Assessing the Organic and Inorganic Pollutants of Oil Field Brine Water in Marmul Area, Sultanate of Oman

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Abstract: The present work aim is to quantifying and assessing the organic and inorganic pollutants in the study area. In this study, the data from 19 Monitoring Wells (MWs) and from Marmul Main Production Station (MMPS) were used to assess the Total Petroleum Hydrocarbon (TPH) concentrations ranged from 0.170ppm and 1.582ppm with average of 0.435ppm. The concentrations and distribution of total Poly Aromatic Hydrcarbons (PAHs) in the Marmul study area were measured in MWs ranged between 0ppm and 0.806ppm. There are 7 individual PAHs observed in the monitoring wells of the studying area. Naphthalene has the highest concentration among other individual PAHs with 0.616ppm and the lowest concentration is Fluorine with concentration of 0.004ppm. The distribution of TPH and PAHs in the area trend is to increase toward the area of disposal of brines in the shallow aquifer. Also, water sample collected form well no. MW-10 which is located north of the SWD has shown highly concentrations in both TPH and PAHs over the study area. The Gas Chromatography (GC) device fingerprints of the sampling indicated that the type of petroleum hydrocarbons is same and it is similar to the one from MMPS. In this case the source of organic pollution in the area is attributed to the activity of oilfield brines. All fingerprints contain around 19 of hydrocarbon compounds from C21 to C39 and did not include pristane and phytene isprenoids. The Carbon Preference Index (CPI) in samples of the study area was ranging from 0.6 to 1.7 with average 1.18, reflecting in almost similar anthropogenic sources of pollution rather than biogenic. There are 11 trace metals had results of concentration. The lowest concentration average is for Co of 0.0002ppm and it is detected in only one monitoring well. The average concentrations of the rest of 9 trace metals are range between zeros to 1.2ppm (Sr 11.56ppm, B 1.18ppm, Mn 0.08ppm, Ba 0.03ppm, Mo, Zn and P 0.02ppm, V 0.004ppm and Cr 0.002ppm). No concentration of Cd, Pb, Al, Fe, Cu, and Ni not found in the study area. In addition, trace metals results may regard to anthropogenic and/or natural sources and its level not indicated as trace metal pollution case. Patterns in groundwater pollution are consistent with produced water contamination that affirms the pollution originating is from one source (point source) of a produced water reinjection disposal wells in the study area.

Key words: TPH, PAHs, Hydrocarbon, oil, pollution, Marmul oilfield, and Sultanate of Oman.

INTRODUCTION

The Sultanate of Oman is located in the south-eastern corner of the Arabian Peninsula. The United Arab Emirates is present to northwest, Republic of Yemen to the southwest, and the Kingdom of Saudi Arabia to the west of the Sultanate Fig. (1). The coast is formed by the Gulf of Oman on northeast and Arabian Sea on the south and east. Marmul concession area is located approximately 900km south of Muscat and 260km north of Salalah. It covers an area of approximately 26,963km^2. The study area of this thesis will cover Marmul camp and the area around it which has all oil production activities it is area around 120km^2.The study area which coverage an area of approximately 120km^2 of more than 26,900km^2 Marmul Oilfield concession in Dhofar region. Dhofar is an historical region in southern Oman Fig. (2). There are oil fields in the northeast in Marmul area. It consists by based of the geographical, social and economic diversity of three natural landscapes; the coastal strip, the mountain district and the Nejd. Marmul site lays in Nejd, meaning plateau, is one of the major physiographic features of the Arabian Peninsula. Nejd constitutes the greater part of Dhofar; it covers an area of some 50,000km^2 north and west of the Dhofar Mountains. The mountains could

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be termed nature's dividing line determining the distribution of water between the mountain region and the Nejd. The principal drainage of Nejd consists of a number of northerly and north easterly trending Wadi systems that carry water only seasonally. The Wadis have cut deeply incised canyons into thick limestone sequences along the southern, mountainous margins. Immediately north of the mountains, foothills merge with a relatively undissected, limestone plateau of gentle to moderate slope. This plateau is overlain by an extensive sand dune system in the north and northwest Rub Al Khali and merges with the Jidat Al Harisis plateau in the west.
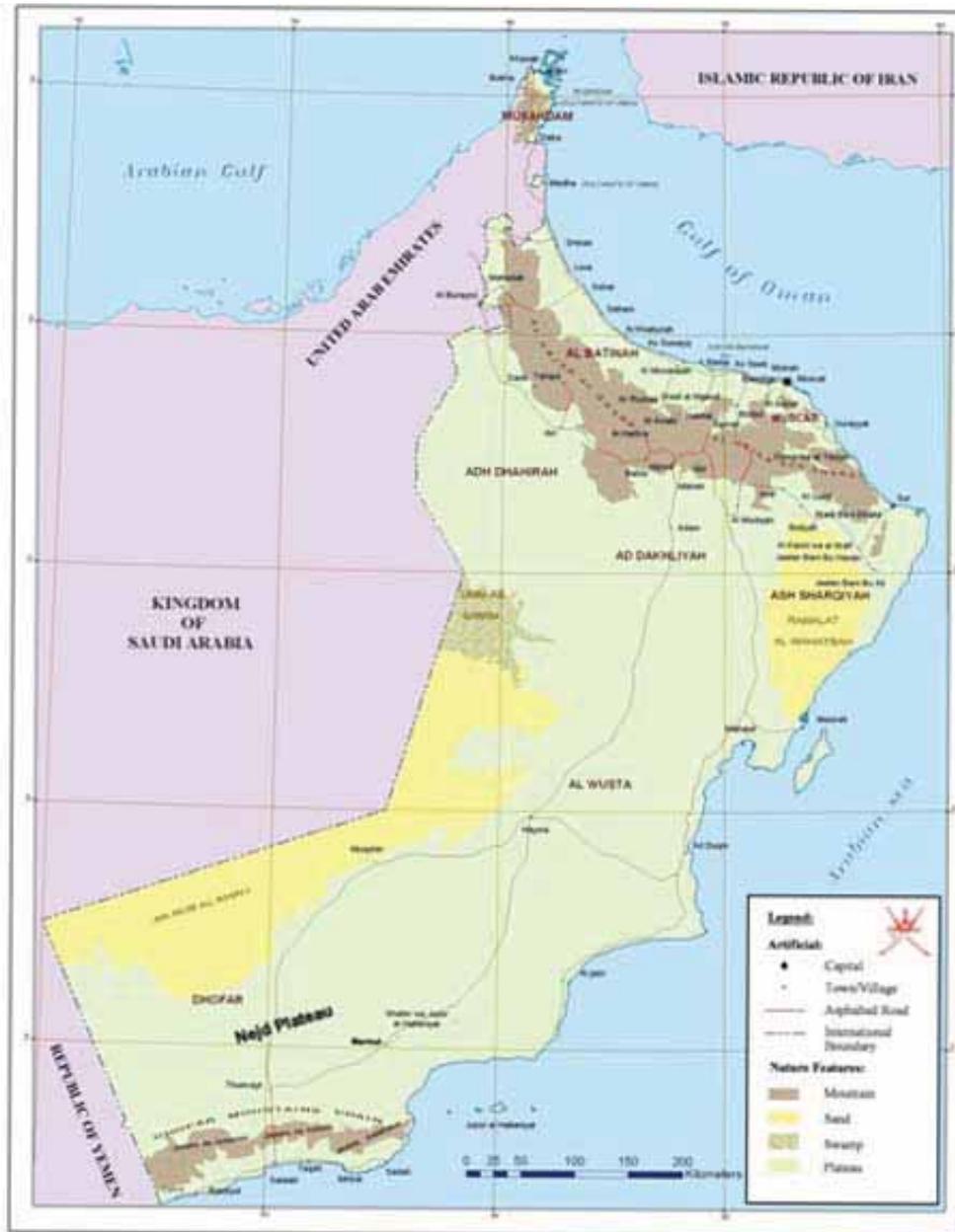
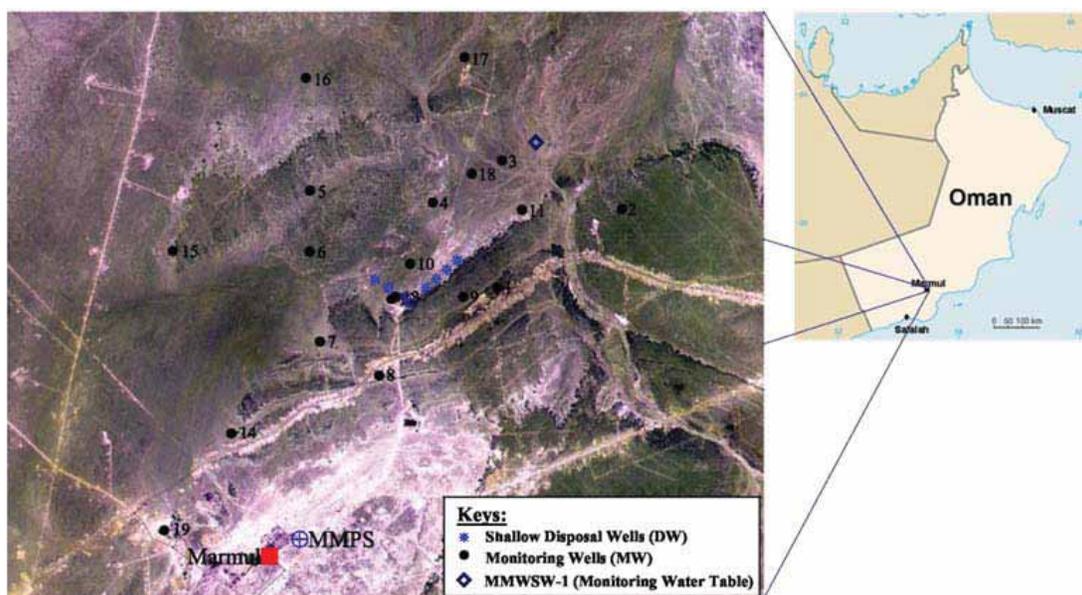**Fig. 1:** Sultanate of Oman location map.

