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Water Quality Assessment and Bottom Sediment in the Coastal Area of the Three Refineries (Mina Al-Ahmadi, Mina Shuaiba and Mina Abdullah), Kuwait

Al-Qattan F., Al-Sarawi M.*

Department of Earth and Environmental Science, College of Science, Kuwait University, Safat, State of Kuwait
*Corresponding author: sarawi500@gmail.com

Abstract The three refineries (Mina Abdullah, Mina Ahmadi and Mina Shuaiba) plays a major role for the oil industries in Kuwait as one of the most important locations along the coast of Kuwait for its transportation of oil and its products composition, The three refineries decompose oil into many product such as Naphtha, Kerosene, High Speed Diesel (HSD), European Gas Oil (EGO), Marine Diesel Oil (MDO) and High Sulfur Fuel Oil (HSFO), these products can cause high pollution if they are in contact with water or sediments and may cause a large environmental impact. This study will focus on analyzing the geochemistry of sea water and bottom sediments. Five water and five sediment samples were collected in front of each refinery with a distance between each sample 200 m away. Physio-chemical parameters (Temperature, Salinity, Conductivity, pH, and Dissolved Oxygen), Inorganic nutrients (N-NH_3, N-NO_2, N-NO_3, P-PO_4, and Si-SiO_3). Total Suspended Solids, Total Petroleum Hydrocarbons and Trace Metals (Pb, V, Cu, Fe, and Ni) were measured in water samples. The Sediments were analyzed for TOC, TPH and trace metals contents. Several sources of pollutants were found alongside the three refineries. These sources were mostly from the refineries sites, ports, storm outlet, oil pipeline transportation, and commercial ships entering toward some refineries. The most amount of pollution was discovered in Mina Abdullah refinery.

Keywords: *refineries, pollutants, trace metals, hydrocarbons, bottom sediments, water quality*

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1. Introduction

Kuwait is located in the northern part of the Arabian Peninsula between latitudes 28°30' and 30°08' north and longitudes 45°30' and 48°30' east. It is bordered by Iraq to the north and west, Saudi Arabia to the south and the Arabian Gulf to the East with a total length of shoreline of 500 km. It covers an area of 17,818 km^2. Kuwait is well known by its significant long, dry and very hot summer with high temperature that varies between 30°C to 45°C reaching a maximum of 54°C. Kuwait winter is a short period, mostly cold and moderately wet. The temperature in winter varies between 7°C to 17°C. Rainfall is low and limited, the total rainfall is less than 125 mm/year. Winds are bidirectional with a primary mode from the NW and a secondary mode from the SE.

1.1. Kuwait Coastal Zone Characteristics

The coast of Kuwait is featured by sandy beaches and mud flats surrounded by a set of fixed and active sand dunes, coastal plains, small bays and tongues extended from the sea into the land which are called inlets (locally known as Khors). Salt marshes are found along the northern and southern coasts due to the gentle slope and the dominant ebb tide phenomena. The Kuwait Bay and the Arabian Gulf distinguish the coast of Kuwait. Kuwait bay is a flooded inlet from the Arabian Gulf heading to the west with an entrance bounded by Ras Al-Subiya in the north and Ras Al-Ardh in the south . The southern coast line undulates forming a number of branched inlets that are separated by headlands such as Ras Ushairej and Ras Kadhma. The coastline is being straight at south of Ras Al-Ardh except some prominent tips such as Ras Az-Zour and Ras Al-Jailaiah.

1.2. Aim and Objectives

The aim of this research is to evaluate the level of pollution at the bottom sediment and water quality in the coastal area for the three refineries in the State of Kuwait (Mina Al-Ahmadi, Mina Shuiaba and Mina Abdullah), to determine the impact of the sources and non-sources pollution on the marine environment, to assess the physical and chemical pollution level and to determine the zones which are highly polluted (Figure 1).

Figure 1. Location map for sampling along the three refineries

The main objectives of this study are:

1. To evaluate the level of pollution in the three refineries coastal area.
2. To investigate the physiochemical qualities of the water and bottom sediment near the three refineries.
3. To compare the extent of pollution between the three refineries and the offshore area.

This will be achieved through:

1) Measuring the oceanographic (physical) parameters (temperature, pH, salinity, and conductivity, total suspended solid and dissolved oxygen) of water. Determining the level of total petroleum hydrocarbons, nutrients, trace metals and total suspended solids in water.
2) Determining the level of total petroleum hydrocarbons, total organic carbons, and trace metals in bottom sediment.
3) Comparing the level of pollution in the three refineries with previous records.

2. Literature Review

Some trace metals and polycyclic aromatic hydrocarbons (PAHs) were evaluated in water and particulate of the State of Kuwait [1, 2] and they found the southern cost is highly contaminated with hydrocarbons. The concentrations of trace metals in seawater, particulate matter, and polycyclic aromatic hydrocarbons were determined in order to assess the environmental consequence of the massive oil spill off Kuwait Coast during the Iraqi invasion [3]. The mean concentration ranges of trace metals Cu, Cr, Mn, Ni, Pb Cd, Zn, and V in particulate matter were (14.13-52.64), (45.6-19.7), (53.2-247.2), (28.96), (140.5), (5.11-24.61), (1.34-78.76), (41.97-189.5), (38.58-101.4) µg/g, respectively. The mean concentration of PAH's ranged from 21.14 to 320.5 µg/L. An oil spill environmental sensitivity index (ESI) was developed for the coastal environments of Kuwait as an aid to oil spill contingency planning and response efforts [4,5] studied the bottom sediment at the Kuwait costal area and also found high amount of trace metals such as Cu, Mn, and Zn. Several studies were implemented at Sulibikat Bay in Kuwait Bay for bottom sediment and most of the findings are confirming the presence of heavy metals and hydrocarbons [6]. The rapid expansion of petrochemical industry has led to a variety of contaminants which includes polycyclic aromatic hydrocarbons (PAHs) and trace metals [7]. Analysis of 30 years' water quality data in Kuwait Bay determined significant increase for dissolve nutrients over the time period. The high sewage content of the costal water from sewage discharges likely favoring the presence of smaller phytoplankton taxa [8,9]. Hot spots of contamination were identified for PAHs, PCBs and PBDES, that were mainly associated with the Shuaiba Industrial Area, located south of the city and known to contain a diverse mix of both light and heavy industry [10]. A study by [11] in, Dubai Creek showed higher levels of ammonia (8.22 times), nitrite (10.93 times), nitrate (5.85 times), phosphate (10.64 times), silicate (1.60 times), total phosphorus (3.19 times), and total silicon (1.54 times) and it was due to domestic sewage waters. A study was carried out on the mud size fraction sediments of Saudi Arabia in order to determine the total metal content in the bulk sediments [12,13,14] and most of the findings showed high amount of trace metals. [15] showed that total organic carbon (TOC) content in the Gulf sediments vary between 0.46 and 2.8%, and exceeding the Gulf natural background level (average 0.7% ±0.3). [16,17] studied the trace metals in the Gulf sediments and reported high amount of trace metals. In New Zealand, Evaluation of heavy metals improvement elements and the level of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand Eight sediments cores recouped from Tamaki Estuary were examined for Cu, Pb, Zn, and Cd utilizing downward-cored sub-samples. The outcomes show a huge upward enhancement in heavy metals with the most astounding fixations found in the highest 0–10 cm layer. [20].

3. Material and Methods

A total of thirty of water and bottom sediment samples were collected from fifteen stations (Figure 1) covering the marine environment of the three refineries (Mina Al-Ahmadi, Mina Shuiaba and Mina Abdullah).

Concentrations of trace metals were measured by the EPA 3050B method using instrument Perkin-Elmer-A Analyst 700. All equipment used for sample preparation and analysis were soaked in 0.1 M nitric acid for 24 h and then rinsed several times with Milli-Q deionised water (18.2 MΩ.cm @ 25°C) prior to use. About 0.1 g of dried sediment samples were digested with HNO_3–HCl–H_2O_2 mixture according to method developed previously in our laboratory (EPA 3050B Method). All other chemical analysis was performed according to Ropme manual [19]. In each station five water samples were collected to determine:

- Physical-chemical parameter such as (temperature, salinity, PH and dissolved oxygen (DO) of seawater),
- Level of nutrients (PO_4), (NH_3), (NO_3), (NO_2) and (SiO_2)
- Total suspended solids (TSS),
- Trace metals and total petroleum hydrocarbons (TPH's), and total organic carbon (TOC).

