Characterize the Process of Denitrification in Contaminated Shallow Groundwater by Hydrocarbon Using GIS System in Nizwa Area, Oman

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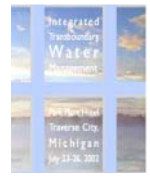

Abstract

Hydrocarbon and chemical data from groundwater wells in the Nizwa area of Oman have been compiled and integrated into a GIS system in order to characterize the contamination and the hydrocarbon behavior in groundwater. TPH screening analysis for hydrocarbon shows that all the peaks for the contaminated wells ranging between C_{15} to C_{32}, which means that the hydrocarbon contamination originated from oil product sources. The absence of low molecular weight hydrocarbons below C_{12} indicates that the hydrocarbon is old and has been subject to weathering and biodegradation. Denitrification process under anaerobic conditions prevailed in the hydrocarbon contaminated groundwater wells, which resulted in degradation of the hydrocarbon and disappearance of nitrate completely from the contaminated groundwater wells. It is suggested that a bioremediation process involving the addition of groundwater with high nitrate concentration to the contaminated aquifer could be possible under these conditions

Introduction

Groundwater resources in Oman are considered very precious and play a great role in the economical development. It is used practically as a main source for various purposes, domestic, agricultural, industrial, commercial and most important as a main source for drinking. The public water suppliers are obligated to furnish water to their consumer that meet the Omani drinking-water standard. Therefore, the government of Oman took all the precaution necessary to protect the groundwater from over exploitation and contamination.

In Oman there are more than 128,000 wells tapping the major aquifers and around 4,100 different types of Aflajes; 3,095 of them functioning and some of them its water originates from the groundwater (Fig.1).

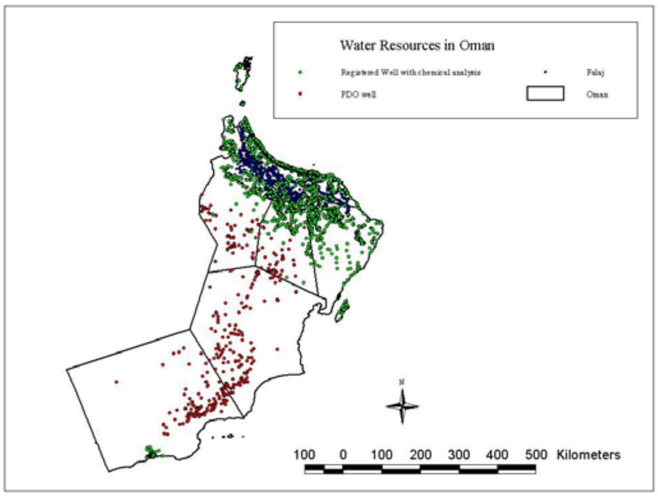

Fig.1Groundwater Resources in Oman

Groundwater contamination is one of the major problems facing the country and of great concern for the Ministries dealing with water and environment. The contaminated groundwater is not only reducing the available water resources for use, but also pose a threat to human health.

In Oman there are wide variety of materials that have been identified as contaminants in groundwater such as synthetic organic chemicals, hydrocarbons, inorganic cations & anions, and pathogens. These contaminants could originate from under storage tanks (UST), oil pipeline, septic tanks, municipal landfills, saltwater intrusion, oil injection wells and others. Nevertheless, some of these potential sources pose a greater threat to groundwater than others. Hydrocarbon leakage through UST or oil pipelines is an extremely great threat to the groundwater in different areas in the country. Groundwater contamination by hydrocarbons either dissolved in water or present as a separate liquid is an extremely serious threat to the quality of groundwater and soil facing Oman at different locations (Bajjali, 2000).

There are important health effects related to drinking water contaminated by hydrocarbon. Certain carcinogenic effects have been associated with benzene, which is an Environmental Protection Agency (EPA) defined class ***"A"*** carcinogen. Therefore, the maximum contaminant-level goal (MCLG) is set to zero by WHO and US-EPA for drinking water supplies. In addition, chlorinating water contaminated with hydrocarbon for the purpose of disinfecting the water (standard procedure in Oman) could cause chlorinated hydrocarbon, which is also harmful for human health.