Fig. 2: Satellite image of the study area.

MATERIALS AND METHODOS

Sample Collection:

Water samples were collected from 19 MWs and MMPS in Marmul oilfield area, all samples were taken in glass bottles, refrigerated by ice (< 4ºC), acidified by nitric acid (HNO_3) 5 ml for inorganic chemical samples and hydrochloric acid (HCl) 5 ml or sodium sulfate (Na_2SO_4) for organic chemical analyses and kept frozen prior to in the mentioned laboratories. This is to prevent any change in the elements or volatile compounds from evaporation or chemical degradation Table (1).

Table 1: Details of water sampling from MMPS and monitoring wells at Marmul oilfield.

No.	Date of sampling	No.	Place	Purpose of the samples	Laboratories
1	1st October, 2006	2	MMPS	Inorganic elements test.	Central Laboratories Unit (CLU) at the United Arab Emirates University (UAEU
3	31st October, 2007	19	MW and MMPS		Petroleum hydrocarbons and inorganic elements test. Geochemistry Lab Geology Dept.-UAEU Water, Soil, and Fertilizers Laboratories Center, Al-Ain – UAE (WSFLC)
4	7th February, 2008	19	MW	Chemical elements test.	Food, Environment and Water Monitoring Centre, Muscat – Sultanate of Oman (FEWMC)
5	21st March, 2008	20	MW and MMPS		TPH and PAHs test Central Laboratories Unit (CLU) at the United Arab Emirates University (UAEU)

Analytical Methods:

Determination of total TPH by Fourier Transform InfraRed (FTIR) system provides information on the contamination of water with petroleum products. After the procedure of preparing the sample, place the solution in the Nicolet Fourier Transform Infrared Manga-IR 560 (FTIR). Select appropriates working standards and cell path length. The Nicolet FTIR 560 system with flexible configuration that offers highest accuracy and sensitivity in a variety of wavelength ranges. The spectrometer has more than 4 external beams, DTGS and MCT detectors, IR microscope and Thermal Gravimetric Analysis (TGA). Analysis of PAH was carried out by High Performance Liquid Chromatography (HPLC) in the CLU as per the SOP-CH-HPLC-02 procedure. Quantitatively transfer into a 5ml volumetric flask and make up to volume. HPLC system equipped with auto sampler fluorescence detector and UV detector (two waters Alliance Separation 2695), water photo-diodearray detector (2996) and other devices like tunnel absorbance UV detector (486). HPLC column: Chromosphere 3 PAH column (100mm x 4.6mm ID, 3mm).

To determine the qualitative of petroleum hydrocarbon pollution, GC then further GC/MS instruments will used to test the water sample contamination by oil. In the following there are three stages to follow. Firstly,

extract the hydrocarbons from the sample by the extraction method, inject GC by extracted samples, and then inject GC/MS by same extracted if the sample need further test to show Biomarker. After a thorough investigation the solvent mixture of hexane and dichloromethane (7/3; v/v) has been found to be appropriate for the extraction of petroleum hydrocarbons from water sample. Sample extraction should be performed as soon after collection is possible. Samples should never be stored more than 3 - 4 hours and should be kept in refrigerator or icebox during the Storage. The extraction is performed with a solvent mixture of fluorescence free hexane and dichloro-methane (7/3; v/v). After the hydrocarbon extraction procedure, the extract is quantitatively transferred to a 100 ml measuring cylinder. Transfers apportions to a 2 ml GC auto-sampler vial and inject 1μl in the GC-FID. The Varian CP-3800 GC 2000 will running the samples, then the result will processing and final results printing in the workstation. The Waters Quattro micro™ GC is a mass spec-trometer configured for Integrated LC/MS/MS. A tandem quadrupole mass spectrometer is a versatile instrument and can be used to perform a wide variety of experiments. Ion sources, EI is standard - Cool CI optional - GC interface - Solids probe option. Desorption chemical ionization probe option.4 to 1500Da mass range. MRM dwell time and ICD of only 10ms each. Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then be measured. ICP hardware is designed to generate plasma, which is a gas in which atoms are present in an ionized state. The basic set up of an ICP consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a Radio Frequency (RF) generator. As flowing gases are introduced into the torch, the field is activated and the gas in the coil region is made electrically conductive. This sequence of events forms the plasma. An ICP requires that the elements which are to be analyzed be in solution. An aqueous solution is preferred over an organic solution, as organic solutions require special manipulation prior to injection into the ICP. Solid samples are also discouraged, as clogging of the instrumentation can occur.

Statistical methods in this study include correlation matrix and cluster analysis. The statistical correlation matrices are multivariate analyses used to correlate the relationships between variables. A correlation matrix is always a symmetric matrix to locate the correlation for any pair of variables, find the value in the intersection for those two variables (Al Katheeri, 2004 and Al Adba, 2008). Statistical method can produce hierarchical clusters of items (cases) or variables based on distance measures of dissimilarity or similarity. The items being clustered are usually cases from the active dataset, and the distance measures are computed from their values for one or more variables. Cluster assumes that the items being clustered are cases and uses the squared Euclidean distances between cases on the variables in the analysis as the measure of distance. Average Linkage (a compromise) of the distance between two clusters is defined as the average distance between points in them (SPSSTM v.15.0, 2006).

Geological Settings:

The rocks of Dhofar represent deposition on an extensive carbonate shelf that existed from Cretaceous times through into the Tertiary (Cheverl *et al.,* 1992).The deposits are predominantly of marine although the Middle Eocene (Bartonian) shelf deposits pass northwards into continental deposits of the Qitabit Formation. Retreat of the sea at the end of the Late Eocene led to the emergence and weathering of the Eocene landmass. A new transgression from the Arabian Gulf in the Middle Miocene (Burdigalian) deposited sediments of the Dam Formation southwards across the area. This was followed at the end of the Langhian by a final transgression from the Indian Ocean in the east which laid down the deposits of the Ghubbarah Formation. The margins of these Miocene seas were sites of continental deposition, represented by the Dawkah Formation in the Burdigalian-Langhian and the Montasar Formation in the Langhian-Serravallian. A new retreat of the sea towards the end of the Middle Miocene resulted in the deposition of continental, mainly detritus or palustrine sediments, which constitute the Shisr, Nar and Atinah formations. Uplift of the southern part of Dhofar, related to the opening of the Gulf of Aden (Aden Rift) from the end of the Eocene but mainly during Oligocene-Miocene times, tilted the sedimentary succession to the north to produce a very gentle regional homocline dipping into the Rub Al-Khali. In the geological study area map in Fig. (3), the tilting of this homocline led to the development of a series of parallel pinched synclines with a SW-NE or WSW-ENE trend. Diapiric salt movements were responsible for the development of broad domal features, such as the Marmul dome, in the overlying sedimentary cover. Chevrel *et al.* (1992) broadly explained that the tertiary of Marmul area divided into marine and continental domains. The Eocene marine/continental boundary corresponds roughly to the course of Wadi Qitabit. The marine domain is being to the southeast and the continental domain to the northwest of Marmul. The Hadhramaut Group comprises the entire Paleocene-Eocene marine succession
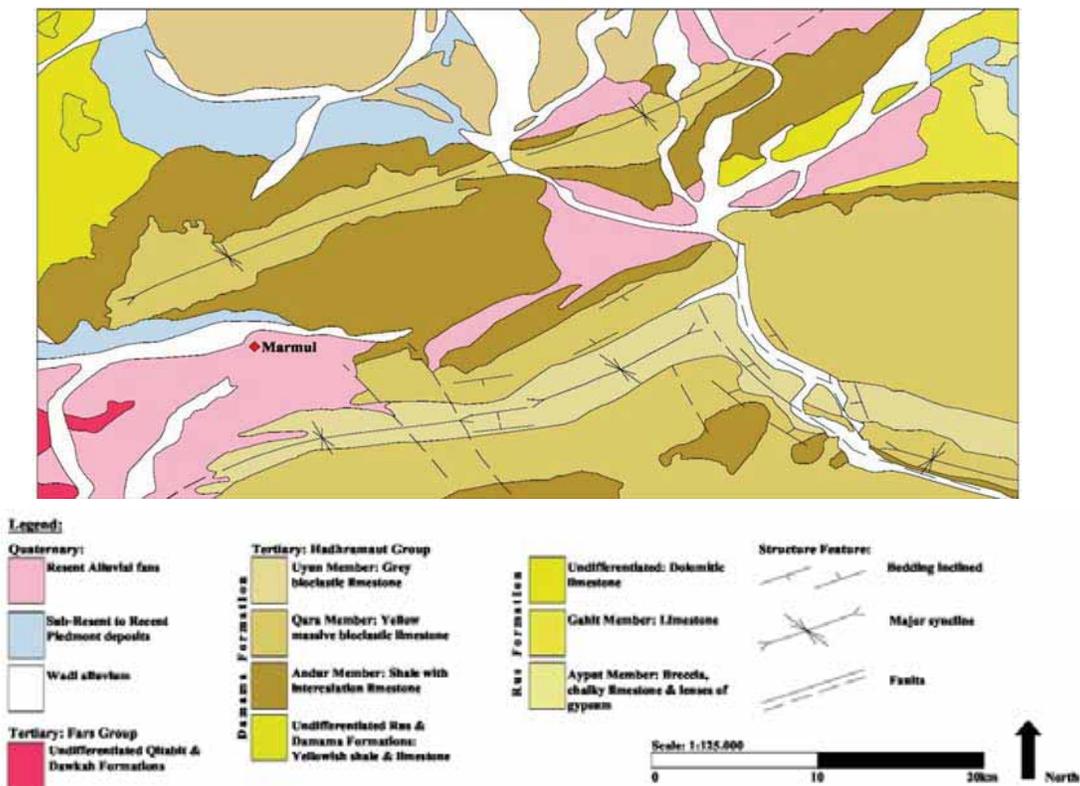
Fig. 3: Geological map of Marmul Oilfield Area.

between the Cretaceous-Tertiary unconformity at their base and the unconformity at the base of the overlying the Late Eocene to Early Miocene deposits of the Dhofar Group. The Hadhrarmaut Group divided into a basal transgressive sequence (the UeR) overlain by a regressive evaporite sequence (the Rus Formation) and further transgressive sequence (The Dammam Formation) overlain by the bioclastic limestone of the Aydim Formation which marks the start of the Late Eocene regression.