4. Results

The three refineries (Mina Abdullah, Mina Ahmadi and Mina Shuaiba) plays a major role for the oil industries in Kuwait as one of the most important locations along the coast of Kuwait for its transportation of oil and its hydrocarbon products , the three refineries decompose oil into many product such as Naphtha, Kerosene, High Speed Diesel (HSD), European Gas Oil (EGO), Marine Diesel Oil (MDO) and High Sulfur Fuel Oil (HSFO), these products can cause high pollution if they are in contact with water or sediments.

This study focuses on evaluating the level of pollution within the three refineries by several chemical and physico-chemical analyses for water quality parameter and bottom sediments samples. All analysis were following [18].

4.1a. Mina Ahmadi Refinery

Mina Al-Ahmadi Refinery is located in the South of Kuwait 45 km away from Kuwait city on the Arabian Gulf and it has a total area of 10,534,000 m^2 (Fig. 2). In 1949, Mina Al-Ahmadi refinery was constructed as a small refinery with a capacity not exceeding 25,000 bpd to refine but at present it is able to refine 460,000 bpd to supply Kuwait with gasoline, kerosene and diesel.

4.1b. Physio-Chemical Parameters (Water Samples)

In Mina Al-Ahmadi (MAH) refinery we evaluated the physical properties in 5 water samples collected in 5 stations shown in (Figure 2). It is found that MAH-5 station had the highest peak of salinity with 37 (ug/L), and an average DO (0.3 mg/L) in all stations, with an average PH (8.2) ranging from 8.3 to 8.2. The temperature had a small variation with 1 degree Celsius as it shown in (Figure 3). The conductivity of the study area MAH increased from station MAH-1 to station MAH-5. (791, 785, 769, 810 and 856 respectively).

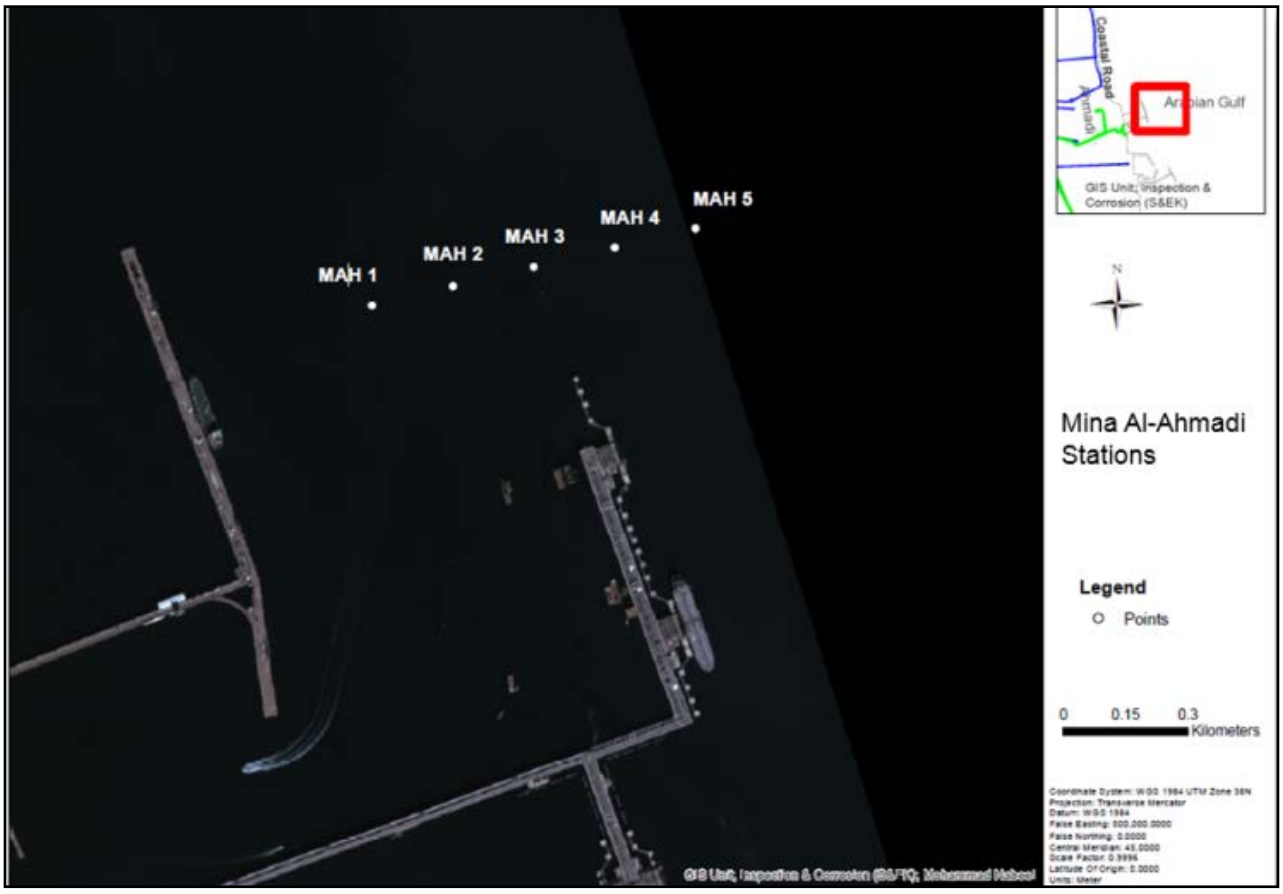

Figure 2. Location for Mina Al - Ahmadi sampling sites

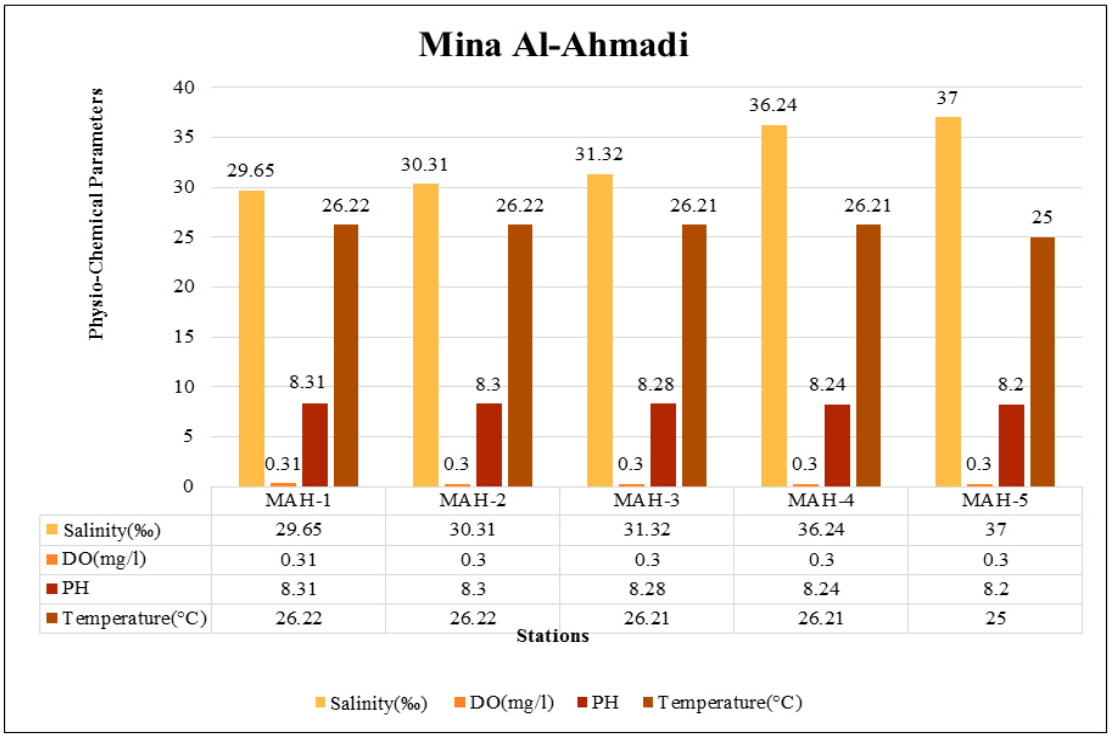

Figure 3. Physio-chemical parameters in MAH stations

Table 1. Nutrient parameters in Ahmadi refinery.