2. Water Resources in Nizwa Area

This paper deals with hydrocarbon contamination and the process of denitrification in Nizwa area. Nizwa is the regional headquarters of the Interior Region and is considered a important major town, which provides all the public and private sector services to the citizens. The population of the Wilaya is estimated to be around 50,000 in 1999 around 70% of them is living in the town of Nizwa.

Groundwater sources are brought into production mainly via boreholes and dugwells. These are generally located in the wadi channels, which are the natural conduits for occurrence and movement of water. In Wilayat Nizwa there are a number of private and governmental wells and different types of Aflaj, which are scattered all over the Wilaya. The MWR database shows that in this Wilaya there are around 3,410 wells and 99 Falaj, with the majority being of the Ayni type (55 %) (Fig.2).

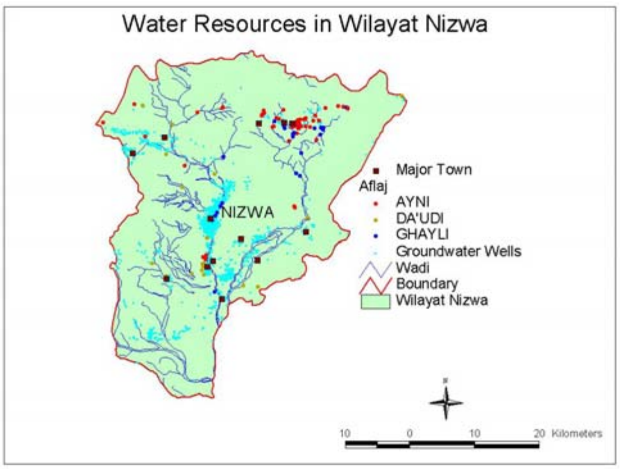

Fig2 Location of the Groundwater Wells and Falajs in the Wilayat Nizwa.

3. Hydrocarbon Contamination in Nizwa

In 1980, a free oil layer was detected floating on the top of the water table in some of the shallow groundwater wells located along Wadi Abyad. The groundwater contamination was presumably caused by oil product leakage from three sources; UST of old Shell fuel station, Electric Power Station (EPS) and repair garages next to Shell station (Fig.3).

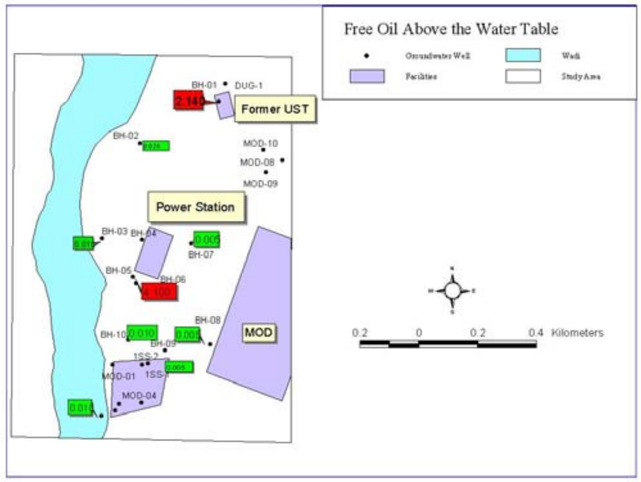

Fig.3 Thickness of free oil above the water table of the groundwater in Nizwa

Figure 3 shows the maximum thickness of the free oil in meters in a number of wells in the effected area. The recorded maximum thickness was 2.14 and 4.1 meters and found in BH-01 and BH-06, wells respectively. These two wells are located within less than one-kilometer radius from each other. Other wells (BH-03, BH-07, BH-08, BH-10) recorded free oil above the water table to be less than 1 cm.

Figure 4 shows the fluctuation of free oil in the BH-01 well from June 1992 to October 1999. The well is located some few meters from a former UST gas service station. The well is around 12 m deep and its water table fluctuated sharply. Fluctuations in the BH001 well were recorded to be between 4.85 and 10.14 meters for the last 7 years. The sharp rise and fall of the water table is due to the heavy pumping and groundwater abstraction from the wells in the vicinity and also to the recharge events during the rainy seasons. The fluctuation of the water table could effect and complicate the movement and thickness of the hydrocarbon in the groundwater wells. For example, if the water table rises faster than the oil table can rise "pocket" of free oil might become left below the water table.

