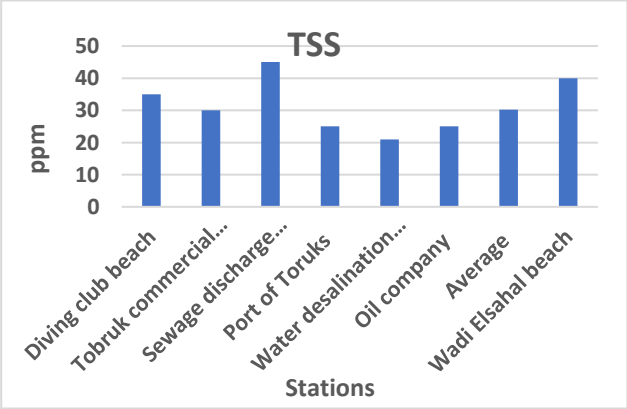

Fig. (4): Bar graph distribution for total suspended solids (TSS) concentrations.

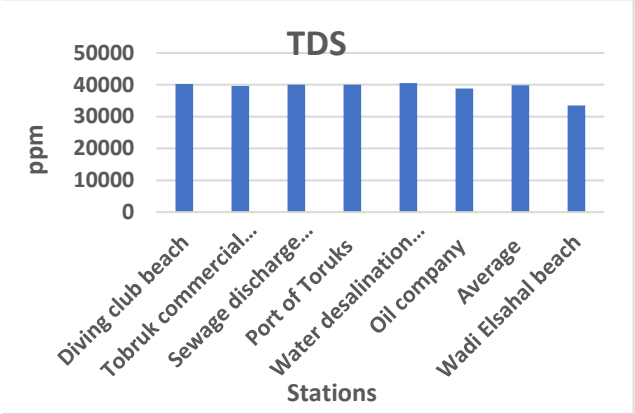

Fig. (5): Bar graph distribution for total dissolved solids (TDS) concentrations.

- **Total Nitrogen (TN)**

The total nitrogen, as a commonly used parameter, consists of many compounds such as; NH_3, NH_4 -N, NO_3 -N, NO_2 -N, urea, Organic-N (EPAP, 2002). Nitrogen data is required to evaluate the treat ability of waste water by biological processes. Insufficient nitrogen can necessitate the addition of nitrogen to make the waste water treat able.(Emara et al., 2013).

Total nitrogen concentrations in Tobruk bay water are listed in Table (2) and represented graphically in Fig. (6). TN values fluctuate between 8.5 and 19.3 ppm with an average of 12.5 ppm, which is higher than TN value determined in Wadi Elsahal beach (3.5 ppm). The highest (TN) value was recorded at Oil Company due to oil pollution.

- **Total Phosphorus (TP)**

Phosphorus is an essential nutrient for the living organisms and appears exclusively as phosphate in an aquatic environment. Total phosphorus (TP) concentrations are listed in Table (2) and illustrated in Fig. (7). Total phosphorus (TP) has concentration varies from 0.034 to 0.095 ppm with an average of 0.063 ppm, which is higher than the concentration at Wadi Elsahal beach 0.026 ppm and the average value given in the Gulf of Suez and indicates highly pollution water in Tobruk bay.

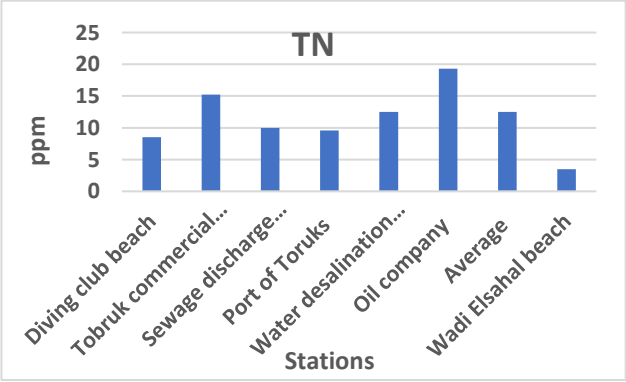

Fig. (6): Bar graph distribution for total nitrogen (TN) concentrations

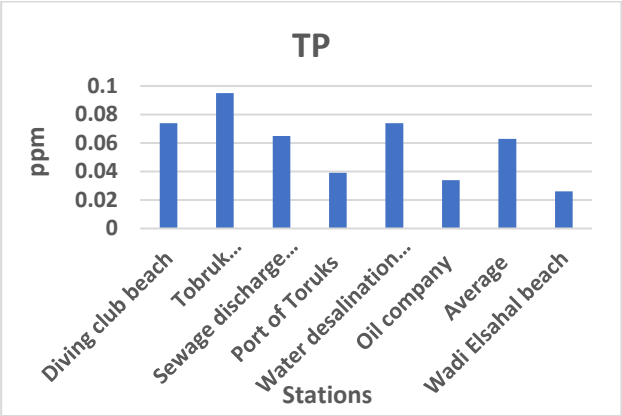

Fig. (7): Bar graph distribution for total phosphorus (TP) concentrations.