Stations	NH_3	NO_2	NO_3	PO_4	SiO_3	TSS	TOC	TPH
MAH 1	0.03	0.001	0.02	< DL	0.52	29	10323	290
MAH 2	0.04	0.001	0.01	< DL	0.43	16	28542	370
MAH3	0.04	0.002	0.01	< DL	0.38	7.0	69362	680
MAH4	0.05	0.003	0.01	< DL	0.36	7.0	15675	150
MAH5	0.07	0.003	0.01	< DL	0.30	7.0	57878	490
AVG.	**0.046**	**0.002**	**0.012**	**<DL**	**0.398**	**13.2**	**36356**	**396**

4.1c. Inorganic Nutrients

Ammonia (N-NH3):

In station, MAH-5 had the highest peak with 0.0756 (mg/L), whereas MAH-1 had the lowest concentration with 0.0305 (mg/L) shown in Table 1. According to data results Ammonia concentration is increasing toward station MAH-5

Nitrite (N-NO2):

Nitrite analysis showed that MAH-1 had lower detection than other stations, whereas station MAH-5 had the highest concentration with 0.00311 (mg/L), the values are decreasing towards station MAH-1as shown in Table 1.

Nitrate (N-NO3):

Nitrate concentration was constant in stations MAH-5 to MAH-2 with 0.01 (mg/L), where MAH-1 had the highest with 0.02 (mg/L) shown in Table 1,

Phosphate (P-PO4):

Phosphate was below the detection limit in MAH stations (from MAH-1 to MAH-5) as shown in Table 1.

Silicates (Si-Si03):

Station MAH-1 had the highest concentration with 0.52 (mg/L), whereas station MAH-5 had the lowest with 0.3 (mg/L), Si-Si03 is increasing towards station MAH-1 as shown in Table 1.

4.1d. Total Suspended Solids (TSS)

According to the Total Suspended Solids (TSS) analysis, MAH-1 had the most with concentration of 29 (mg/L). Station MAH-2 had the second most TSS with 16 (mg/L) as shown in Table 1.

4.1e. Total Organic Carbon (TOC) (Water and Sediments Samples)

The Highest station with TOC (sediment samples) was MAH-3 with 13872 ± 1318 (µg/g), Station MAH-1 was Low of detection whereas the TOC variations was depending on the stations bottom sediments MAH-3 was softer and more darker in color, Station MAH-4 and MAH-2 coarser and lighter in color.

Station MAH-1 had the highest concentration of (TOC) with 2.419% whereas stations MAH-5 and MAH-4 had the lowest with 1.763% shown in Table 1.

As per Total petroleum hydrocarbons (TPH) for the bottom sediments samples results are showed in Table 1. Station MAH-3 had the highest concentration of TPH with 680 (mg/kg), whereas station MAH-4 had the lowest with 150 (mg/kg).

4.1f. Trace Metals (T.M) (Water and Sediments Samples)

Trace metals analysis revealed a variety of elements shown in (Table 2.) Cu, Fe, Pb, Ni, and V measurements were taken for water samples from the five stations in Mina Al-Ahmadi refinery Table 2.

Table 2. Metal Analysis results for MAH Stations (Water samples).mg/L

Metal Analysis for MAH Stations						
#	1	2	3	4	5	Lower Detection Limit
Sample ID	**MAH-1**	**MAH-2**	**MAH-3**	**MAH-4**	**MAH-5**	
Silver	0.021	0.023	0.022	0.021	0.019	**0.01**
Aluminum	<DL	<DL	<DL	<DL	<DL	**1**
Arsenic	0.03	0.021	0.025	0.021	0.02	**0.01**
Barium	0.004	0.003	0.003	0.002	<DL	**0.01**
Beryllium	0.007	0.007	0.006	0.007	0.005	**0.01**
Calcium	427.8	411.3	416.7	424	415.3	**1**
Cadmium	0.008	0.008	0.009	0.008	0.005	**0.01**
Cobalt	0.003	0.003	0.003	<DL	<DL	**0.01**
Chromium	0.005	0.006	0.002	0.004	0.004	**0.01**
Copper	0.008	0.006	0.009	0.005	0.001	**0.01**
Iron	<DL	<DL	<DL	<DL	<DL	**1**
Potassium	566.5	550.3	548.9	559.1	553	**1**
Magnesium	1537	1776	1691	1542	1654	**1**
Manganese	0.012	0..012	0.012	0.013	0.011	**0.01**
Sodium	15230	15000	15024	14990	15090	**1**
Nickel	0.003	0.004	0.003	0.006	0.005	**0.01**
Lead	0.009	0.009	0.007	0.009	0.006	**0.01**
Antimony	0.013	0.005	0.011	0.012	0.006	**0.01**
Selenium	1.12	1.881	1.514	1.7	1.366	**0.01**
Thallium	0.404	0.489	0.398	0.401	0.388	**0.01**
Vanadium	0.002	0.003	<DL	<DL	<DL	**0.01**
Zinc	0.01	0.01	0.01	0.012	0.01	**0.01**

Table 3. Trace Metal Analysis results for MAH Stations (Sediments samples)

#	1	2	3	4	5	Lower Detection Limit
Sample ID	**MAH-1**	**MAH-2**	**MAH-3**	**MAH-4**	**MAH-5**	
Cadmium	0.40	0.90	2.40	0.90	2.60	**0.01**
Chromium	3.70	17.50	70.60	13.80	76.80	**0.01**
Copper	1.70	9.30	30.60	9.60	31.20	**0.01**
Iron	728.00	4668.00	17930.00	4729.00	20660.00	**1**
Nickel	1.20	18.50	84.30	14.30	94.00	**0.01**
Lead	4.90	3.80	7.40	3.50	6.50	**0.01**
Vanadium	4.10	14.90	49.30	13.20	50.40	**0.01**
Zinc	3.60	21.70	70.00	14.80	73.00	**0.01**
Mercury Mg/l	0.345	0.340	0.338	0.324	0.198	**0.1**

The highest concentration of Copper (Cu) in station MAH-3 with 0.009 (mg/L), with an average Lead (Pb) ranging from 0.006 (mg/L) to 0.009 (mg/L), iron (Fe) was below the detection limit, nickel (Ni) was average ranging from 0.003 (mg/L) to 0.006 (mg/L) which was in station MAH-4, Vanadium appeared in stations MAH-1 and MAH-2 with 0.002 (mg/L) and 00.3 (mg/L) respectively.

Trace metals results in the bottom sediments samples showed results above the stander limits shown in Table 3.

Stations MAH-3 and MAH-5 had the highest Copper (Cu) with 30.60 (mg/kg) and 31.20 (mg/kg) respectively. Iron (Fe) highest concentration was in station MAH-5 20660.00 (mg/kg) whereas the lowest was in station MAH-1, Nickel (Ni) highest amount was in station MAH-5 with 94.00 (mg/kg) the lowest was in station MAH-1 with 1.20 (mg/kg). Lead (Pb) largest peak was in station MAH-3 with 7.40 (mg/kg) and the lowest peak was in Station MAH-4 with 3.50 (mg/kg).Vanadium (V) highest concentration appeared in station MAH-5 with 50.40 (mg/kg) and the lowest concentration in station MAH-1 with 4.10 (mg/kg). Other trace metals where included such as Zinc (Zn) were the highest amount showed in station MAH-5 with 73.00 (mg/kg) whereas the lowest was in station MAH-1 with 3.60 (mg/kg), Chromium (Cr) showed that station MAH-5 had the highest concentration with 76.80 (mg/kg) and Station MAH-1 had the lowest with 3.70 (mg/kg). The Cadmium appeared in the analysis with the highest in station MAH-5 with 2.60 (mg/kg) and

lowest in station MAH-1 with 0.40 (mg/kg).Mercury is relatively high and ranging between 0.345 and 0.198 mg/l.