Oil Production in Marmul:

The Marmul Oilfield is located within Petroleum Development of Oman Company (PDO) Block 6 of more than 74 PDO oilfield areas in the Sultanate of Oman and it is part of PDO's Southern Oman operating facility. PDO's exploration, development and production activities are centred upon the main camp at Marmul, and there are approximately 500 producing oil wells in this concession area. The Marmul Main Production Station (MMPS) is one of PDO oilfields in the company's concession area in southern Oman developments. The primary function of MMPS is to dry the crude oil received from the nearby Marmul Gathering Stations and adjacent fields (MMPS - PDO Operation Manual, 2002). The original production facilities came on stream in 1980. In the original scheme of the MMPS plant, the liquid production was heated and the crude and water were separated in Wash Tanks. The free-floating oil was skimmed off from this water in Skim Tanks. The Marmul Oilfield currently produces approximately 12,000 m3/day of crude oil and a large quantity of produced water (water cuts well above 80%). Target crude specification is 0.5% Base Sediment and Water in the export crude and 150ppm oil in the disposal water. Marmul oil is producing from Hushi formation (Late Carboniferous – Middle Permian) and the source rock type was Marine Marl aged between Precambrian to Cambrian (Geomark, 2008). Marmul oil is classified as heavy or extra heavy oil. Wikipedia URL, Heavy crude oil is any type of crude oil which does not flow easily. It is a relative term, compared to light crude oil, but relates to specific technical issues of its own on production, transportation and refining. Physical properties that distinguish heavy crudes from lighter ones include higher viscosity and specific gravity, as well as heavier molecular composition (MECA, 2008a). Heavy oil from the Marmul area has a viscosity of over 10,000 centipoise (cP). Marmul oil API gravity is 12.4° and it is in mild biodegradation (Geomark, 2008); the

biodegradation level sits between 5 and 6 of Table (2). Generally diluents are added at regular distances in a production wells and pipeline carrying heavy crude to facilitate its flow. As Waples and Machihara (1997) most geologists agree that crude becomes heavy as a result of biodegradation in which lighter ends are preferentially consumed by bacterial activity (bacteria attack) in the reservoir leaving heavier hydrocarbons behind. This hypothesis leans heavily on the techniques of petroleum geochemistry.

Table 2: Stages of biodegradation of crude oils based on the presence or absence of certain classes of compounds (after John K. Volkman *et al.*, 1983).

Level of Biodegradation	Compounds Removed	Extent of Biodegradation
1	None	Undegraded
2	Short n-aIkane	Minor
3	>90% of n-alkanes	Moderate
4	Alkvlcyclohexanes; isoprenoids reduced	Moderate
5	Isoprenoids	Moderate
6	Bicyclic alkanes	Extensive
7	>50% of regular steranes	Very extensive
8	Steranes; hopanes reduced; demethylated hopanes abundant	Severe
9	Demethylated hopanes predominate; diasieranes formed; steranes gone	Extreme

Lily and Young (2005) explained that during the past 15 years researchers have made great strides in understanding the metabolism of hydrocarbons by anaerobic bacteria. The findings of these researches were degradation can be demonstrated for all Hydrocarbons under the different anaerobic conditions. The anaerobic biodegradation pathways for reduced hydrocarbon compounds include a series of metabolites unique to the anaerobic degradation of these hydrocarbons Table (2). Because they are specific and identifiable with these anaerobic processes, the metabolites can be used to assess the in situ biodegradation of these contaminants in anoxic subsurface. Strontium sulfates which precipitate sulfate can be used as an oxygen source by bacteria.

Statistical Analysis:

Simply the statistics of the result parameters which tested in the study area illustrate the correlation between them and the plot of a cluster dendogram shows the relationships between these variables. There are negative as well as positive correlation coefficients between the parameters. The value (0.0) – (-1.0) represents a perfect negative correlation of the Parameters. The value of (0.0) – (1.0) represents a perfect positive correlation that is with pair of the parameters. A value of zero represents a lock of correlation between the variables. A correlation matrix is always a symmetric matrix to locate the correlation for any pair of variables, find the value in the intersection for those two variables. The strongest positive correlation was between Alkalinity and HCO_3 with the value of 1.00 and the lowest negative correlation was between TPH and SO_4 with value of -0.55.

RESULTS AND DISCUSSION

Organic Compounds Pollutants:

Crude oil represents a common source of organic contamination in the environment because of the large volumes of these liquids and their byproducts (Deutsch, 1997). There are a lot of organic parameters using to determine the hydrocarbon pollution in groundwater, especially measuring the TPH and PAHs in the water samples.

Total Petroleum Hydrocarbon (TPH):

The Total Petroleum Hydrocarbons (TPH) in produced water quality from produced waters range between 50 to 250 mg/l. The average concentrations reported are 100 mg/l, but there is considerable variation. The distribution of TPH and TOC in Dubai sediments was discussed in detail by Haifa *et al.* (2005). Concentrations of TPH in Dubai sediments showed drastic fluctuations from 2 to 48,018 μg g^{-1}. The total petroleum hydrocarbon concentration (TPH) results from Port Said area ranges from 1.86ppm to 32.25ppm. It was found that the TPH of the most of the bottom sediments are within high levels (4 to 26ppm) (El Tokhi *et al.,* 2008). With reference to Oman regulations OS 8/98, MD145/93 and RD 115/2001, the oil in water concentrations for produced water disposed at Marmul exceed the prescribed limits for both potable water and wastewater discharge standards respectively. The limit prescribed is 0.5ppm. Oil in water is considered to be a major pollutant and is a parameter for which consideration is required for any proposed remediation of contaminated aquifers. ATSDR (1999) defined that TPH is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which

can contaminate the environment. Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at a site. TPH is a mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons. Determination of TPH provides information on the contamination of ground water with petroleum products. TPH is an estimate of the amount of hydrocarbons present between the carbons ranges from C_8 to C_{40}. This range of carbon extends from the volatile hydrocarbons compounds with the lower boiling to the non-volatile compounds found at the higher boiling point range.

The TPH concentration and distribution map variation in study area shown in Figs. (4 and 5) respectively. The maximum TPH concentration values were recorded in monitoring well no. MMWMW-10 which is 1.582μg/ml (1.582ppm) and the minimum TPH concentration values were recorded is 0.170μg/ml (0.170ppm) in wells no. MMWMW-5, MMWMW-14, MMWMW-15, MMWMW-16, MMWMW-17 similarly Table (3). It is clear in Fig. (4) that increasing trend of TPH is to the central of the area where the place of re-injected produced water is. The TPH variation in Marmul field area is within low limits except 5 samples which are exceeding 0.5ppm regarding to RD 115/22001 as illustrated in Fig. (5). The TPH result of the produced sample from MMPS is relatively high 273μg/ml (273ppm). Regarding to the Production Water Management Plan (PDO-PWMP, 1993), the excess limit of oily contents or TPH in produced brine should be 100ppm. Whatever, this situation need more investigation to confirm the high concentration as it appears may due to some failure in MMPS in time of sampling and its not to be seemed as dangerous because PDO have adhered to phase out the shallow injection of brines since April 2008.
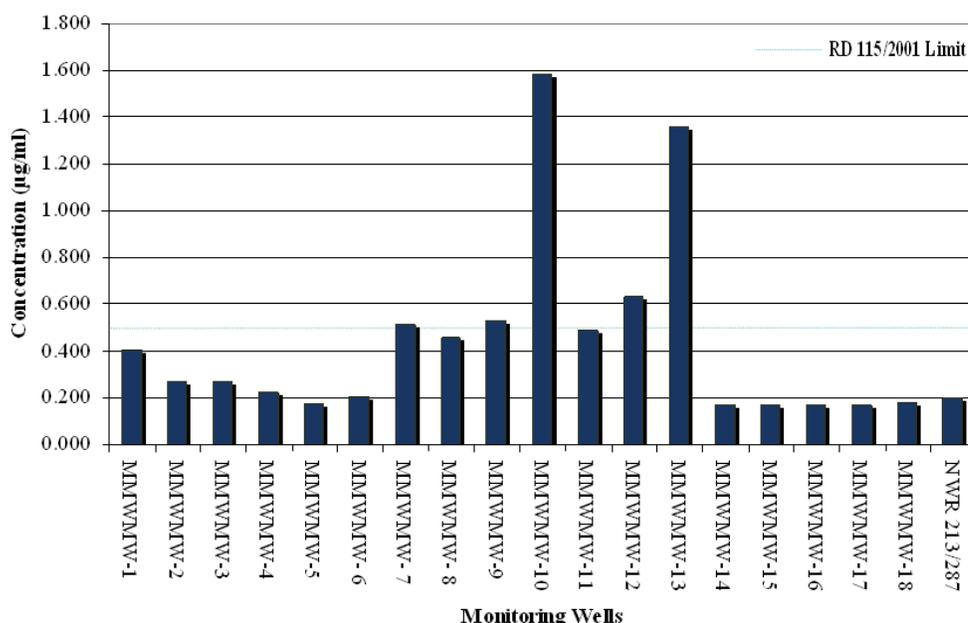

Fig. 4: TPH concentration in study area.