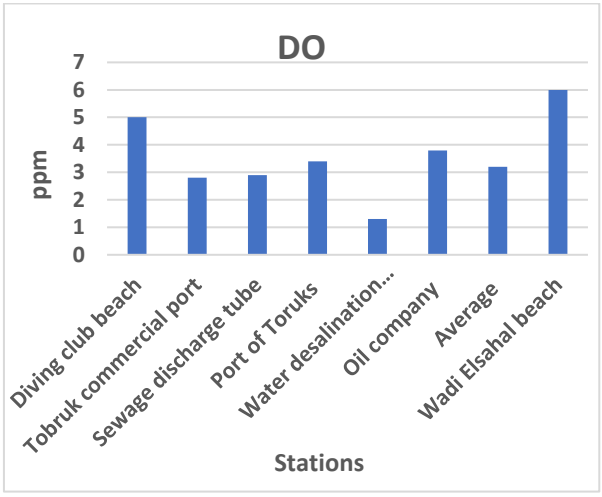

Fig. (8): Bar graph distribution for Dissolved Oxygen (DO) concentrations.

- **Dissolved Oxygen (DO)**

Concentrations of the dissolved oxygen (DO) in Tobruk surface water vary between 1.3 and 5 ppm with an average of 3.2 ppm which appears higher than the average given in the Gulf of Suez (2.87 and 1.9 ppm). Their concentration distribution has been shown in Fig. (8). The lowest concentration of DO (1.3 ppm) is exhibited by station no. 4 (Water desalination plant) due to the warming of the seawater where dissolved oxygen reaches the minimum. It is not surprise to find low water quality at some stations in Tobruk bay. This is caused by the combination of any factors including industrial and domestic waste discharges. Thus, negative effects were focused in the vicinity of pollution point sources. The consumption of a high rate of oxygen in the decomposition of organic matter discharged in Tobruk bay is considered as the main cause of diminishing the oxygen. The solubility of oxygen increases with decline the temperature (Singh et al., 1990). The highest value of DO was recorded at station no.7 (Wadi Elsahal beach).

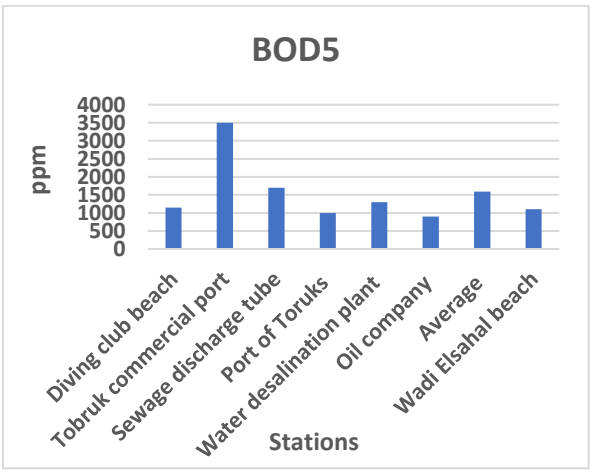

Fig. (9): Bar graph distribution for Biochemical Oxygen Demand (BOD5) concentrations.

- **Biochemical Oxygen Demand (BOD_5)**

The measurement of the dissolved oxygen used by organisms in the biochemical oxidation of organic matter. The difference in oxygen levels between the control bottle and the bottles with oxygen remaining is used to calculate the BOD_5 in mg/l (EPAP, 2002). BOD_5 concentrations in Tobruk bay vary between 900 and 3500 ppm with an average of 1591ppm, which is generally higher than the average given for seawater in the Gulf of Suez. Table (2). This reflects pollution of seawater in Tobruk bay. The marked local variations in BOD_5 are attributed to the effect of pollution point sources where water quality deterioration is pronounced for receiving considerable amounts of untreated domestic sewage wastes and industrial effluents. It was observed that Tobruk commercial port location represents the most polluted area.