4.2a. Mina Shuiaba (MSH)

Mina Shuiaba refinery is viewed as the first world hydrogen refinery that fully uses hydrogen gas in process units and capable of taking care of generally high Sulphur crude oil. The hydrogen gas assumes a huge part in reducing and removing sulphur and nitrogen from products and upgrading the quality of the products to meet the required international product specifications. The refinery is situated 50 km south the city of Kuwait and possesses an area of 1,332,000 m^2 shown in (Figure 1).

Kuwait national petroleum company built the refinery in 1966 and it considered the first refinery in the region. The initial Crude Oil limit of the refinery was 95,000 BPD and now the refinery is operating at a limit of 200,000 BPD.

4.2b. Physio-Chemical Parameters (Water Samples)

Five water samples have been gathered from five stations in Mina Shuiaba refinery (Figure 4), to assess the physical-chemical properties.

Figure 4. Mina Shuiaba sampling stations profile

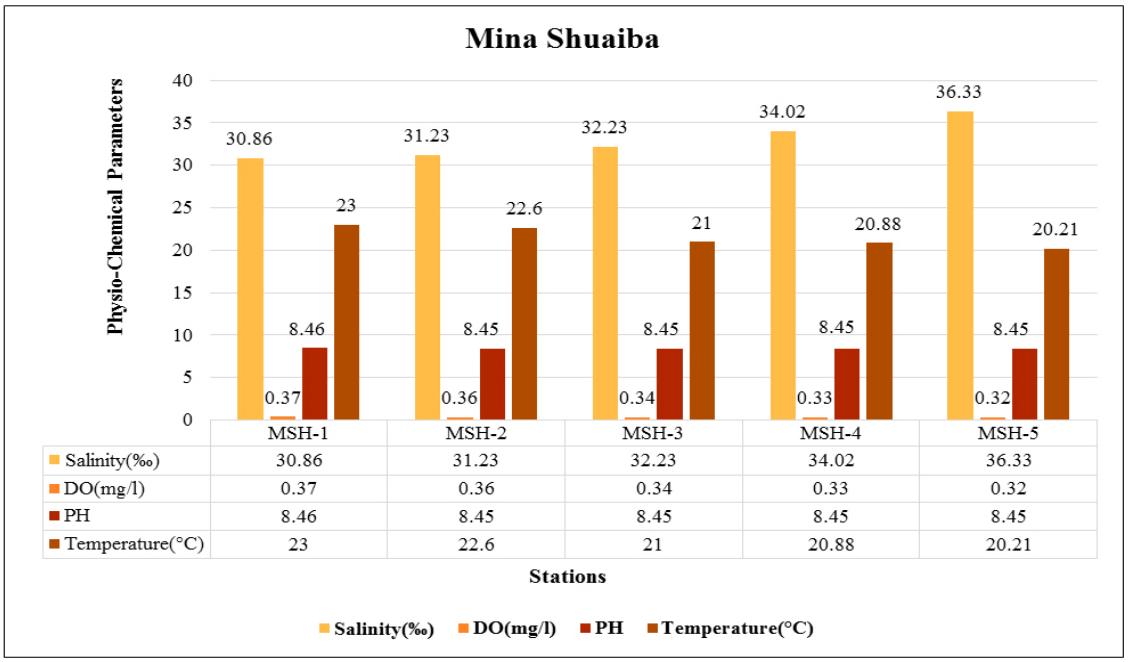

Figure 5. Physio-chemical parameters in MSH stations

Salinity concentration was recorded in station MSH-1 with 30.86 mg\L while the top peak was recorded in MSH-5 station with 36.33 (mg\L) (Figure 5). The dissolved oxygen (DO) was average from MSH-1 station to MSH-5 station. The PH (hydrogen exponent) reached its highest peak in MSH-1 and from MSH-2 until MSH-5, the PH remains constant. The temperature dropped from MSH-1 station to MSH-5 station by 2.8 degree Celsius. Conductivity in Mina Shuiaba Refinery stations was increasing from MSH-1 (769) and reaches its highest in MSH-5 (890).

4.2c. Inorganic Nutrients:

Nitrite (N-NO2):

Station MSH-5 had the highest concentration with 0.0912 (mg/L), where the lowest concentration obtained in station MSH-1 and MSH-2 with 0.088 (mg/L) which is shown in Table 4.

Nitrate (N-NO3):

Nitrate concentration was constant in stations MSH-3, MSH-4 and MSH-5 with 0.01 (mg/L) for all, where MSH-1and MSH-2 had the highest with 0.02 (mg/l) as shown in Table 4

Phosphate (P-PO4):

Phosphate was limited deducted in MSH stations from MAH-1 to MAH-5 as shown in Table 4.

Silicates (Si-Si03):

Station MSH-1 had the highest peak with 0.42 (mg/L), whereas station MSH-5 had the lowest with 0.27 (mg/L), Si-Si03 is increasing towards station MSH-1as shown in Table 4.

4.2d. Total Suspended Solids (TSS)

According to the Total Suspended Solids (TSS) analysis all stations MSH from station MSH-1 to MSH-5 had a standard amount with 5 (mg/L) as it shown in Table 4.

4.2e. Total Petroleum Hydrocarbons (TPH) (Water and Sediments Samples)

Total petroleum hydrocarbons (TPH) was below the detection limit in all MSH stations (water samples), the limit of detection (LOD) is 0.175 (µg/L) and the limit of quantitation (LOQ) is 0.35 (µg/L) shown in Table 4. For the guidelines for pollution level of TPH [2].

4.2f. Total Suspended Solids (TSS)

According to the Total Suspended Solids (TSS) analysis all stations MSH from station MSH-1 to MSH-5 had a standard amount with 5 (mg/L) as it shown in Table 4.

4.2g. Total Petroleum Hydrocarbons (TPH) (Water and Sediments Samples)

Total petroleum hydrocarbons TPH was low of detection in all MSH stations (water samples), the limit of detection (LOD) is 0.175 (µg/L) and the limit of quantitation (LOQ) is 0.35 (µg/L) shown in Table 4. For the guidelines for pollution level of TPH [2].

4.2h. Total Organic Carbon (TOC) (Water and Sediments Samples)

The concentration station with TOC (sediment samples) (Table 4) was in station MSH-4 with 51095 ±636 (µg/g), station MSH-2 was the lowest with 10120 ±108 (µg/g), whereas the TOC variations was related on the stations bottom sediments MSH-4 was softer and more darker in color .The Total Organic Carbon (TOC) (water samples) results are shown in Table 4.

All stations were close in percentage; station MSH-1 had the highest concentration of (TOC) with 1.796% whereas stations MSH-5 had the lowest with 1.763% as shown in Table 4.

4.2i. Trace Metals (T.M) (Water and Sediments Samples)

Trace metals analysis announced a variety of elements shown in Table 5. Cu, Fe, Pb, Ni, and V measurements were taken for water samples from the five stations in Mina Al-Shuiaba refinery.

The highest concentration of Copper (Cu) in station MSH-1 with 0.006 (mg/L), Lead (Pb) highest concentration was in station MSH-5 with 0.05 (mg/L) whereas the lowest was in station MSH-4 with 0.004 (mg/L), nickel (Ni) was average ranging from 0.004 (mg/L) to 0.006 (mg/L), Vanadium appeared in all stations with 0.002 (mg/L) in MSH-1, 0.003 (mg/L) in MSH-2 ,0.003 (mg/L) in MSH-3, 0.001 (mg/L) in MSH-4 ,0.001 (mg/L) in MSH-5.

Trace metals results in the bottom sediments samples showed high concentration in some metals as shown in Table 6.

Copper (Cu) highest concentration was found in station MSH-4 with 24.00 (mg/kg). Iron (Fe) largest amount was in station MSH-4 with 14540.00 (mg/kg), whereas the lowest was in station MSH-1, Nickel (Ni) highest concentration was in station MSH-4 with 69.70 (mg/kg) the lowest was in station MSH-1 with 3.40 (mg/kg). Lead (Pb) highest amount was in station MSH-4 with 5.60 (mg/kg) and the lowest was in Station MSH-1 with 1.00 (mg/kg).Vanadium (V) highest peak appeared in station MSH-4 with 42.70 (mg/kg) and the lowest concentration in station MSH-2 with 5.30 (mg/kg). Other trace metals where included such as Zinc (Zn) were the highest amount showed in station MSH-4 with 59.60 (mg/kg) whereas the lowest was in station MSH-1 with 5.40 (mg/kg). Chromium (Cr) showed that station MSH-4 had the highest amount with 58.60 (mg/kg) and station MSH-2 had the lowest with 5.10 (mg/kg). The Cadmium revealed in the results with the highest in station MSH-4 with 2.10 (mg/kg) and lowest in stations MSH-1 and MSH-2 with 0.50 (mg/kg) and 0.50 respectively.