Poly Aromatic (Cyclic) Hydrocarbons (PAHs):

ATDSTR (1995) highlighted PAHs in dwell. Its definition in brief is "PAHs are a group of chemicals that are occur naturally or formed during the incomplete burning of oil or other organic substances". There are more than 100 different PAHs. PAHs generally occur as complex mixtures not as single compounds. As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. They can have a faint, pleasant odor. They can be found in crude oil. PAHs in general do not easily dissolve in water and some of them evaporate into the atmosphere from waters. The 16 types of PAHs that analyzed are divided into 7 individual PAHs was detected and other 9 individual PAHs not detected in the laboratory instruments. The Benzo(a)pyrene (BaP), which is the most acute deadly carcinogenic, not included in the detected PAHs. There are two primary sources of PAHs to the marine environment, pyrogenic and petrogenic: pyrogenic PAHs are derived from combustion sources and petrogenic PAHs are derived from petroleum inputs. The highest amount of PAHs is usually associated with sediments that have a high TOC. The distribution pattern appeared to be related to oil pollutant sources (Abdel Gawad, *et al.*, 2008). The concentration and distribution map of total
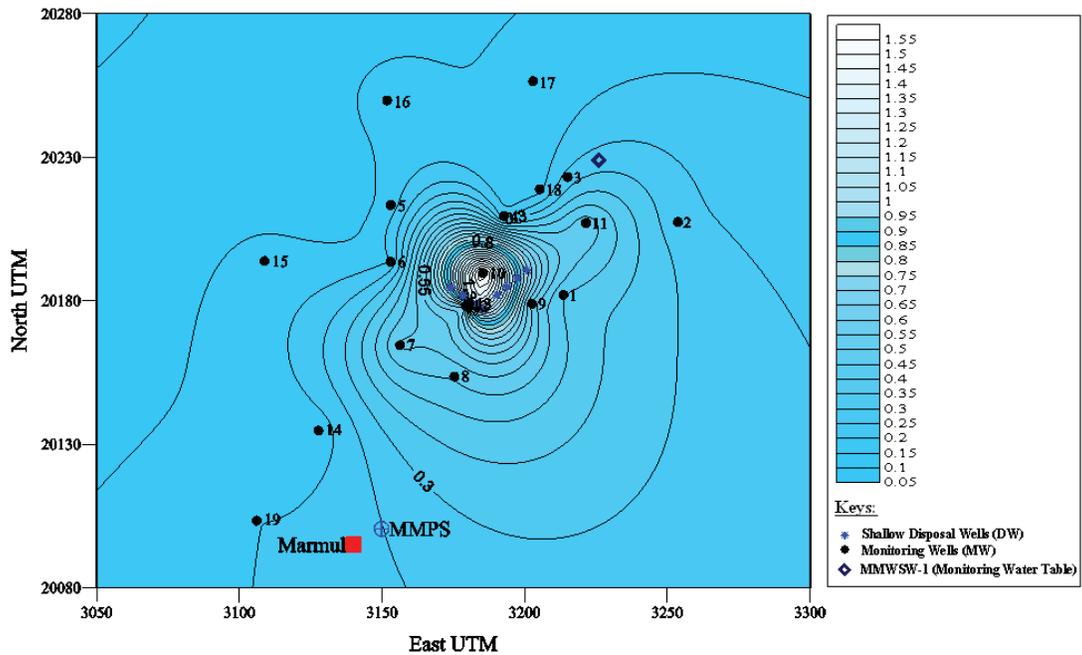
Fig. 5: Contour map of TPH distributions in the study area.
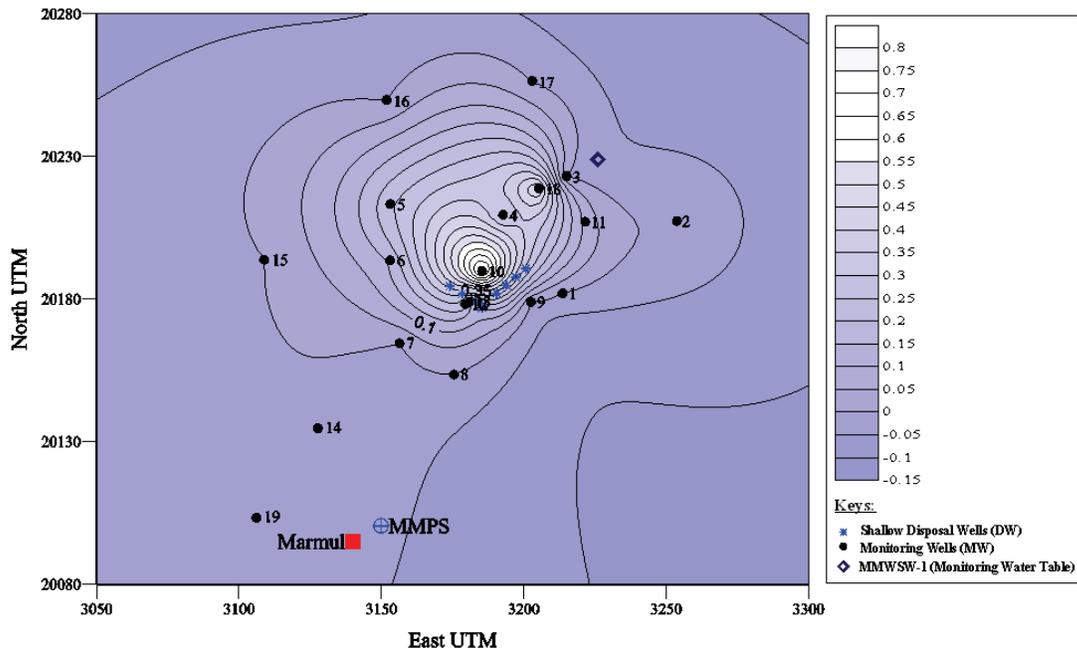
Fig. 6: Contour map of PAHs distributions in the study area.

total PAHs in the Marmul study area are illustrated in Fig. (6). The total PAHs found in 8 monitoring wells and they ranges between 0μg/ml (in case of not detected in other 11 wells) and 0.806μg/ml (0.806ppm) Fig. (7). The maximum value was recorded in monitoring well no. MMWMW-10 well shows highly concentrations in both TPH and PAHs over the study area. Various high concentration spots of Total PAHs concentration trend increases towards middle of upper north of the study area. However, the central part of the study field shows low of PAHs concentration. As it is shown above (Fig. 7) and in Table (3) there are 7 individual PAHs

Table 3: Total TPH Concentrations (µg/ml), Total PAHs Concentrations (µg/ml), Concentration (µg/ml) of detected individual PAHs and CPI in the study area.

Sample ID	TPH (µg/ml)	TPAHs (µg/ml)	Naphthalene	Acenaphthene	Flourene	Phenanthrene	Anthracene	Pyrene	Indeno (1,2,3-cd) pyrene	CPI
MMWMW-1	0.402	0	0	0	0	0	0	0	0	0.7
MMWMW-2	0.269	0	0	0	0	0	0	0	0	1.1
MMWMW-3	0.270	0	0	0	0	0	0	0	0	1.6
MMWMW-4	0.222	0.28	0	0.03	0	0.07	0.03	0.15	0	0.6
MMWMW-5	0.176	0.243	0	0.03	0	0.07	0.03	0.043	0.07	0.6
MMWMW-6	0.203	0.158	0	0.03	0	0	0.03	0.098	0	1.5
MMWMW-7	0.510	0	0	0	0	0	0	0	0	1.7
MMWMW-8	0.457	0	0	0	0	0	0	0	0	0.9
MMWMW-9	0.528	0	0	0	0	0	0	0	0	1.3
MMWMW-10	1.582	0.806	0.636	0.03	0.04	0.07	0.03	0.04	0	1.3
MMWMW-11	0.487	0.089	0	0	0	0	0.03	0.059	0	1.2
MMWMW-12	0.634	0.245	0.14	0.03	0	0.005	0.03	0.04	0	1.2
MMWMW-13	1.362	0.094	0	0.03	0	0	0	0.064	0	1.3
MMWMW-14	0.170	0	0	0	0	0	0	0	0	1.4
MMWMW-15	0.170	0	0	0	0	0	0	0	0	0.9
MMWMW-16	0.170	0	0	0	0	0	0	0	0	1.4
MMWMW-17	0.170	0	0	0	0	0	0	0	0	1.2
MMWMW-18	0.182	0.509	0.14	0.095	0	0.244	0.03	0	0	1.2
NWR 213/287	0.199	0	0	0	0	0	0	0	0	1.4
MMPS	-	-	0	0	0	0	0	0	0	1.1
Individual PAHs Total	-	-	0.916	0.275	0.04	0.459	0.21	0.494	0.07	-
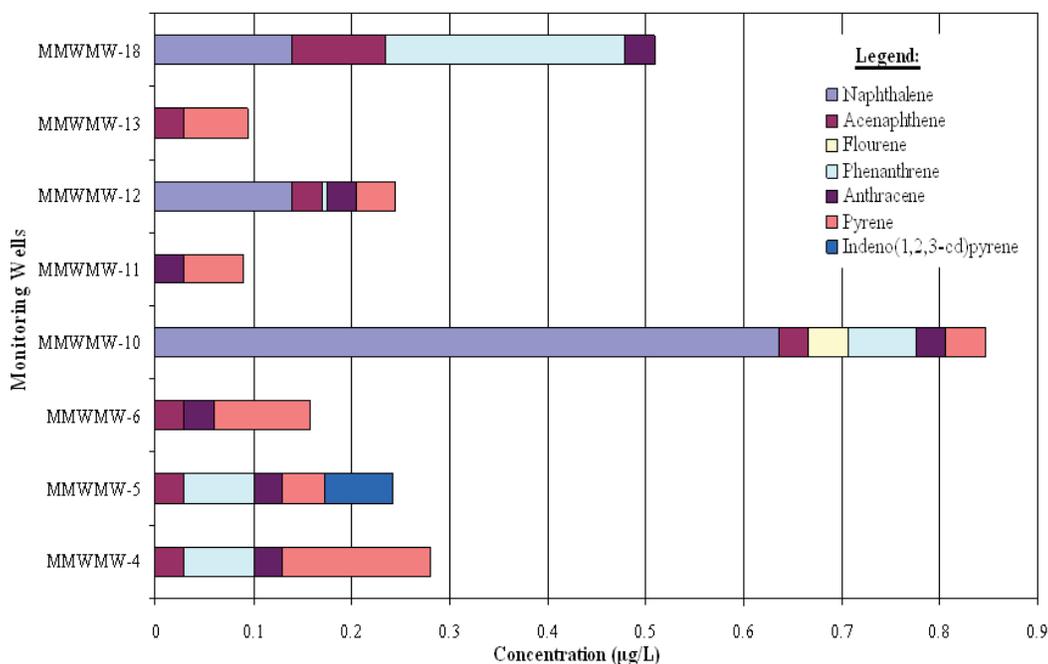
Fig. 7: Total PAHs concentration in the study area.