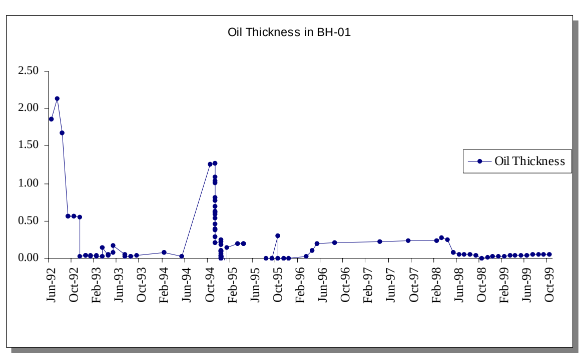

Fig.4 Fluctuation of the free oil above the water table in BH-01 well in Nizwa area

The flow of water and hydrocarbons is controlled by Darcy's law and depends upon the effects of density, viscosity, and relative permeability. Depending upon these factors, either the hydrocarbon or the water could have a greater velocity as the water table rises and falls. The thickness of floating LNAP in monitoring wells decreases when the water table rises. Oil will be trapped in the soil as the water table rises and hence there is less mobile oil able to enter the well. A sharp increase in the water level has been observed in BH-01 well in June-October 92, 94, 96, and 97 (Fig.4).

If the water table drops to a point where it is lower than any pervious time, the floating LNAPL may disappear. This may be due to the fact that the hydrocarbon may move slowly through the soil and does not drop at the same rate as the water table. Water table measurement between 1992-1999 showed that BH-02 and BH-07 wells had been reached almost to the bottom of the wells (Table 1).

NAME	Depth (m)	WL (min)	WL (max)	Oil Thickness (min)	Oil Thickness (max)
BH-01	12.20	4.86	10.14	0.000	2.140
BH-02	8.35	6.11	8.34	0.000	0.020
BH-03	12.26	4.90	7.30	0.000	0.010
BH-04	11.70	6.69	7.80	0.000	0.010
BH-05	10.85	5.30	7.72	0.000	0.005
BH-06	20.37	9.90	15.90	0.000	4.100
BH-07	12.84	2.42	12.49	0.000	0.005
BH-08	12.90	7.01	12.50	0.000	0.005
BH-09	13.57	6.44	9.71	0.010	0.005
BH-10	7.60	1.60	5.00	0.000	0.010
BH-11	12.10	2.46	4.57	0.000	0.010
BH-12	12.25	3.60	9.79	0.000	0.010
Note: WL - Water Level					

Table 1 Fluctuation of water table and thickness of hydrocarbon in groundwater

From the above we can see that the behavior of the LNAPL in the wells is extremely complex. The sharp fluctuation of the water table of the wells within the study area, which is listed in table 1, could give a false impression about the actual thickness of the hydrocarbon.

4. Geology and Hydrogeological Setting

The contaminated site is relatively flat with an average elevation of approximately 495 meters above mean sea level.

The local geology of the area consists of Samail Ophiolite Nappes, tertiary limestone and the alluvium. The contaminated shallow aquifer consists of gravel, which is more or less heterogeneous. At various location in the study area an outcrop layer of cemented gravels were observed. These impermeable layers exist also at depth and form one hydraulic unit with the gravel formation of the aquifer. The heterogeneity of the water bearing formation plays a big role in the movement and direction of the NAPL. Dissolved hydrocarbon pathways are different from NAPL pathways. It is also worthwhile to mention that sharp fluctuations of the water table and decreased volume of water in the aquifer, increase the time period to dissolve of contaminated mass. Other factors such as the natural attenuation due to advection, adsorption, biological degradation, dispersion, and volatilization can effectively reduce contaminant mobility.

Because the monitoring system in the area is limited to only specific wells that have been drilled in the early 1990, it is difficult to verify the existing phase of the hydrocarbon and its extent in the subsurface. Nevertheless, the hydrocarbon contamination, either as a free oil or dissolved in groundwater, is still posing a great threat to the water resources in the Nizwa area. The majority of the contaminated wells had become unused for water supply, but some of them still in use for irrigation.