Table 4. Nutrients sampling in Al Shuaiba refinery

Stations	NH_3	NO_2	NO_3	PO_4	SiO_3	TSS	TOC	TPH
MSH 1	0.03	0.003	0.02	< DL	0.42	5.0	12513	200
MSH 2	0.03	0.003	0.02	< DL	0.39	5.O	10120	180
MSH3	0.03	0.003	0.01	< DL	0.34	4.5	12798	170
MSH4	0.01	0.003	0.01	< DL	0.30	5.3	51095	510
MSH5	0.01	0.001	0.01	< DL	0.27	5.4	30880	400
AVG.	**0.002**	**0.0026**	**0.014**	**<DL**	**0.344**	**5.04**	**2348.12**	**292**

Table 5. Trace metal analysis results for MSH Stations (water samples)mg/l

Metal Analysis for MSH Stations						
#	1	2	3	4	5	Lower Detection Limit
Sample ID	**MSH-1**	**MSH-2**	**MSH-3**	**MSH-4**	**MSH-5**	
Silver	0.026	0.024	0.026	0.022	0.022	**0.01**
Aluminum	<DL	<DL	<DL	<DL	<DL	**1**
Arsenic	0.021	0.019	0.018	0.02	0.017	**0.01**
Barium	<DL	<DL	<DL	<DL	<DL	**0.01**
Beryllium	0.005	0.004	0.0019	0.005	0.03	**0.01**
Calcium	1915	1890	1900	1875	1900	**1**
Cadmium	0.009	0.006	0.006	0.009	0.008	**0.01**
Cobalt	0.004	0.004	0.004	0.006	0.003	**0.01**
Chromium	0.004	0.005	0.006	0.003	0.004	**0.01**
Copper	0.006	0.005	0.003	0.001	0.002	**0.01**
Iron	<DL	<DL	<DL	<DL	<DL	**1**
Potassium	186.7	179.8	168.2	172.5	176	**1**
Magnesium	1955	1820	1945	1790	1800	**1**
Manganese	0.012	0.011	0.009	0.009	0.011	**0.01**
Sodium	16070	16020	16040	16000	15090	**1**
Nickel	0.006	0.004	0.006	0.005	0.005	**0.01**
Lead	0.005	0.006	0.007	0.004	0.05	**0.01**
Antimony	0.01	0.007	<DL	<DL	0.01	**0.01**
Selenium	0.001	0.001	<DL	<DL	<DL	**0.01**
Thallium	0.001	0.002	0.002	0.01	<DL	**0.01**
Vanadium	0.002	0.003	0.003	0.001	0.001	**0.01**
Zinc	0.007	0.008	0.005	0.004	0.006	**0.01**

Table 6. Trace metal analysis results for MSH stations (sediments samples) mg/kg

#	1	2	3	4	5	Lower Detection Limit
Sample ID	**MSH-1**	**MSH-2**	**MSH-3**	**MSH-4**	**MSH-5**	
Cadmium	0.50	0.50	0.60	2.10	1.30	**0.01**
Chromium	5.20	5.10	8.40	58.60	27.30	**0.01**
Copper	3.10	3.00	4.20	24.00	11.90	**0.01**
Iron	1042.00	1256.00	2359.00	14540.00	8264.00	**1**
Nickel	3.50	3.40	7.00	69.70	32.20	**0.01**
Lead	1.00	1.70	2.10	5.60	4.10	**0.01**
Vanadium	5.90	5.30	9.10	42.70	20.60	**0.01**
Zinc	5.40	6.50	8.70	59.60	25.80	**0.01**
Mercury (mg/L)	0.345	0.225	0.435	0.271	0.612	**0.1**

Figure 6. Mina Abdulla sampling stations profile

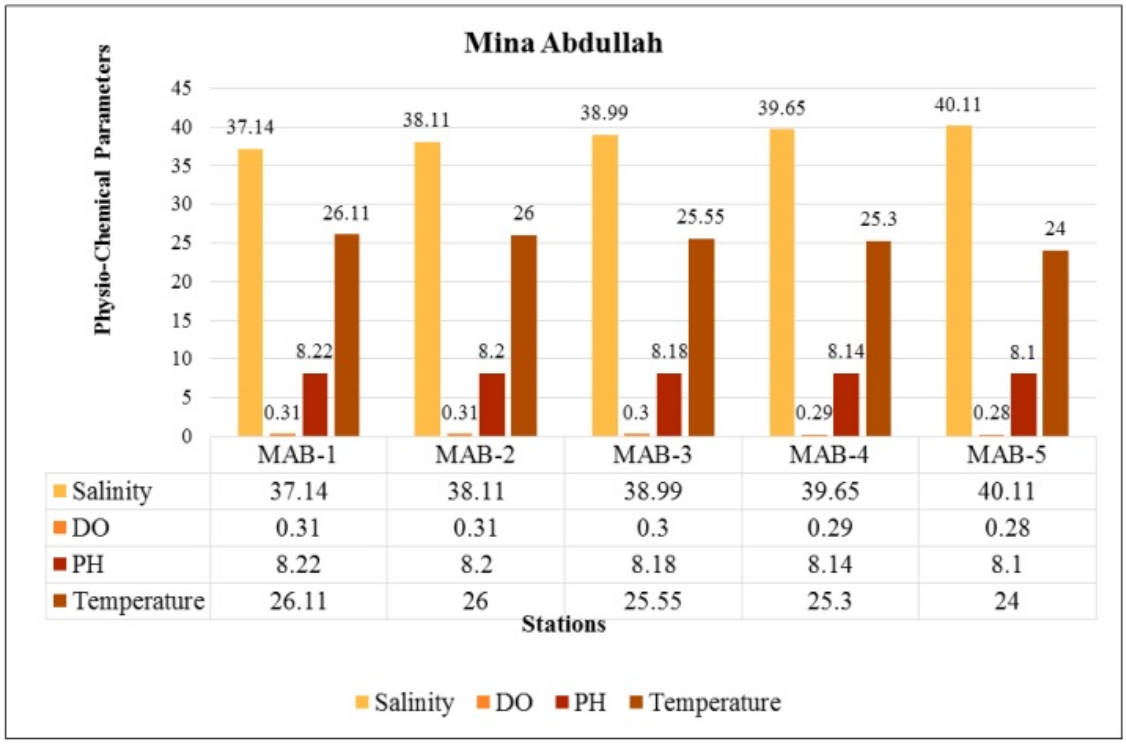

Figure 7. Physio-chemical parameters in MAB stations

4.2j. Mercury (Hg) (Water and Sediments Samples)

Mercury (Hg) in the sediment samples results are shown in Table 6. Where station MSH-5 had the highest peak of mercury with 0.612 (mg/L), and the lowest was in station MSH-2 with 0.225 (mg/L).

4.3a. Mina Abdullah Refinery (MAB)

Mina Abdullah is located in the southern part of Kuwait with an area of 7,935,000 m^2 (Figure 1). In 1958, the American Independent Oil Company "AMINOIL" constructed Mina Abdullah refinery, and it increased its capacity from 30,000 bpd to 145,000 bpd approximately.

4.3b. Physio-Chemical Parameters (Water Samples)

Five water samples have been collected in five stations in Mina Abdullah (Figure 6), to evaluate the physical and chemical properties. According to the Physio-Chemical Parameters shown in (Figure 7), the lowest peak of salinity concentration was recorded in MAB-1 with 37.14 (mg\L) while the highest peak was recorded in station MAB-5 with 40.11 (mg\L).

The dissolved oxygen DO was decreasing from station MAB-1 to MAB-5 and the PH (hydrogen exponent) ranging from 8.22 to 8.1.The temperature drops from MAB-1 station to MAB-5 station by 2.1 degree Celsius (Figure 7).