- **Chemical Oxygen Demand (COD)**

COD is the rate of oxygen required to oxidize organic matter and oxidize compounds present in the water sample into CO_2 and H_2O (APHA, 1995). The COD parameter is used to measure the organic matter in industrial waste water that contains toxic compounds to biological life (EPAP, 2002). COD can be determined in 3 hours, compared with 5 days for the BOD**5**. COD concentrations measure in Tobruk bay fluctuate between 462 and 1208 ppm with an average of 675.8 ppm. Distribution of COD values is shown in Fig. (10). High COD value is found in (Tobruk Commercial Port) whereas, low COD concentration is recorded in (An Oil Company).

Variation trends of COD concentrations show a high concentration at Tobruk Commercial Port station due to the high decomposition rate of organic matter as a result of low DO content

- **Ammonia (NH_3)**

Ammonia (NH_3) can be produced by bacteria decomposition of organic matter containing nitrogen in the aquatic system (Vanloon and Duffy, 2000). Ammonia concentrations in Tobruk bay water range from 0.59 to 2.06 ppm with an average of 1.23 ppm, which is lower than the average of ammonia exhibited by seawater in the Gulf of Suez (Table 2, Fig.11). Strong wide variation trend of ammonia concentrations is documented depending on the location of collected water sample in the bay. Highest value (2.06 ppm) is exhibited at (sewage discharge tube-Corniche beach) where the direct inflow of domestic water runs. The lowest ammonia value (0.59 ppm) was exhibited by stations no. 2 and no. 6, while at Wadi Elsahal beach there was no ammonia concentration. The average content of NH_3 (1.23 ppm), generally higher than the permissible limit of WHO (2011) for drinking water.

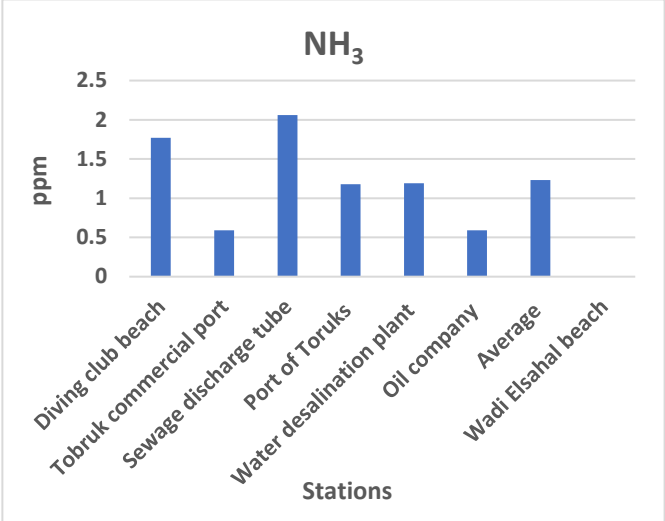

Fig. (11): Bar graph distribution for Ammonia (NH_3) concentrations.

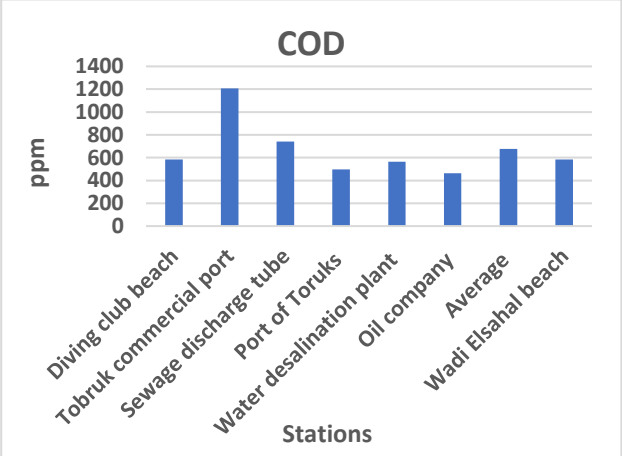

Fig. (10): Bar graph distribution for Chemical Oxygen Demand Concentrations

Heavy metals:

concentration in Tobruk bay seawater.

Heavy metals can endanger our health by being incorporated in the food chain or released into overlying water layers. Different industrials, population growth, and technological developments nowadays have led to a huge increase and accretion of heavy metals in the environment (Liu et al., 2009). The heavy metals can lead to a serious health hazard to humans and marine ecosystem. Heavy metals, such as Pb, Cr, and Cd, are highly toxic even at minute quantities and these metals go to the environment mainly by human activities. On the other hand, some heavy metals, such as Mn, Fe, and Cu are useful to the environment in limited quantities by providing nutrition to plants (Alsaffar et al., 2016).