5. Sampling and analysis

A field trip had been made on February 8, 2000 to the ISS wells in Nizwa area in order to characterize the groundwater condition in terms of hydrocarbon contamination.

Three wells within the territory of the ISS buildings had been tested to verify if the groundwater is still contaminated by hydrocarbon. The results of the analysis of the major cations and anions, oil and grease, and the total petroleum hydrocarbon (TPH) are presented in Table 2

Well No	Owner	Date	TPH	Oil & Grease	pH	TDS	Ca	Mg	Cl	SO4	HCO3	NO3	Mn
			mg/l	Mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
010/565	ISS-1	08-Feb-00	6.0	8.0	8.7	705.3	1.6	51.8	204.0	127.0	270.0	0.0	0.024
010/566	ISS-2	08-Feb-00	1.5	1.8	7.4	1184.0	33.6	97.0	300.0	1.6	420.0	0.0	0.24
010/567	MOD1	08-Feb-00	0.4	0.5	7.7	909.4	16.0	100.8	200.0	2.6	488.0	0.0	0.34

Table No2 Hydrocarbon and chemical analysis

6. Discussion

The total petroleum hydrocarbon (TPH) is not the perfect parameter to use in order to characterize the groundwater contamination by hydrocarbon (Zemo, D.A, Bruya, J.E, Graf, T.E, 1995). Nevertheless, it is the only parameter that could be analyzed at the laboratory of MEW and gave an indication of the level of hydrocarbon contamination of the groundwater. TPH analysis has numerous limitations and it is not recommended as a stand-alone method unless the results can first be consistently correlated over time as the oil ages.

The TPH concentration was found to vary between 0.4 to 6 mg/l. The highest value was recorded in the ISS-1 well. A thickness of 2.28 meters of free oil floating at the top of the well was measured in December 1994 (Ministry of Water Resources file, 1994). The well is located inside the ISS building and currently is abandoned due to the contamination.

In addition, a value of 8.0 mg/l of oil and grease, which also very high was recorded for the same well. Currently there is no free oil on the well, but a thin film of dissolved hydrocarbon was observed during the sampling.

The TPH is analyzed using gas chromatography, which separates the hydrocarbon compounds on the basis of their boiling point. All of the peaks that fall in a certain boiling point range are assumed to come from a petroleum hydrocarbon. Their mass is combined and the sum is assigned to the particular compound. For example, the entire peak that would fall in the C_4 to C_{10} range are assumed to come from gasoline and all in the C_{10} to C_{24} peaks are assumed to come from diesel fuel (Fetter, C, 1999). Table 3 shows that the peak for the three wells is ranging between C_{15} to C_{32}. This simply means that the hydrocarbon contamination is old and had been subject to weathering. The lower molecular weight (less than C12), which is more volatile and mobile have been lost due to volatilization and biodegradation. The unweathered hydrocarbon, especially the gasoline has peaks that in general elute between C_4 and C_{12}. Gasoline has a high concentration of monoaromatic hydrocarbons: benzene (C_6), toluene (C_7), ethylbenzene & xylene (C_8). The highest sum of C_{15} to C_{32} was recorded for the ISS-1 well, which means that the groundwater in this particular location still has the highest contamination level.

Parameters	Units	ISS-1	ISS-2	MOD-1
TPH	mg/l	6.00	1.50	0.40
C15	µg/l	2.40	3.60	< 0.001
C16	"="	12.10	6.30	0.06
C17	"="	29.80	9.30	0.30
C18	"="	54.10	10.30	0.47
C19	"="	47.90	7.60	0.50
C20	"="	70.40	9.70	0.73
C21	"="	39.50	6.10	0.67
C22	"="	19.50	4.00	0.87
C23	"="	12.40	2.00	1.10
C24	"="	10.40	2.00	< 0.001
C25	"="	3.80	1.00	1.60
C26	"="	8.00	0.86	1.90
C27	"="	6.00	0.48	1.60
C28	"="	5.20	0.16	1.50
C29	"="	4.40	0.24	1.50
C30	"="	3.40	0.20	1.30
C32	"="	2.00	< 0.003	0.90
Sum C15-C32	"="	331.30	63.80	15.00