4.3c. Inorganic Nutrients

Ammonia ($N\text{-}NH_3$):

Table 7, shows that in Mina Abdullah stations, ammonia concentration was increasing from MAB-1 station 0.0321 (mg\L) and reached its highest peak in MAB-5 station 0.09 (mg\L). However, MAB-2, MAB-3, and MAB-4 stations were sharing the same ammonia concentration 0.089 (mg\L). The average ammonia concentration in Mina Abdullah stations is 0.0778 (mg\L).

Table 7. Nutrients in Mina Abdullah refinery

Stations	NH_3	NO_2	NO_3	PO_4	SiO_3	TSS	TOC	TPH
MAB 1	0.03	0.004	0.06	< DL	0.43	4.0	14042	190
MAB 2	0.08	0.004	0.02	< DL	0.43	4.0	12020	190
MAB3	0.09	0.003	0.02	< DL	0.40	4.5	20713	180
MAB4	0.09	0.003	0.01	< DL	0.38	5.0	22012	290
MAB5	0.09	0.003	0.01	< DL	0.34	5.0	18337	190

Nitrite ($N\text{-}NO_2$):

Nitrite concentration highest peak is in station MAB-1 with 0.0048 (mg\L) the lowest peak in station MAB-5 with 0.003 (mg\L). Table 7, the average Nitrite concentration in Mina Abdullah stations is 0.0039 (mg\L).

Phosphate ($P\text{-}PO_4$)

Phosphate was below the detection limit in all MSH stations from MAH-1 to MAH-5 shown in Table 7.

Silicates ($Si\text{-}Si0_3$):

Silicates concentration varies between all five stations Table 7. MAB-1 and MAB-2 stations had the highest concentration peak with 0.43 (mg\L) while MAB-5 station had the lowest concentration peak with 0.34 (mg\L). According to Table 7, silicates concentration is decreasing towards MAB-5 station with an average concentration of 0.396 (mg\L).

4.3d. Total Suspended Solids (TSS)

Total Suspended solids (TSS) analysis shows that both MAB-1 and MAB-2 stations had the same TSS value of 5.0 (mg\L) and then the TSS dropped by 1.0 (mg\L) to reach 4.0 (mg\L) for MAB-3, MAB-4, and MAB-5 stations Table 7.

4.3e. Total Petroleum Hydrocarbons (TPH) (Water and Sediments Samples)

Total petroleum hydrocarbons (TPH) was below the detection limit in all Mina Abdullah (MAB) stations

(water samples), the limit of detection (LOD) is 0.175 (µg/L) and the limit of quantitation (LOQ) is 0.35 (µg/L).

Bottom sediments samples for total petroleum hydrocarbons (TPH) results are shown in Table 7. Station MAB-4 had the highest amount of TPH with 290 (mg/kg), whereas station MAB-3 had the lowest with 180 (mg/kg).

4.3f. Trace Metals (T.M) (Water and Sediments Samples)

Trace metals analysis revealed a variety of elements shown in Table 8. Cu, Fe, Pb, Ni, and V measurements were taken for water samples from the five stations in Mina Al-Abdullah refinery.

The highest amount of Copper (Cu) is in station MAB-1 with 2.598 (mg/L) and the lowest was in station MAB-2 with 0.424 (mg/L), Lead (Pb) highest concentration was in station MAB-1 with 2.244 (mg/L) whereas the lowest was in station MAB-4 with 0.656 (mg/L), iron (Fe) was below the detection limit in all stations, nickel (Ni) highest peak was in station MAB-1 with 2.026 (mg/L).Vanadium highest concentration was in station MAB-1 with 1.474 (mg/L) and the lowest was station MAB-2 with 0.123 (mg/L).

Copper (Cu) highest amount was in station MAB-5 with 7.30 (mg/kg). Iron (Fe) highest peak was in station MAB-5 with 4915.00 (mg/kg), whereas the lowest was in station MAB-1 with 1053.00 (mg/kg), Nickel (Ni) highest concentration was in station MAB-5 with 20.50 (mg/kg) the lowest was in station MAB-1 with 5.20 (mg/kg). Lead (Pb) highest amount was in station MAB-5 with 1.70 (mg/kg) and the lowest was in station MAB-1 with 0.40 (mg/kg).Vanadium (V) highest peak appeared in station MAB-5 with 14.20 (mg/kg) and the lowest concentration in station MAB-2 with 3.20 (mg/kg). Other trace metals where included such as Zinc (Zn) were the highest concentration was in station MAB-5 with 15.50 (mg/kg) whereas the lowest was in station MAB-2 with 2.10 (mg/kg). Chromium (Cr) showed that station MAB-5 had the highest amount with 18.20 (mg/kg) and station MAB-2 had the lowest with 3.20 (mg/kg). The Cadmium appeared in the results with its highest amount in station MAB-5 with 0.90 (mg/kg) and lowest in stations MAB-2 with 0.40 (mg/kg).

Table 8. Trace metal analysis results for MAB Stations (Water samples)

Metal Analysis for MSH Stations						
#	**1**	**2**	**3**	**4**	**5**	**Lower Detection Limit**
Sample ID	**MSH-1**	**MSH-2**	**MSH-3**	**MSH-4**	**MSH-5**	
Silver	0.315	2.977	1.516	1.92	0.7	**0.01**
Aluminum	<DL	<DL	<DL	<DL	<DL	**1**
Arsenic	3.917	1.042	3.45	2.95	1.082	**0.01**
Barium	<DL	<DL	<DL	<DL	<DL	**0.01**
Beryllium	3.739	0.543	2.469	1.364	0.512	**0.01**
Calcium	287.6	753.1	609.2	465	423	**1**
Cadmium	0.153	0.881	0.662	0.325	0.458	**0.01**
Cobalt	2.203	0.509	1.252	1.99	0.486	**0.01**
Chromium	0.351	0.166	0.321	0.25	0.421	**0.01**
Copper	2.598	0.424	2.369	1.278	1.233	**0.01**
Iron	<DL	<DL	<DL	<DL	<DL	**1**
Potassium	162.9	575.8	337	502.4	241.6	**1**
Magnesium	1852	1742	1780	1809	1813	**1**
Manganese	1.261	1.084	1.25	1.187	1.079	**0.01**
Sodium	14890	14960	15010	14800	14790	**1**
Nickel	2.026	0.442	1.025	1.362	1.044	**0.01**
Lead	2.244	0.656	1.258	1.669	1.199	**0.01**
Antimony	3.899	0.715	0.895	2.215	2.09	**0.01**
Selenium	1.057	1.147	1.059	1.127	0.991	**0.01**
Thallium	3.893	0.575	2.003	2.074	1.254	**0.01**
Vanadium	1.474	0.123	1.126	0.245	0.261	**0.01**
Zinc	0.044	0.359	0.124	0.087	0.236	**0.01**
Unit	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**

Table 9. Trace metal analysis results for MAB stations (Sediments samples).mg/kg.

#	1	2	3	4	5	Lower Detection Limit
Sample ID	**MAB-1**	**MAB-2**	**MAB-3**	**MAB-4**	**MAB-5**	
Cadmium	0.50	0.40	0.60	0.70	0.90	**0.01**
Chromium	7.60	3.20	8.80	11.70	18.20	**0.01**
Copper	4.30	1.30	4.70	5.40	7.30	**0.01**
Iron	1053.00	634.30	2129.00	3017.00	4915.00	**1**
Nickel	5.20	0.90	8.40	12.30	20.50	**0.01**
Lead	0.40	1.50	0.90	1.40	1.70	**0.01**
Vanadium	5.00	3.20	8.30	9.50	14.20	**0.01**
Zinc	4.70	2.10	7.80	11.50	15.50	**0.01**

4.3g. Total Organic Carbon (TOC) (Water and Sediments Samples)

The highest peak concentration station with TOC (sediment samples) was in MAB-4 with 22102± 1781 (µg/g), station MAB-1 was the lowest with 14042 ± 1485 (µg/g), whereas MAB-2 was below the detection limit.

All stations were close in percentage, except station MAB-1 which had the highest concentration of (TOC) with 1.978% whereas stations MAB-3 and MAB-4 had the lowest with 1.773% shown in Table 7.