The results are listed in Table (3) and represented graphically as bar graphs in Figs (12-20). The summary of correlation coefficients of metal and chemical parameters concentrations is summarized in Table (4).

Table (3): Heavy metal concentrations in seawater of Tobruk bay.

Locations	Fe ppm	Zn ppm	Mn ppm	Cu ppm	Ni ppm	Co ppm	Pb ppm	Cd ppm	Cr ppm
1	0.391	0.21	1.1227	0.159	21.289	2.926	4.412	0.010	0.2128
2	0.518	0.32	1.2858	0.098	27.019	7.895	2.021	0.006	0.2344
3	0.813	0.12	1.4571	0.062	27.586	5.475	8.254	0.250	0.2746
4	1.006	0.14	1.2278	0.191	22.200	12.885	3.110	0.012	0.2256
5	0.530	0.35	1.1889	0.063	23.901	17.774	5.400	0.007	0.2319
6	0.315	Zero	0.9558	0.059	21.287	14.478	6.300	0.008	0.1613
Average (present study)	0.595	0.19	1.206	0.105	23.880	10.238	4.916	0.0488	0.223
Average in Suez Canal (El-Moselhy etal., 2005)	35.0	4.32	2.89	1.71	1.46	0.33	3.52	0.51	0.23
Average in Gulf of Suez (Hamed, 1996)	15.5	7.91	2.5	2.68	2.96	0.7	0.39	0.23	-
7	0.787	0.1	0.8925	Zero	21.555	9.308	0.036	0.005	0.208
Perm. limits WHO (2011)	0.3	0.5	0.1	2.0	0.07	-	0.01	0.003	-

Table (4): Correlation coefficients (r) for metals and chemical parameters concentrations in Tobruk bay seawater.

Water variables	TSS	TDS	TN	TP	DO	BOD_5	COD	NH_3	Fe	Zn	Mn	Cu	Ni	Co	Pb	Cd	Cr
TSS	1																
TDS	-0.392	1															
TN	-0.572*	0.528*	1														
TP	-0.049	0.618*	0.258	1													
DO	0.507*	-0.725	-0.549*	-0.539*	1												
BOD_5	0.090	0.181	0.270	0.743*	-0.327	1											
COD	0.199	0.119	0.183	0.724*	-0.242	0.993**	1										
NH_3	0.227	0.737*	-0.031	0.419	-0.345	-0.094	-0.082	1									
Fe	0.287	-0.203	-0.593*	-0.336	0.041	-0.105	-0.075	0.073	1								
Zn	-0.296	0.400	-0.001	0.819*	-0.555*	0.564*	0.530*	0.153	-0.116	1							
Mn	0.196	0.684*	0.099	0.063	-0.629*	0.487	0.480	0.723*	0.324	0.408	1						
Cu	-0.080	0.242	-0.594*	-0.138	0.525*	-0.176	-0.156	0.145	0.417	0.024	-0.037	1					
Ni	0.308	0.350	0.179	0.649*	-0.578*	0.760*	0.761*	0.329	0.182	0.420	0.834*	-0.434	1				
Co	-0.791*	0.048	0.397	-0.299	-0.502*	-0.282	-0.376	-0.380	-0.014	0.057	-0.273	-0.282	-0.228	1			
Pb	0.029	0.654*	0.456	0.175	-0.507*	-0.194	-0.218	0.730*	-0.219	-0.164	0.490	-0.612	0.306	0.037	1		
Cd	0.667*	0.211	-0.106	0.116	-0.202	0.076	0.122	0.632*	0.340	-0.206	0.681*	-0.357	0.646*	-0.392	0.653*	1	
Cr	0.449	0.309	-0.352	0.513*	-0.409	0.413	0.444	0.579*	0.538*	0.465	0.864*	-0.016	0.789*	-0.348	0.218	0.689*	1

- **Iron (Fe)**

Iron content ranges from 0.315 to 1.006 ppm with an average of 0.595 ppm, which is generally lower than those recorded in Suez Canal and Gulf of Suez (Table 3, Fig.12). Iron content in the unpolluted seawater of Wadi Elsahal (0.787 ppm), appears higher than the average Fe content in the polluted seawater of Tobruk bay and the permissible limits given by WHO (2011) for drinking water (not exceed 0.3 ppm). The highest iron content (1.006 ppm) is recorded at station no. 4 (Port of Toruks).