Table No.3 High molecular weight of hydrocarbon

When the hydrocarbon contamination reach the groundwater and dissolve in it, their fingerprint changes dramatically due to differing solubilities of the various components of each product. For example, the solubility of benzene is 1780 mg/l, while the ethylbenzene is only 150 mg/l at 25 ^{o}C. Most of the compounds in petroleum distillates have very low water solubility. Gasoline will yield primary BTEX, other benzene and naphtallenes. Diesel fuel will yield the same compounds plus phenanthrene and anthracene.

From the results of our analysis it is impossible to determine the parent product of the dissolved phase hydrocarbons. In other-word it is not possible to verify if the dissolved hydrocarbons originated from the leakage of the UST of gas service station or the leakage of the waste oil from the EPS of the MEW. In addition, the results of the TPH analysis may indicate the presence of gasoline or diesel fuel when none is there. There are numerous petroleum distillates that are neither gasoline nor diesel fuel that fall within these two ranges (Powers, Villaume and Ripp, 1997). The result of the oil and grease concentration simply states that the groundwater is contaminated and the hydrocarbon biodegraded to a certain degree. Because BTEX compounds are absent at this stage of study, it is difficult to judge to which degree the biodegradation of the aromatic hydrocarbon had been gone.

The aromatic compounds, especially the BTEX are more volatile, soluble and mobile in groundwater. If we accept that the hydrocarbon contamination in groundwater originated from the UST of the gas service station and the pit of the EPS of the MEW, the contaminants will travel as LNAPL and aqueous phase liquid (APL) long distances depending on the velocity of the groundwater. The aquifer material consists mainly of quaternary alluvium and the average saturated thickness in the Abyad wellfield is around 12 m and the average permeability is around 40 m/d. This simply means that the groundwater velocity is fast and could spread the contaminant from its source faraway within a relatively short period of time. Nevertheless, the local geology shows that the aquifer materials is heterogeneous, a thick layer of compacted sediment had been documented in the lithology of the wells during the drilling. The impermeable formation usually decreases the velocity of the contaminated groundwater by hydrocarbon and also adsorbs it making it less mobile.

Once the hydrocarbon leaks into the groundwater it will be released at a rate that exceeds the ground water's ability to dissolve and carry away the hydrophobic constituents. Hence, the free phase fluids will flow away from the UST of the old gas service station and from the disposal pit facility at EPS as neat organic fluids. As these fluids flow through the porous media, they will leave a trail of residual saturated media behind. At some point, the entire mass of highly saturated organic fluid will be dissipated in the tail of residual saturated media. Dissolution into surrounding ground water will occur as the primary NAPL plume moves through the water saturated media and forms the secondary (cloud) APL plume. The contamination in the three sampled wells demonstrates only the dissolved hydrocarbon phase.

The aromatic hydrocarbon of the contaminant associated with the UST and the waste disposal pit can undergo biological degradation. The degradation of the hydrocarbon in general can be degraded under aerobic condition by microbes. The presence of dissolved oxygen in groundwater is an essential step to help the bacteria to consume the hydrocarbon. If all the oxygen is consumed, the oxidation of the hydrocarbon can still occur, but the oxidizing agents could be other chemical compounds such as the nitrate. The nitrate in the aquifer is an oxidizing agent that could be reduced by the action of the bacteria. This course is called denitrification, a process in which NO_3^- is reduced to N_2O or N_2. The nitrate concentration of the three wells is zero (table 2), while the groundwater in the vicinity has nitrate concentration higher than the natural abundance of nitrate in groundwater, which is around 5 mg/l. This emphasizes the important factor that nitrate plays an important role in consuming and degrading the hydrocarbon through what is called denitrification. Certain compounds in groundwater such as NO_3^- and SO_4^{2-} can be considered oxidizing agents (Stumm, W., and J.J.Morgan. 1970). The oxidized compound is the organic matter and in this particular case is the hydrocarbon. The NO_3^- is the most common contaminant in groundwater in Oman and it is very well documented in the shallow groundwater throughout the country (Bajjali, 1999). The NO_3^- concentration in the groundwater wells, in the vicinity area of the ISS contaminated wells by hydrocarbon is high. The concentration of NO_3^- in the groundwater wells located within 3-km radius from the ISS contaminated wells by hydrocarbon varies between 30 to 47 mg/l (Fig.5). The high concentration of nitrate in the area is due to the agricultural activities and leakage of sewage from septic tanks.