4.3h. Mercury (Hg) (Water and Sediments Samples)

Mercury (Hg) in water samples are below the detection limits, while in sediment samples results are shown in (Figure 8). Where station MAB-5 had highest peak of mercury with 0.612 (mg/L), and the lowest was in station MSH-1 with 0.345 (mg/L). The lower detection limit is 0.2 ppb for the analysis.

5. Discussion

The coastal area and off shore of the three refineries showed high level of pollutions especially at the bottom sediments. The sources of pollutions were primarily from the refineries sites, ports, storm outlet, oil pipeline transportation, and commercial ships entering toward some refineries. The hydrodynamics play a major role in pollutants movement as surface water move from north to south. Average mean longshore current around 20-25cm/sec.

This study exposes the following:

5.1. Mina Abdullah Statement

Mina Abdullah refinery is highly contaminated with superior percentages of trace metals. Comparing to Table 10 (maximum limits of pollutants in industrial water waste permissible to be discharged into the seawater) issued by KEPA (Kuwait environment public authority). The measurement of trace metals in Mina Abdullah is exceeding the limits of pollutants. The percentage of Arsenic, Cadmium, Chromium, Copper, mercury, and Lead is higher than the limits range. However, the zinc percentage in all Mina Abdullah stations is lesser than the maximum limits of zinc percentages to be discharged into the seawater. Nutrients (Phosphate PO4, Ammonia NH_3-N and Nitrate NO_3) are in safe range and less than the permissible limits. Most of the pollutants move with the current from north to souths which mainly end at Mina Abdullah.

Mina Abdullah's results showed massive increase in the measurements of the trace metals in the refinery. The percentage of Arsenic in MAB is ranging from (1.042) mg\L in (MAB-2) up to (3.917) mg\L in (MAB-1) and is exceeding the maximum limits of arsenic in industrial water waste to be discharged into the seawater (0.1) mg\L. The percentage of Cadmium in all MAB stations is also exceeding the limits allowed to be discharged into the seawater. However, not all MAB stations have higher Chromium percentages, for example, in Station 2 (MAB-2), the percentage of chromium concentration is (1.66) mg\L is not exceeding the maximum limits of chromium to be discharged into the seawater which equivalents is (0.2) mg\L. Lead percentages in all MAB station is higher than the maximum lead limits, whereas MAB-2 is exceeding the limits by (0.15) mg/L. The Zinc percentage in MAB's stations is however less than the limits of the maximum zinc percentages to be discharged into seawater.

As a conclusion to this refinery, Mina Abdullah Refinery is considered to be contaminated with an extreme amount of trace metals greater than the maximum limits of pollutants in industrial waste water to be discharged into the seawater .

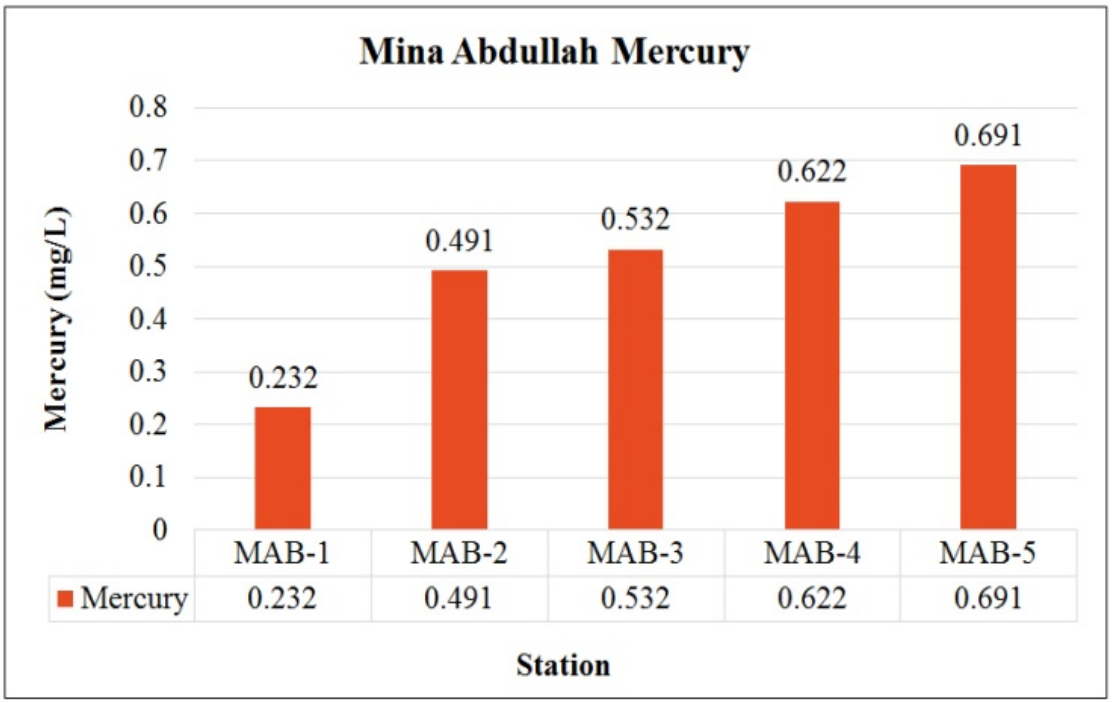

Figure 8. Mercury (Hg) (Sediment Samples) results in MAB

Table 10. KEPA Maximum limits of Pollutants in Industrial Water Waste Permissible to be discharged into the seawater

Pollutant	Symbol	Unit	Maximum Limit
Colour	-	-	clear
pH	pH	-	6-8
Temperature		°C	*10
Biological Oxygen Demand	BOD (5 days, 20 °C)	mg/L	30
Chemical Oxygen Demand	COD	mg/L	200
Oil / grease		mg/L	10
Total Suspended Solids	TSS	mg/L	10
Total Soluble Solids		mg/L	1500
Phosphate	PO_4	mg/L	2
Ammonia	NH_3-N	mg/L	3
Nitrate	NO_3	mg/L	30
Total Kaldal Nitrogen		mg/L	5
Total Nitrogen		mg/L	30
Total Recoverable Phenol		mg/L	1
Fluorides	F	mg/L	25
Sulfides	S	mg/L	0.5
Chlorine	Cl_2	mg/L	0.5
Dissolved Oxygen	DO	mg/L	>2
Turbidity		NTU	50
Floatables		mg/L	Nil
Aluminum	Al	mg/L	5
Arsenic	As	mg/L	0.1
Barium	Ba	mg/L	2
Boron	B	mg/L	0.75
Beryllium	Br	mg/L	0.1
Cadmium	Cd	mg/L	0.01
Cyanides	Cn	mg/L	0.1
Chromium	Cr	mg/L	0.2
Nickel	Ni	mg/L	0.2
Mercury	Hg	mg/L	0.001
Cobalt	Co	mg/L	0.2
Iron	Fe	mg/L	5
Antimony	Sb	mg/L	1.0
Copper	Cu	mg/L	0.2
Manganese	Mn	mg/L	0.2
Zinc	Zn	mg/L	2.0
Lead	Pb	mg/L	0.5
Lithium	Li	mg/L	2.5
Molybdenum	Mo	mg/L	0.01
Vanadium	V	mg/L	0.1
Silver	Ag	mg/L	0.1
All herbicides		mg/L	0.2