observed in the monitoring wells of the studying area. Naphthalene has the highest concentration among other individual PAHs with 0.916µg/ml (0.916ppm), which may attribute to its situation in the way of contaminated water way in the study place from the Shallow Disposal Wells SDW and hence the almost of PAHs concentrated is Naphthalene. The concentration of Naphthalene shows variation in Marmul oilfield area throughout the monitoring well stations. Naphthalene was detected in three monitoring wells with highest concentration of 0.636µg/ml (0.636ppm) in monitoring well no.MMWMW-10. The concentration of Acenaphthylene ranges between 0.0µg/ml and 0.095µg/ml (0.095ppm). The maximum concentration recorded was in MMWMW-18. Flourene was detected only in monitoring well no.MMWMW-12 with concentration of 0.095µg/ml (0.095ppm). Also, Indeno(1,2,3-cd)pyrene was noticed in MMWMW-5 with concentration of

0.07μg/ml (0.07ppm). Phenanthrene is identified at 5 of 8 monitoring wells with highest concentration of 0.244μg/ml (0.244ppm) in MMWMW-18 and lowest concentration of 0.005 μg/ml (0.005ppm) in MMWMW-12. Anthracene is identified at all wells of 8 monitoring wells expect well no. MMWMW-13 with same concentration that is 0.03 μg/ml (0.03ppm) in MMWMW-18. In otherwise, Pyrene was founded at all detected wells without well no. MMWMW-18 and the concentrations are 0.15μg/ml (0.15ppm), 0.043μg/ml (0.043ppm), 0.098μg/ml (0.098ppm), 0.04μg/ml (0.04ppm) and 0.064μg/ml (0.064ppm) from wells MMWMW-12 to MMWMW-17 respectively. In general the distribution of PAHs in the area trend to increase toward the area of disposal of brines in the shallow aquifer. And this is a determinism consequence of disposal of oilfield produced water by re-injection in the shallow aquifer. The following identify 9 of PAHs were not detected in any of the 19 sampling monitoring wells in Marmul study area are Acenaphthylene, Fluoranthene, Benzo(a)anthracene, Chrycene, Benzo(k)flouranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(b)flouranthene and Benzo(g,h,i)perylene.

Recognizing Petroleum Hydrocarbons by GC and GC/MS:

The Plate 4.1 of the GC device fingerprints of three selected samples; Marmul Main Production Station (MMPS) produced water, monitoring wells no.MMWMW-17 and NWI 213/287 clarify that the type of petroleum hydrocarbons is same and its similar to the once from MMPS. In this case, the source of hydrocarbon pollution in the area trend to the activity of oilfield brines disposal of in shallow aquifer. The other samples fingerprints are quite similar to that presented for both samples of MMWMW-17 and NWI 213/287. All fingerprints contains around 19 of hydrocarbon compounds from C21 to C39 (some have additional C8 and/or C40). All samples did not include pristane and phytane isprenoids i.e., Plate 4.2 shows of the chromatograms of GC of three mentioned above samples. Carbon Preference Index (CPI), which is a ration between the amounts of normal alkanes of odd and even numbered carbon atoms between C24 and C34, was calculated from the GC chromatograms. The distinct characteristics of biogenic hydrocarbons including much higher abundance of odd n-alkanes in wide range of n- C21 to n- C33 and high CPI and pristane/phytane values. However, the presence of petrogenic hydrocarbons were also obvious, indicated by the distribution of n- alkanes in a wide range from C15 to C40 and the notable presence of the chromatographic UCM (Abd El Gawad *et al.*, 2008). Within the study area, the CPI in samples was ranging from 0.6 to 1.7 with average 1.18 of the area, reflecting in almost similar anthropogenic sources of pollution rather than biogenic, as in Table (3). In addition, the correlation matrix shows there is strong negative relationship between sulfate and TPH. This situation may refer to the presence of sulfate reducing bacteria, the type of bacteria find in subsurface and can make hydrocarbon biodegradation primarily under anoxic conditions availability of dissolved sulfate. CPI was calculated in the present study according to the following equation:

$$CPI = 0.5 * \frac{\sum(C_{25}:C_{33})}{\sum(C_{24}:C_{32})} + \frac{\sum(C_{25}:C_{33})}{\sum(C_{24}:C_{34})} \quad ....$$

Fig. (8) shows the chromatograms of GC/MS instrument for the three samples of MMPS, MMWSW-17 and NWI 213/287. The chromatograms illustrated no Biomarkers are found in these samples, which may attribute to the highly oil biodegradation in the Marmul oilfield area Fig. (9). So, it is not detected of steranes and hopanes biomarker in chromatograms in Plate 4.3. Finally, the results of chromatograms of GC and GC/MS clarified that the origin of petroleum hydrocarbon pollution in Marmul shallow aquifer is one source from the activity of re-injected of produced water in it. Also, hydrocarbons are known to biodegrade in groundwater depending upon the presence of bacteria, oxygen and sulfates and because of the developments of secondary fractures on the surface that observed (Reid, 1992).

Trace Metals:

The previous data review indicates that there are undesirable levels of boron and aluminum present in Marmul's produced water. Concentrations of other metals, including silicon, zinc and barium may also be present at undesirable concentrations. In an alkaline environment, such as may be found in limestone, heavy metals tend to form insoluble compounds. Thus an alkaline aquifer enhances the precipitation of heavy metals. The distributions of heavy metals indicate that three groups of elements were discriminated. Group one includes those elements associated with carbonates (Sr & Mg). Group two are those associated with silicates fractions (Al, Fe & Mn). The third group discriminates those elements associated and used as indicators for petroleum
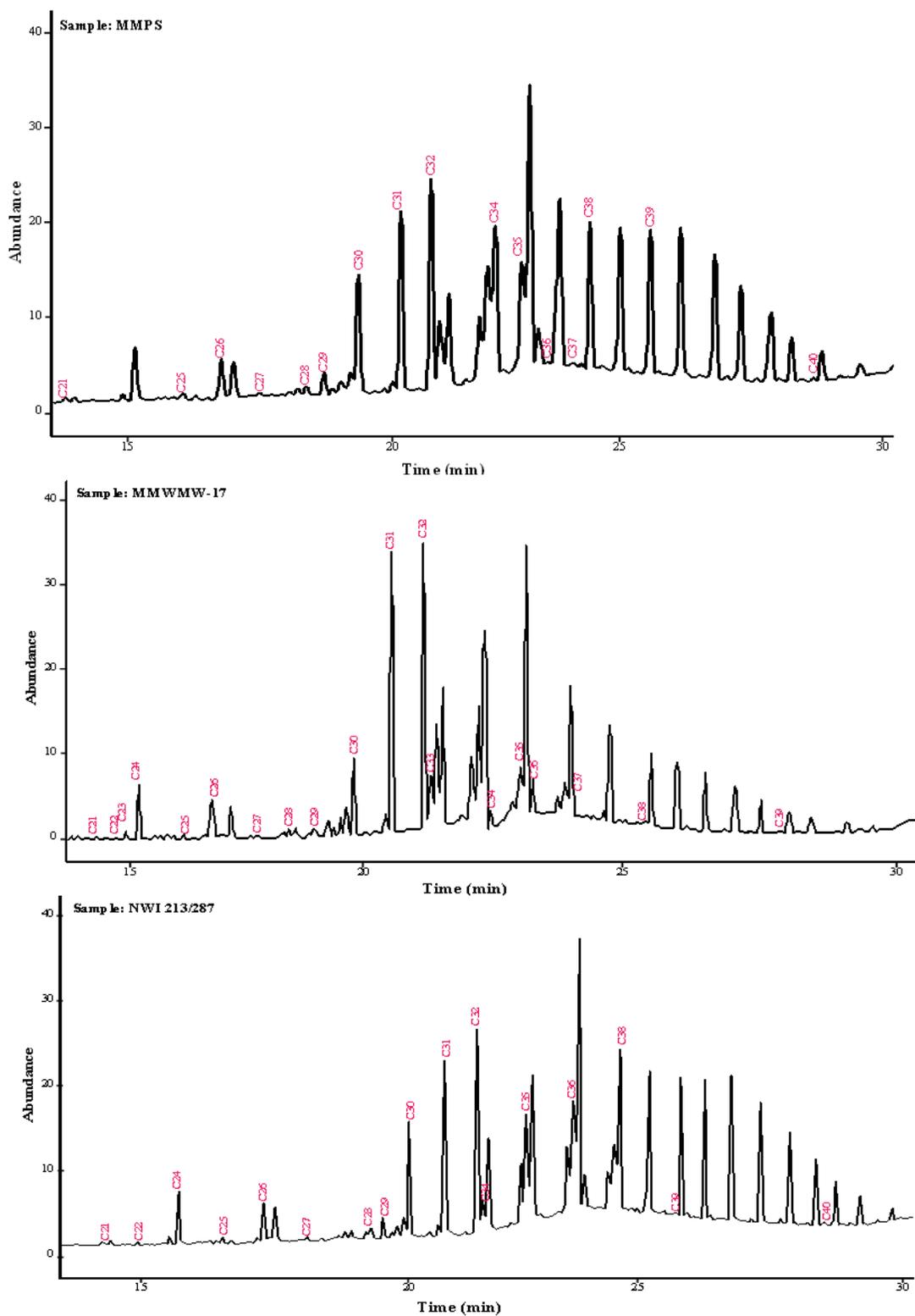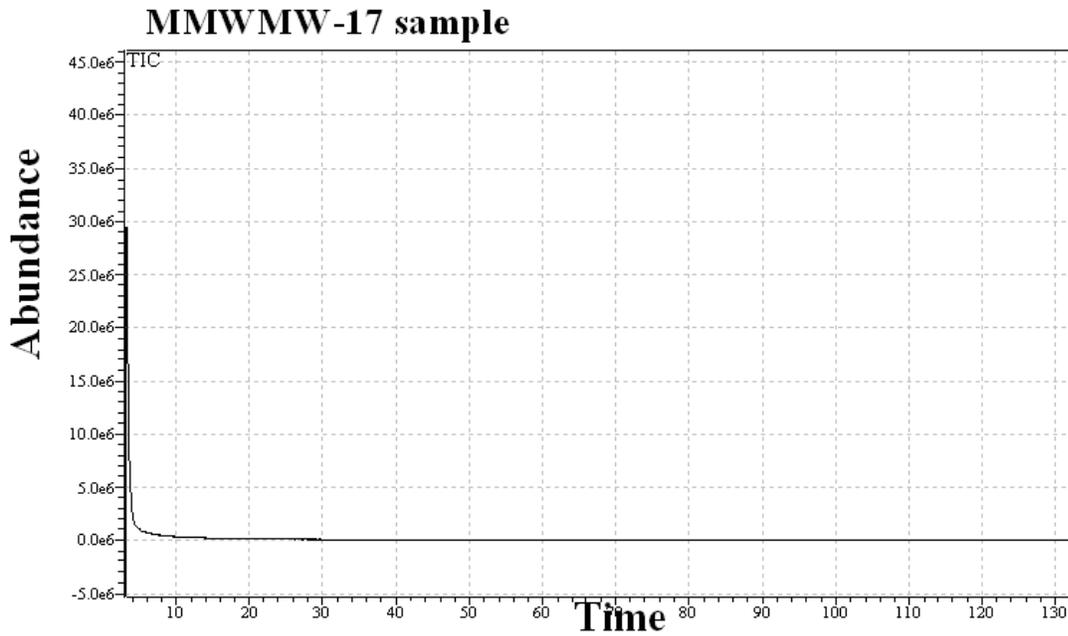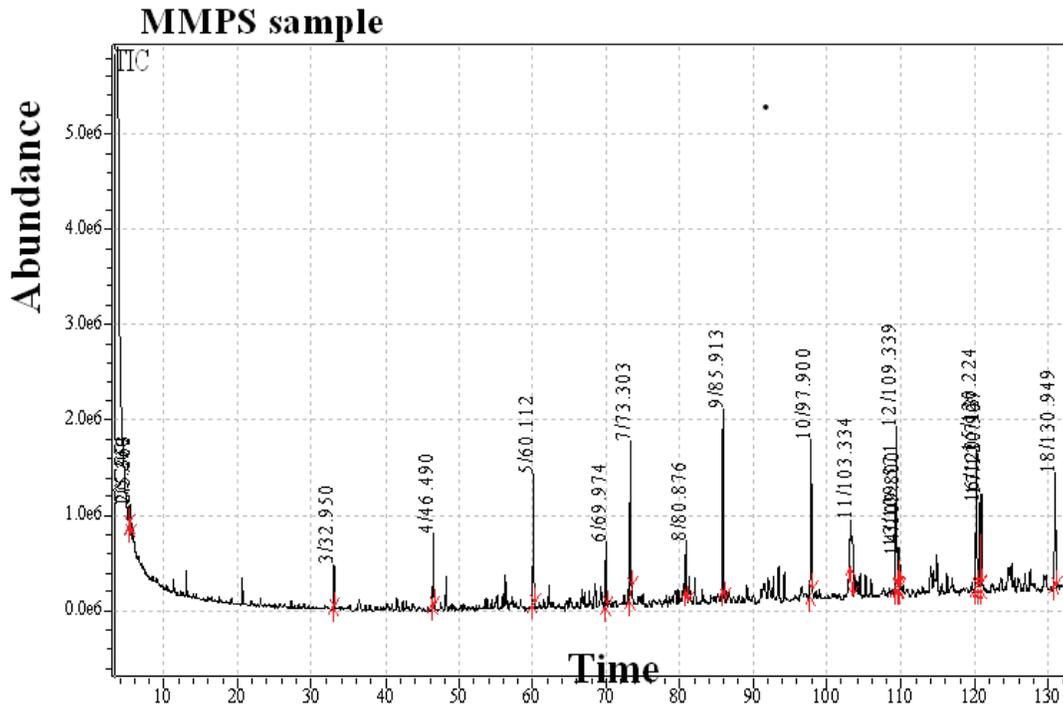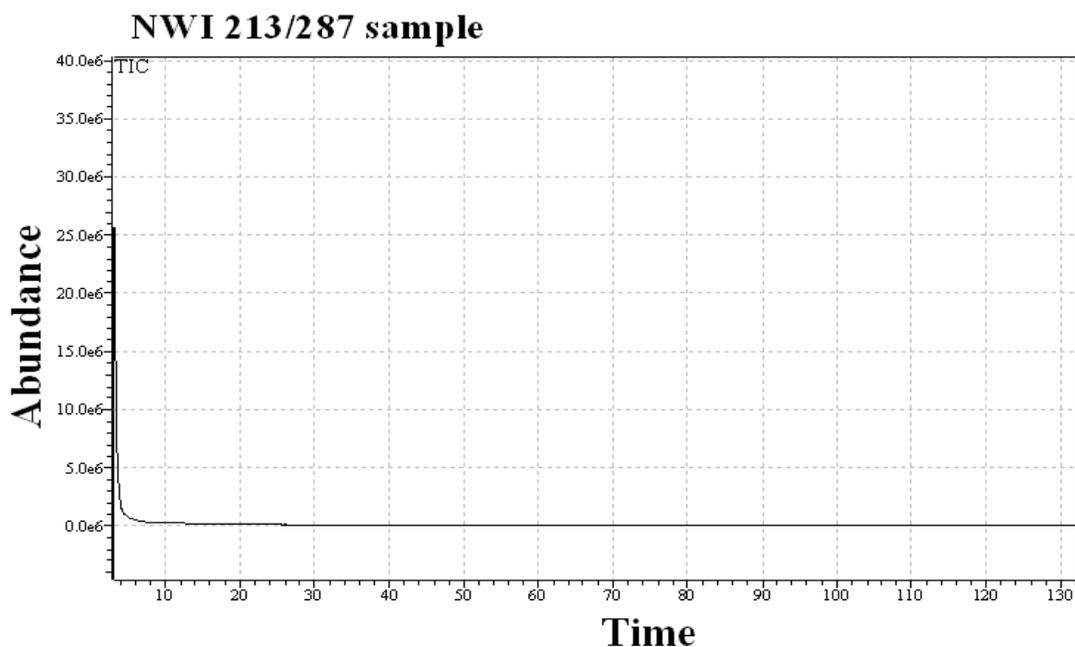
Fig. 8: GC chromatograms of MMPS oilfield brine water, MMWMW-17 and NWI 213/287 water samples.

MMPS sample

MMWMW-17 sample

NWI 213/287 sample

Fig. 9: GC/MS chromatogram of MMPS oilfield brine water, MMWMW-17 and NWI 213/287 samples.

hydrocarbon pollution (Ni, V) (Abdel Gawad *et al.*, 2008). Of the trace elements analyzed, silicon and boron are present in significant concentrations, and are identified as a pollutant. Boron exceeds the limits specified in Drinking Water Quality Standard OS 8/98. There are 17 of trace elements have been analyses in this study i.e., Cadmium (Cd), Chromium (Cr), Lead (Pb), Vanadium (V), Barium (Ba), Boron (B), Phosphorus (P), Zinc (Zn), Strontium (Sr), Silicon Oxide (SiO_2), Molybdenum (Mo), Manganese (Mn), Aluminum (Al), Iron (Fe), Cobalt (Co), Copper (Cu) and Nickel (Ni). The Table (4) shows the results of 11 trace metals concentration which obtained from the study area monitoring wells sampling. The highest concentration detected was for the dissolved silica SiO_2 with an average amount 24.79ppm, which may attribute to chemical weathering of siliceous minerals in the groundwater. It is noteworthy the SiO_2 concentration average of Petroluem Development of Oman (PDO) data in the period from year 2000 to 2005 is 23.2ppm. Also, Sr, one of dissolved polyvalent metallic ions comes from sedimentary rocks, appeared in moderate average amount concentration of 11.56ppm. On other hand, the lowest concentration average is for which Co 0.0002ppm is and it's detected in monitoring well no. MMWMW-2 only. The average concentration of the rest of 8 trace metals are range between zero to 1.2ppm. They gradually are B 1.18ppm, Mn 0.08ppm, Ba 0.03ppm, Mo, Zn and P 0.02ppm, V 0.004ppm and Cr 0.002ppm. As shown in Table (4), the concentration of Sr is distributed in all of the MWs. The highest rate is in well no. MMWMW 15 (25ppm) and the lowest rate in well no. MMWMW-12 (0.7ppm). B found in all MWs and the maximum value is in well no. MMWMW-10 (3.85ppm) and the minimum in well MMWMW-19 (0.05ppm). Mn distributed in 6 wells (MMWMW-10, MMWMW-11, MMWMW-12, MMWMW-13, MMWMW-15, and MMWMW-18). The maximum rate is in well no. MMWMW-13 (0.82) and the minimum rate in well no. MMWMW-12 (0.02ppm).P found only in well no. MMWMW-11 (0.3ppm). Mo distributed in 9 wells (MMWMW-3, MMWMW-4, MMWMW-5, MMWMW-6, MMWMW-7, MMWMW-15, MMWMW-16, MMWMW-17, and MMWMW-19). The maximum rate is in well no. MMWMW-15 (0.19ppm) and the minimum rate in well no. MMWMW - 7 (0.007ppm). Zn found only in 4 wells (MMWMW-1, MMWMW-2, MMWMW-7, and MMWMW-19). The highest value is 0.21ppm found in well no. MMWMW - 19 and the lowest one 0.02ppm in well no. MMWMW-7. Ba distributed in all MWs except MMWMW-2, MMWMW-4, MMWMW-11, MMWMW-12, and MMWMW-15. the maximum value is in well no. MMWMW-10 (0.14ppm) and the minimum value is in well no. MMWMW - 14 (0.003ppm). Cr found only in MMWMW-8, MMWMW-10, MMWMW-15, and MMWMW-17 and the maximum rate 0.02ppm found in well no. MMWMW-16 and the minimum rate 0.001ppm in well no. MMWMW-7. V distributed in 9 MWs (MMWMW-4, MMWMW-4, MMWMW-5, MMWMW-6, MMWMW-7, MMWMW-8, MMWMW-9, MMWMW-14, and MMWMW-19).