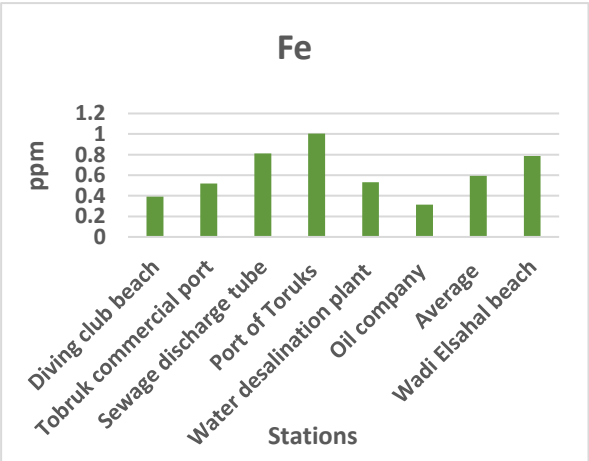

Fig. (12): Bar graph distribution showing Fe concentrations in theTobruk bay water.

This higher level of iron can be related to the function of water stagnation under low flow conditions and thus the water is not sufficiently oxygenated. Iron is positively correlated with chromium (r=0.538), in contrast, iron is negatively correlated with TN (r= -0.593) Table (4)

- **Zinc (Zn)**

Zinc is an essential element for the growth of aquatic organisms. Domestic wastes are considered the main source of zinc (James, 1991). Zn concentration in Tobruk bay water ranges from 0.0 and 0.35 ppm with an average of 0.19 ppm, which is lower than the average given in Suez Canal and Gulf of Suez (4.32 and 7.91 ppm, Table 3, Fig.13) and is lower than the permissible limits given by WHO (2011) (not exceed 0.50 ppm). The lowest content of Zn (0.1 ppm) is exhibited by the Wadi Elsahal beach water which is considered unpolluted station. Zinc has a significant positive correlation with TP (r= 0.819), BOD_5 (r=0.564) and COD (r=0.530). Table (4).

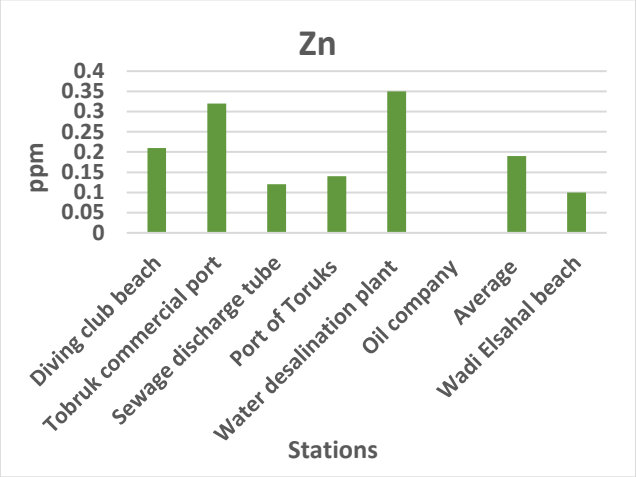

Fig. (13): Bar graph distribution showing Zn concentrations in the Tobruk bay water.

- **Manganese (Mn)**

Manganese concentrations fluctuate between 0.9558 and 1.4571 ppm with an average of 1.2060 ppm, generally lower than those exhibited by Suez Canal and Gulf of Suez Table (3). In addition, Mn concentrations are higher than the permissible limits of WHO (2011) (not exceed than 0.1 ppm). The lowest concentration of Mn is documented in Wadi Elsahal beach water (0.8925 ppm) which was considered unpolluted station. Burning discharge of diesel fuel in the motor cars and the power plants are the major sources for manganese in water and air (Beliles, 1979). High concentration of Mn was explained by mechanisms of diagenetic mobilization produced by changing condition due to sewage discharge (Förstner, 1977). The highest Mn concentration was recorded at Sewage discharge tube (Corniche beach) (Fig.14) where huge amounts of domestic sewage discharge in the bay. Manganese has positive correlation with TDS (0.684), TP (r= 0.636),

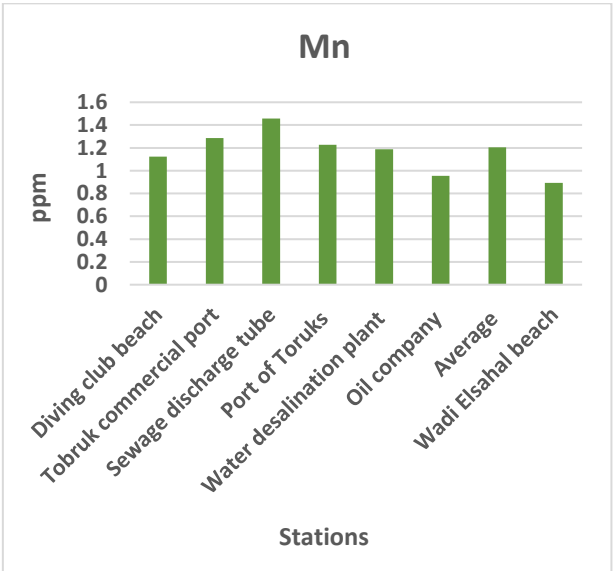

Fig. (14): Bar graph distribution showing Mn concentrations in the Tobruk bay water.