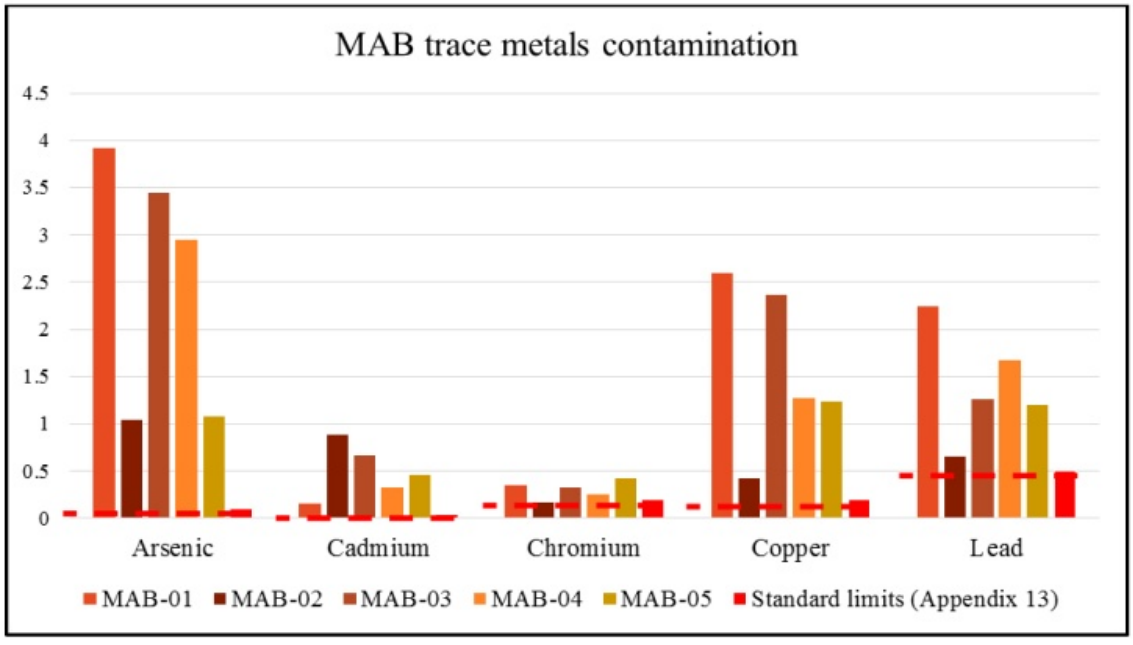

Figure 9. MAB trace metals contamination

5.2. Mina Ahmadi Statement

Contrasting Mina Abdullah refinery with Mina Ahmadi Refinery, the results were lower than the maximum limits of pollutants. Arsenic, Cadmium, Chromium, Copper, Lead, and Zinc percentages in all Mina Ahmadi stations and they were lower than the maximum limits of industrial waste water to be discharged into the seawater .

Mina Ahmadi's results showed steady amount of trace metal concentrations. The average percentage of Arsenic concentration in Mina Ahmadi is lower than the maximum limit of arsenic percentage by 0.0766 (mg/L). Moreover, the highest percentage of Cadmium concentration in MAH stations is lower than the maximum limit by (0.001) Mg/L. The percentage of Lead concentration is also lower than the maximum limits to be discharged into the seawater.

In general, Mina Ahmadi refinery contained a safe percentage of trace metals compared to Mina Abdullah refinery and to the maximum limits of pollutants in industrial waste water to be discharged into the sea (Table 11). Nutrients (Phosphate PO_4, Ammonia NH_3-N and Nitrate NO_3) are in safe range less than the permissible limits.

5.3. Mina Shuaiba Statement

Mina Shuaiba results were lower than the maximum limits of trace metals to be discharged into the seawater. For example, the average Arsenic 0.019 (mg/L), Cadmium 0.0076 (mg/L), Chromium 0.0044 (mg/L), Copper 0.0034 (mg/L), Lead 0.0144 (mg/L), and zinc 0.006 (mg/L) percentages in all stations were lower than the maximum limits of the same trace metals order, and unlike Mina Abdullah. Mina Shuaiba results have shown safe trace metal concentrations according to Table 11. As well, the maximum percentage of copper recorded in all MSH stations is lower than the maximum percentage of copper to be discharged. The total average of the comparable trace metals is lower than the maximum total average of metals to be discharged into the seawater. Nutrients (Phosphate PO_4, Ammonia NH_3-N and Nitrate NO_3) are in safe range less than the limits range. Mina Ahmadi refinery and Mina Shuaiba refinery both have recorded low safe trace metal percentages compared to Mina Abdullah refinery of. However, the average of Calcium and Magnesium concentration in Mina Shuaiba is higher than the other refineries. Both Mina Shuaiba and Mina Ahmadi share the same average concentration of Cadmium with 0.0076 (mg\L). The average Selenium concentration in Mina Ahmadi is higher than Mina Abdullah by 0.44 (mg\L).

According to the sediment samples for trace metals, the declaration is that Mina Abdullah refinery has two Cadmium hot spots of contamination which are MAB-4 and MAB-5 with 0.70 (ppm) , 0.90 (ppm) respectively and a Nickel hot spot at MAB-5 with 20.50 (ppm).

As per Mina Ahmadi refinery sediment samples showed four hot spots for the metal Cadmium at stations MAH-2, MAH-3, MAH-4 and MAH-5 with 0.90 (ppm), 2.40 (ppm), 0.90 (ppm) and 2.60 (ppm) in that order. Two contaminated stations from Chromium in MAH-3 with 70.60 (ppm) and MAH-5 with 76.80 (ppm). Copper is above the limit in stations MAH-3 with 30.60 (ppm) and station MAH-5 with 31.20 (ppm). Nickel concentration, is also above the limit with 84.30 (ppm) at MAH-3.

Mina Shuaiba refinery is no less than the previous refinery, Cadmium recorded high in stations MSH-4 with 2.10 (ppm) and MSH-5 with 1.30 (ppm). As per Chromium, stations MSH-4 and MSH-5 exceeded the limits with 58.60 (ppm) and 27.30 in order. Nickel percentage was over the limit at stations MSH-4 and MSH-5 with 69.70 (ppm) and 32.20 (ppm) respectively.

All stations in the three refineries (Table 12) were compared with the Ontario provincial sediment quality guidelines shown in Table 11.

Table 11. Ontario provincial sediment quality guidelines (ppm dry weight)

Trace metals	Lowest Effect level
Cadmium	0.6
Chromium	26
Copper	16
Iron	21200
Nickel	16
Lead	31
Vanadium	Not Available
Zinc	120

Table 12. All stations sediment samples with the amount of trace metals

Sample ID	Cadmium	Chromium	Copper	Iron	Nickel	Lead	Vanadium	Zinc
MAB-1	0.50	7.60	4.30	1053.00	5.20	0.40	5.00	4.70
MAB-2	0.40	3.20	1.30	634.30	0.90	1.50	3.20	2.10
MAB-3	0.60	8.80	4.70	2129.00	8.40	0.90	8.30	7.80
MAB-4	0.70	11.70	5.40	3017.00	12.30	1.40	9.50	11.50
MAB-5	0.90	18.20	7.30	4915.00	20.50	1.70	14.20	15.50
MAH-1	0.40	3.70	1.70	728.00	1.20	4.90	4.10	3.60
MAH-2	0.90	17.50	9.30	4668.00	18.50	3.80	14.90	21.70
MAH-3	2.40	70.60	30.60	17930.00	84.30	7.40	49.30	70.00
MAH-4	0.90	13.80	9.60	4729.00	14.30	3.50	13.20	14.80
MAH-5	2.60	76.80	31.20	20660.00	94.00	6.50	50.40	73.00
MSH-1	0.50	5.20	3.10	1042.00	3.50	1.00	5.90	5.40
MSH-2	0.50	5.10	3.00	1256.00	3.40	1.70	5.30	6.50
MSH-3	0.60	8.40	4.20	2359.00	7.00	2.10	9.10	8.70
MSH-4	2.10	58.60	24.00	14540.00	69.70	5.60	42.70	59.60
MSH-5	1.30	27.30	11.90	8264.00	32.20	4.10	20.60	25.80
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm

6. Conclusions

From the chemical analysis for the three refineries it was found that the most polluted refinery is Mina Ahmadi for both water quality and bottom sediment. The concentration of trace metals decreases in the following sequences: Ni > Cr > Zn >Vi > Cu > Pb > Cd. The average concentration of Ni, Cr and Zn in all locations is 23.16 ug/g .It can be concluded that Ni is highest in all location at average 25.02 ug/g. In contrast of Cd was the least in all location at average of 1.02 ug/g. There are several uncontrolled out lets which they need special attentions and continuous control. The main sources are industrial effluents and municipal sewage from urban system.

7. Recommendation

The following are recommendations to control and improve water quality along the three refineries:

- Regular surveillance and monitoring for water quality and bottom sediments.
- Specific inspection of waste disposal on board ship while waiting to enter the port.
- The time permitted for vessels should not exceed three days of standby mode.
- Ministry of Public Works should meet the terms with KEPA regulation for controlling discharge of untreated sewage into the sea.
- Illegal discharge of industrial waste into the emergency storm drain outlet should be punished by law
- Inspire marine researches on water quality, hydrodynamics, bottom sediments, fisheries, fate and flux of pollutants.

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