Table 4: The concentration of trace metals in monitoring wells MWs and MMPS.

Parameter	Concentration of MW ppm			Concentration of MMPS ppm	Remark
	Maximum rate	Minimum rate	Average		
Cd	0.0	0.0	-	0	-
Cr	0.02	0.001	0.002	0	Found in 4 samples
Pb	0.0	0.0	-	0	-
V	0.01	0.001	0.004	0	Found in 4 samples
Ba	0.14	0.003	0.03	0.17	Found in 14 samples
B	3.85	0.05	1.18	4.52	Distribution in all samples
P	0.3	0.0	0.02	0.07	Found in one sample only
Zn	0.21	0.02	0.02	0	Found in 4 samples
Sr	25	0.7	11.56	1.61	Distribution in all samples
SiO_2	44.47	2.16	24.79	-	Distribution in all samples
Mo	0.19	0.007	0.02	0	Found in 9 samples
Mn	0.82	0.02	0.08	0.02	Found in 6 samples
Al	0.0	0.0	-	0.01	-
Fe	0.0	0.0	-	0	-
Co	0.004	0.0	0.0002	0	Found in one sample only
Cu	0.0	0.0	-	0	-
Ni	0.0	0.0	-	0	-

Table 5: Hierarchal cluster of the variables of the study area.

Hierarchal Cluster	Clustered Variables	Remark
1st	Cr, Cu, V, Ba, Mo, Zn, P, Mn, PAHs, TPH, B, NO_3, Sr, and K with Mg	May the source of these parameters except PAHs and TPH is not resulting from the pollution source.

The highest value is 0.01ppm found in well no. MMWMW-14 and the lowest one 0.001ppm in Fig. (10) well no. MMWMW-4. Co found in one sample of well no. MMWMW-2 with concentration of 0.004ppm. Cd, Pb, Al, Fe, Cu, and Ni not found in all of MWs. All previous points illustrated that the all results of trace metals fit with WHO Guidelines for drinking-water quality (Chapman,1996) and RD 115/2001 except 4 samples; B in wells no. MMWMW-10 (3.85ppm) and MMWMW-12 (3.12ppm), Mo in well no. MMWMW-15 (0.19ppm) and Mn in well no. MMWMW-13 (0.82ppm). The analyses of MMPS produced water sample which taken in 1/10/2006 showed that there are only 6 trace metals found in it. They are gradually B 4.52 ppm, Sr 1.61ppm, Ba 0.17ppm, P 0.07ppm, Mn 0.02ppm, and Al 0.01ppm. So, there are limited trace metals in Marmul oilfield produced water and they are corresponding with RD 115/2001 and not upper the limits of WHO Guidelines for drinking-water quality (Chapman, 1996). So, we think no effect of trace metals cause from produced brines in the shallow aquifer. Then, all trace metals found in the MWs samples may regard to both anthropogenic and natural sources and its level not indicated as trace metal pollution case.

Multivariate cluster analysis used to study the similarities between monitoring wells. Applying the cluster for all parameters on all MWs has resulted in Fig. (11) which mainly shows a high similarity between all wells except wells no. MMWMW-1, MMWMW-2, MMWMW-6, MMWMW-13, and MMWMW-15. The cluster analysis i.e., average linkage and euclidean distance were performed on the data matrix comprising 24 variables. The obtained cluster dendrogram in Fig. (12) shows 23 major clusters which are simplified successively from the strongest cluster to the weakest cluster in the next following Table (5).The strongest cluster was among Cr, Cu, V, Ba, Mo, Zn, P, Mn, PAHs, TPH, B, NO_3, Sr, and K and Mg as one positive relation cluster; this can indicate a source of pollution was from pollution source point without may be the trace metals.

During the period of 28 years of re-injected of more than 96 Mm³ of oilfield produced water in the shallow aquifer, it must be change more of groundwater characteristics. In this thesis the result data from 19 monitoring boreholes and from MMPS were used to assess the lateral effect in the shallow groundwater. Groundwater Pollution (GWP) from oilfield activities is becoming a serious environmental problem in Oman. To alleviate this problem the Government of Oman cooperates with other specific companies and organization to study and find solutions to solve serious contamination. One of the GWP problems is the re-injection of oilfield brine water into shallow geological formations. This function is performed in around 16 oilfield areas in Oman including Marmul Oilfield Site. In the Oman oil fields, the underground water had drawn up with oil production amounts to more than three times the volume of the oil. Produced water in Marmul area appears to forecast to be increased year after year from around 40,000 m³/ day in 1999 to 200,000 m³/day in 2020. The produced water in Marmul oilfield is moderately brackish. This water is likely to be contaminated by a range of organic and inorganic matter. A Petroleum Development of Oman Company (PDO) activity includes exploration, development and production of oil are centered upon the main camp at Marmul, and there are
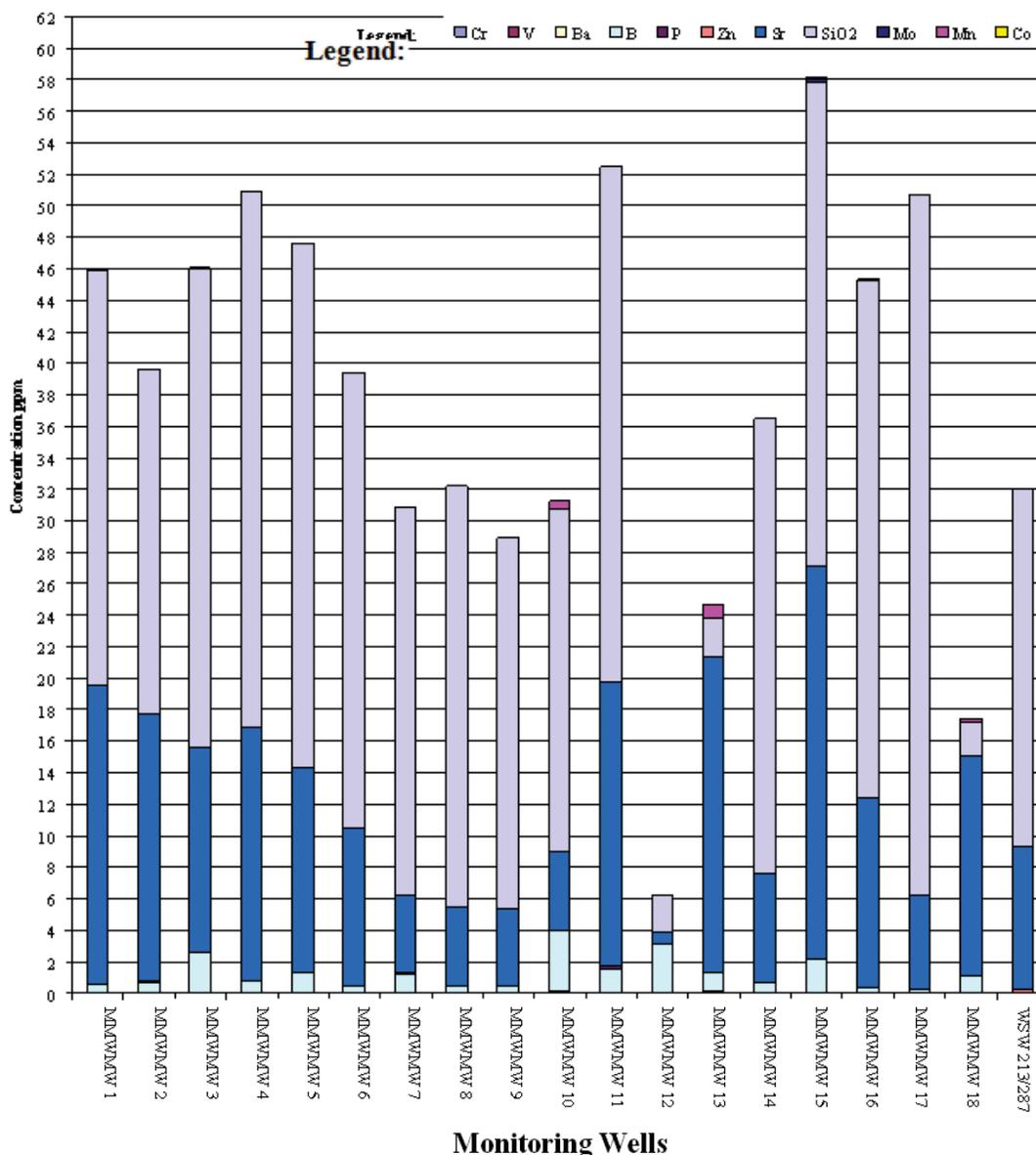
Fig. 10: Trace Elements concentration in study area.

approximately 500 producing oil wells in this concession area. The Marmul Main Production Station (MMPS) function is to dry the crude oil received from the nearby Marmul Gathering Stations and adjacent fields. At MMPS, removed produced water is lined up to the MMPS water disposal pumps. The main goal of this study is representing an approach to assess the major trace metals, and organic pollutants such as TPH and PAHs. Identify the sources of petroleum pollution in such aquifers using Biomarker approach.