- **Copper (Cu)**

Copper concentrations in the study area vary between 0.059 and 0.191 ppm with an average of 0.105 ppm, which is generally lower than the permissible limits of WHO (2011) for drinking water (not exceed than 2 ppm) and lower than the average given in Suez Canal and Gulf of Suez. Table (3). While seawater of Wadi Elsahal (unpolluted station) has zero concentration (Fig. 15). Highest Cu concentration (0.191 ppm) was recorded at (Port of Toruks). Copper exhibits a positive correlation with DO (r= 0.525) and a negative correlation with TN (r= -0.594).

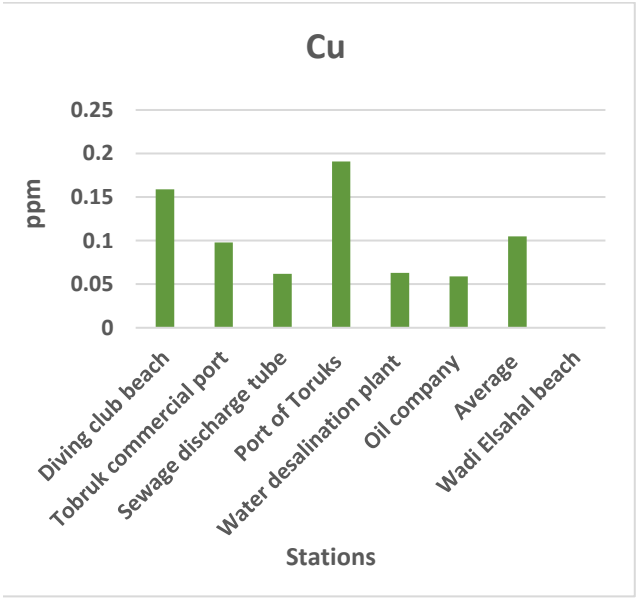

Fig. (15): Bar graph distribution showing Cu concentrations in the Tobruk bay water.

- **Nickel (Ni)**

The distribution of Ni content is shown in Fig. (16), it fluctuates between 21.287 ppm and 27.586 ppm with an average of 23.880 ppm, which is higher than the average given in Suez Canal and Gulf of Suez waters (1.46 and 2.96 ppm respectively). While Wadi Elsahal station has Ni value 21.555 ppm higher than the permissible limits of WHO (2011) (not exceed 0.07 ppm) for drinking water. Ni is always used in gasoline improvement (Helal et al, 1984). Nickel has a positive correlation with TP (r= 0.649), BOD5 (0.760), COD (r= 0.761), and Mn (0.834). On the other hand, it exhibits a negative correlation with DO (r= -0.578). Thus, Tobruk bay water is considered polluted by Ni concentrations.

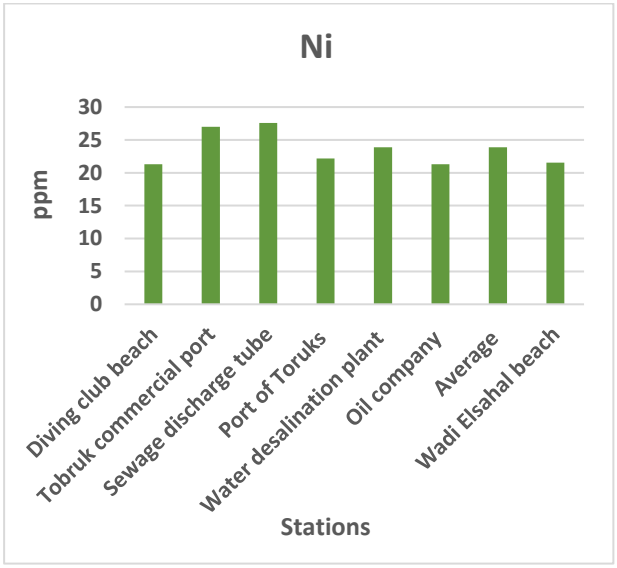

Fig. (16): Bar graph distribution showing Ni concentrations in the Tobruk bay water.

- **Cobalt (Co)**

Cobalt contents range from 2.926 to 17.774 ppm with an average of 10.238 ppm (Fig. 17), which is generally higher than the averages in Suez Canal and Gulf of Suez (0.33 and 0.7ppm, respectively). Tobruk bay seawater is much polluted for Co. The highest Co content was recorded in station no. 5 (water desalination plant). Cobalt has a strong negative correlation with TSS (r= -0.791) and DO (r= -0.502) probably due to changes in redox conditions (Förstner, 1977).

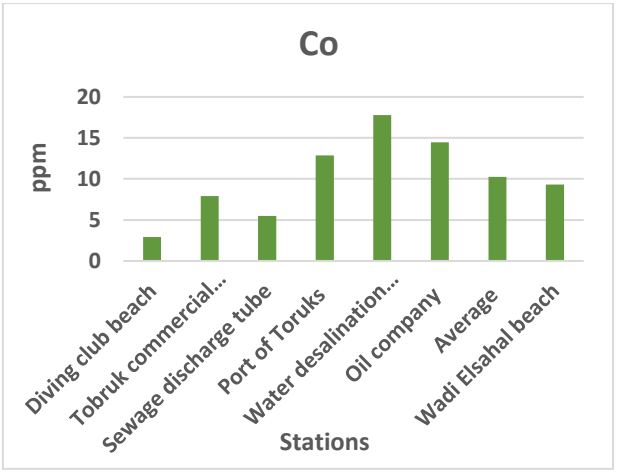

Fig (17): Bar graph distribution showing Co concentrations in the Tobruk bay water.

- **Lead (Pb)**

Lead distribution in Tobruk bay (Fig.18) ranges from 3.110 to 8.254 ppm with an average of 4.916 ppm, which is higher than those given in Wadi Elsahal beach (0.036 ppm), Suez Canal (3.52 ppm) and Gulf of Suez (0.39 ppm). In mean times Pb concentration is higher than the permissible limits of WHO (2011) (not exceed 0.01 ppm) for drinking water. Lead is a toxic metal to the environment (Nicolau et al., 2006). Civilizational influences are mostly reflected by elevated contents of lead, cadmium and zinc (Förstner, 1977). Thus, Pb is considered the main pollutant metal in Tobruk bay. Higher level of lead often occurs in water bodies beside high ways due to high combustion of gasoline (Banat el al., 1998). A high positive correlation exists between Pb and TDS (r= 0.654) and NH_3 (r= 0.730).

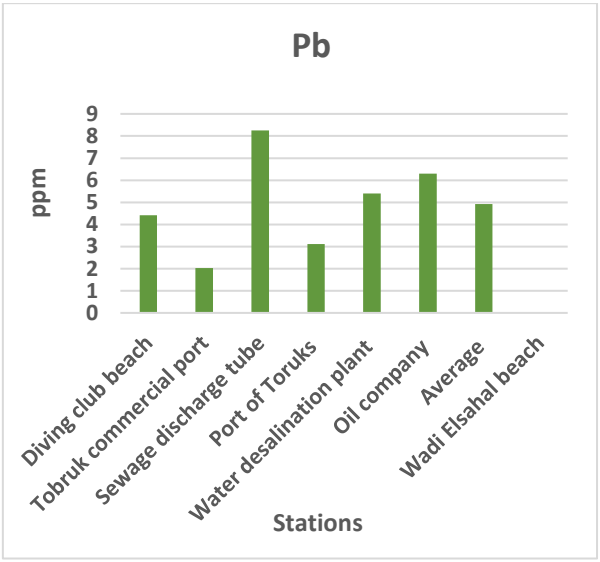

Fig. (18): Bar graph distribution showing Pb concentrations in the Tobruk bay water.

- **Cadmium (Cd)**

Cadmium is an extremely toxic to biota and living organisms even at low concentration and has long biological life of 20 to 30 years in kidney (Green et al., 1986). The distribution of Cd content is shown in Fig. (19). Cd fluctuates between 0.006 and 0.250 ppm with an average of 0.0488 ppm. The highest Cd concentration is recorded in (Corniche beach 0.025 ppm), while the lowest value of Cd (0.005 ppm) was recorded in (Wadi Elsahal beach). Cd concentration in Tobruk seawater is higher than the permissible limits of WHO (2011) (not exceed 0.003 ppm), and is higher than those exhibited in Suez Canal and Gulf of Suez. Thus, Cd is considered one of the pollutant metals beside Pb in Tobruk bay water. Cd has a strong positive correlation with TSS (r= 0.667), NH_3 (r= 0.632), Mn (r= 0.681), Ni (r= 0.646) and Pb (r= 0.653).