The maximum TPH concentration values in the study area were recorded in monitoring wells is 1.582ppm and the minimum is 0.170ppm. Clearly, the increasing trend of TPH is to the central of the area where the place of re-injected produced water is. The TPH variation in Marmul field area is within low limits except 5 samples which are exceeding 0.5ppm regarding to RD 115/22001 as illustrated by Fig. (4). The 16 types of PAHs that analyzed are divided into 7 individual PAHs was detected and other 9 individual PAHs not detected in the laboratory instruments. The Benzo(a)pyrene (BaP), which is the most acute deadly carcinogenic, not included in the detected PAHs. The concentration and distribution of total PAHs in the Marmul study area
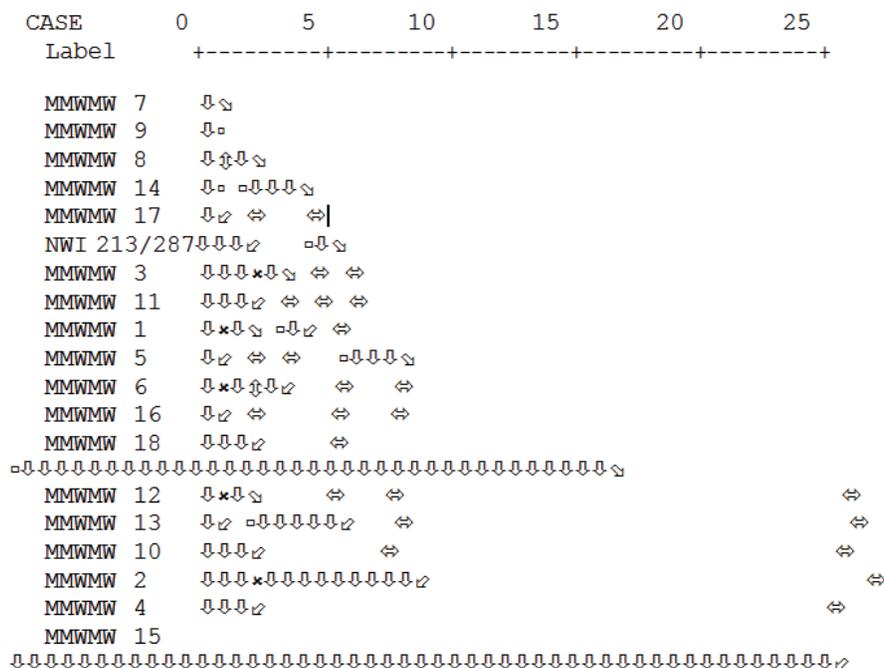
Rescaled Distance Cluster Combine

```
    CASE       0         5        10        15        20        25
    Label      +---------+---------+---------+---------+---------+

    MMWMW  7   ⇩⤸
    MMWMW  9   ⇩□
    MMWMW  8   ⇩⇧⇩⤸
    MMWMW  14  ⇩□ □⇩⇩⇩⤸
    MMWMW  17  ⇩↙ ⇔    ⇔|
    NWI 213/287⇩⇩⇩↙  □⇩⤸
    MMWMW  3   ⇩⇩⇩×⇩⤸ ⇔ ⇔
    MMWMW  11  ⇩⇩⇩↙ ⇔ ⇔ ⇔
    MMWMW  1   ⇩×⇩⤸ □⇩↙ ⇔
    MMWMW  5   ⇩↙ ⇔ ⇔  □⇩⇩⇩⤸
    MMWMW  6   ⇩×⇩⇧⇩↙  ⇔  ⇔
    MMWMW  16  ⇩↙ ⇔    ⇔   ⇔
    MMWMW  18  ⇩⇩⇩↙    ⇔
  □⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⤸
    MMWMW  12  ⇩×⇩⤸   ⇔   ⇔                                    ⇔
    MMWMW  13  ⇩↙ □⇩⇩⇩⇩⇩↙  ⇔                                   ⇔
    MMWMW  10  ⇩⇩⇩↙      ⇔                                    ⇔
    MMWMW  2   ⇩⇩⇩×⇩⇩⇩⇩⇩⇩⇩⇩⇩↙                                ⇔
    MMWMW  4   ⇩⇩⇩↙                                          ⇔
    MMWMW  15
  ⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩↙
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Fig. 11: Cluster analysis dendrogram for the monitoring wells in the study area.

Rescaled Distance Cluster Combine

```
    CASE       0         5        10        15        20        25
    Label      +---------+---------+---------+---------+---------+

    Cr         ⇩⤸
    Cu         ⇩□
    V          ⇩□
    Ba         ⇩□
    Mo         ⇩□
    Zn         ⇩□
    P          ⇩□
    Mn         ⇩□
    PAHs       ⇩□
    TPH        ⇩□
    Sr         ⇩□
  □⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⇩⤸
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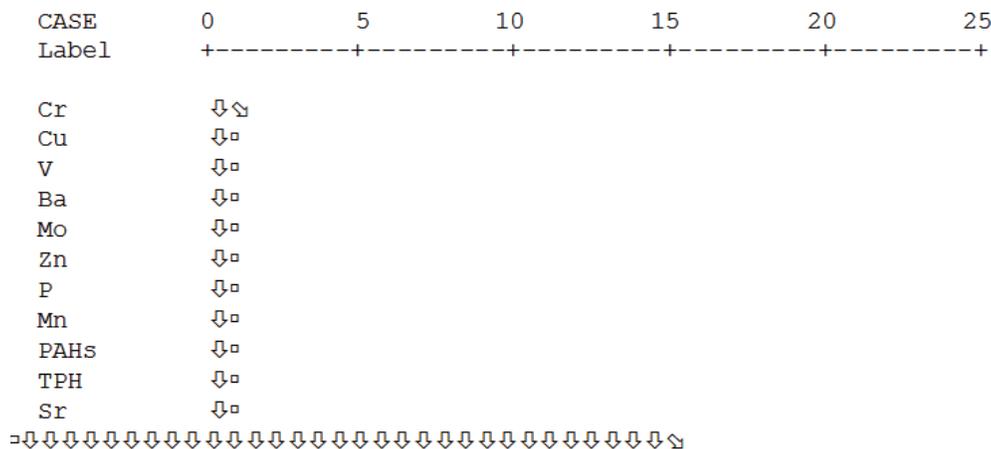
Fig. 12: Cluster analysis dendrogram for the tested parameters in the study area.

found in 8 monitoring wells and they ranges between 0ppm and 0.806ppm. Various high concentration spots of total PAHs concentration trend increases towards middle of upper north of the study area. However, the south part of the study field shows low of PAHs concentration. There are 7 individual PAHs observed in the monitoring wells of the studying area. Naphthalene has the highest concentration among other individual PAHs with 0.916ppm and the lowest concentration is Flourene with concentration of 0.004ppm. Generally, the distributions of PAHs in the area tend to increase toward the area of disposal of brines in the shallow aquifer. And this is a determinism consequence of disposal of oilfield produced water by re-injection in the shallow aquifer. Also the well no MMWMW-10 has shown highly concentrations in both TPH and PAHs over the study area. This well located north of the SWD.

The GC device fingerprints of the samples clarify that the type of petroleum hydrocarbons is same and it's similar to the once from MMPS. In this case, the source of hydrocarbon pollution in the area trend to the activity of oilfield brines disposal of in shallow aquifer. All fingerprints contain around 19 of hydrocarbon compounds from C_{21} to C_{39} and did not include prestane and phytene isprenoids.

Carbon Preference Index (CPI) was calculated from the GC chromatograms. The CPI in samples of the study area was ranging from 0.6 to 1.7 with average 1.18, reflecting in almost similar anthropogenic sources of pollution rather than biogenic. The chromatograms of GC/MS instrument for the three chosen samples. The chromatograms illustrated no Biomarkers are found in these samples, which may attribute to the highly oil biodegradation in the SWD area. So, it does not detected of steranes and hopanes biomarker in chromatograms in these samples.

There are negative as well as positive correlation coefficients between the studied parameters. The strongest positive correlation was between Alkalinity and HCO_3 with the value of 1.00 and the lowest negative correlation was between TPH and SO_4 with value of -0.55. Multivariate cluster analysis used to study the similarities between monitoring wells. Applying the cluster for all parameters on all MWs shows a high similarity between all wells except 6 wells (MMWMW-1, MMWMW-2, MMWMW-6, MMWMW-13, and MMWMW-15) and Well no. MMWMW-15 has the highest The cluster analysis of average linkage and euclidean distance were performed on the data matrix comprising 24 variables. The cluster shows 23 major clusters which are simplified successively from the strongest cluster to the weakest cluster in the parameters. The strongest cluster was among Cr, Cu, V, Ba, Mo, Zn, P, Mn, PAHs, TPH, B, NO_3, Sr, and K and Mg as one positive relation cluster; this can indicate a source of pollution was from pollution source point without may be the trace metals. The weakest cluster was between all clusters with TDS, This reflects the relationship between these variables with TDS, which indicates the sources may, came from the activity of SWD area and/or natural source.

Patterns in groundwater pollution are consistent with produced water contaminations that affirm the pollution originating is from one source (point source) of a produced water re-injection disposal wells in the study area. Produced water disposal to the shallow groundwater aquifer has been ongoing for over 28 years. The pollution plume appears to be migrating northeast along the direction of groundwater flow. The potential contaminants identified and presumed include heavy metals, hydrocarbons, and major ions. According to PWMP-PDO (1993), PDO handled the option which serve with the least environment impact and phase out the SWD in 2008. In other hand, PDO should do the following measurements to solve the GWP in Marmul SWD area. Groundwater in the area defined by the contamination plume i.e., hydrocarbon pollution, should be declared unfit for any usage without prior treatment. Study the biodegradation in the SWD area to find out if the bioremediation is necessary. In case of the re-use purpose or continuation disposal of produced water there are a technologies available with a clear potential for a significantly reduction of the concentration of TPH, PAHs, and other hydrocarbons in the discharged produced water. Where proven, technologies to reduce or remove the soluble hydrocarbons are best applied as a final "polishing or tertiary" treatment after the removal of the dispersed oil phase (IAOGP, 2002).

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