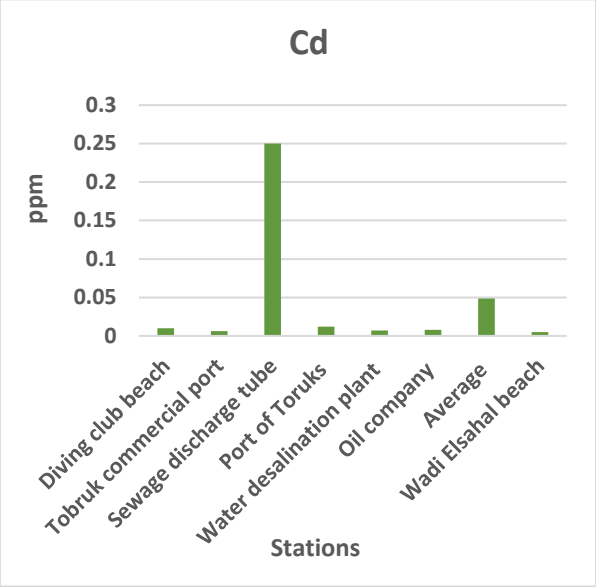

Fig. (19): Bar graph distribution showing Cd concentrations in the Tobruk bay water.

- **Chromium (Cr)**

The Concentrations of Cr concentrations are shown in Fig.20 Chromium varies between 0.1613 and 0.2746 ppm with an average of 0.2230 ppm, which is generally similar to the average exhibited in Suez Canal water (0.23 ppm) and Wadi Elsahal beach (0.208 ppm). The highest Cr concentration is reflected by station no. 3 (Sewage discharge tube - Corniche beach). Strong positive correlations exist between chromium and Mn (r= 0.864), Ni (r= 0.789), Cd (r= 0.689), TP (r= 0.513) and NH_3 (r= 0.579). This behavior reflects periods of reducing conditions on the bay according to Förstner (1977) where these metals can be mobilized.

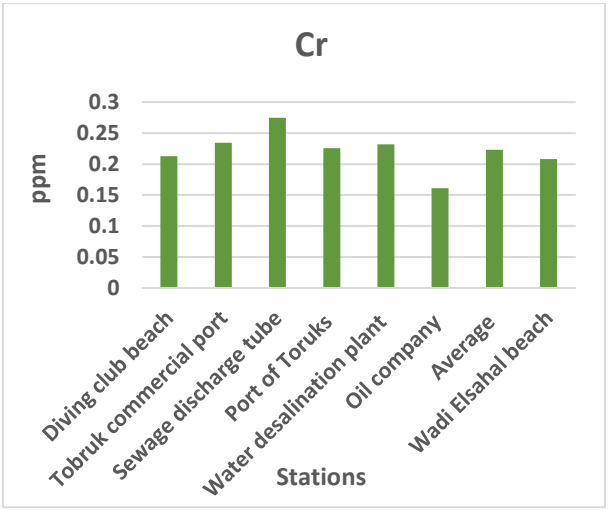

Fig. (20): Bar graph distribution showing Cr concentrations in the Tobruk bay water.

CONCLUSION

Distribution of chemical parameters and heavy metals concentration in Tobruk bay indicate the current state of water quality and the degree of pollution caused by the different sources. Average concentrations of chemical parameters (pH, TSS, TDS, DO, BOD, COD, TN and TP) and heavy metal concentrations (Fe, Zn, Mn, Cu, Ni, Co, Pb, Cd and Cr) are compared with similar averages in Gulf of Suez of Egypt and the permissible limits of WHO (2011). Noticeable local variations and important conclusions are recorded:

1- The average concentrations of TSS, TDS, TN, TP, Do, BOD_5, COD and NH_3 in Tobruk bay are higher than the permissible limits of WHO (2011) and higher than the concentration in Wadi Elsahal beach and Gulf of Suez.
2- The average concentrations of Cr, Fe, Mn, Ni, Co, Pb and Cd are higher than the permissible limits of WHO (2011) while Zn and Cu exhibit lower contents.
3- Noticeable high Ni and Co concentrations are recorded in Port of Toruks (Fishing port), water Desalination Plant, and at Oil Company.
4- Mn, Co, Ni, Pb, Cd and Cr are considered the main polluted metals in seawater of Tobruk bay.

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