This means that there is a hydrochemical process responsible for the reduction of nitrate level in groundwater. In the literature, the phenomenon of the denitrification is very well documented. The denitrification is a process that requires a source of organic matter (hydrocarbon), abundant NO_3^-, and bacterial systems that are capable of denitrifying large amount of NO_3^-. The NO_3^- concentration is considered to be the electron acceptor and in general it will be reduced and also consume the hydrocarbon as illustrated in equation 1 (Freeze & Cherry, 1979).

$$CH_2O + 0.8NO_3^- \rightarrow 0.4N_2 + HCO_3^- + 0.4H_2O + 0.2H^+ \quad \text{Eq.1}$$

In case of toluene (C_6H_5-CH_3), the reaction will proceed if nitrate is available once the oxygen is consumed. Therefore the toluene will degraded as follow:

$$C_6H_5\text{-}CH_3 + 7.2H^+ + 7.2\,NO_3^- \rightarrow 7CO_2 + 7.6\,H_2O + 3.6\,N_2 \quad \text{Eq.2}$$

It is obvious that the denitrification process is the only mechanism responsible for NO_3^- concentration reduction.

The low level of sulfate in the ISS-2 and MOD-1 could also be due to sulfur reducing bacteria. This is a similar process to denitrification. In a closed aqueous systems containing organic materials and other nutrients necessary for growth of bacteria, the oxidation of hydrocarbon accompanied by consumption of oxygen is followed by reduction of NO_3^-, MNO_2, $Fe(OH)_3$, and the last is the SO_4^{2-} (Stumm and Morgan, 1970). The reduction of sulfate can be described as follow:

$$CH_2O + 0.5\,SO_4^{2-} \rightarrow 0.5HS^- + HCO_3^- + 0.2H^+ \quad \text{Eq.3}$$

This process produces more bicarbonate in groundwater. The HCO_3^- concentration recorded in the ISS-2 and MOD-1 is 420 and 488 mg/l respectively, and only 270 mg/l in the ISS-1 well. This phenomenon requires more detailed study in order to verify the effectiveness of the sulfur reducing bacteria under such complex conditions. This raises question as to whether this is related to the high concentration of the heavy molecular weight in the groundwater? We have observed from table 2 that the sum of the heavy molecular weight in ISS-1 is 5 to 22 times higher than the concentration of the heavy molecular weight in MOD-1 and ISS-2 wells respectively. This emphasize that part of the hydrocarbon contaminats are removed by biodegradation.

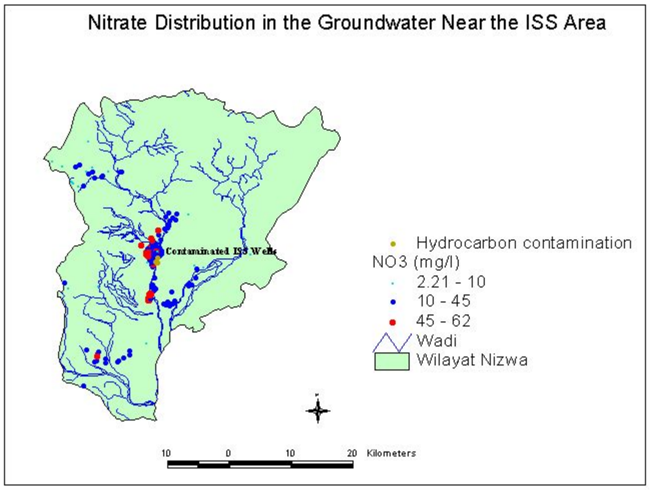

Fig. 5 Nitrate distribution near the contaminated groundwater wells by hydrocarbon

Understanding how hydrocarbons migrate through the subsurface is essential to select an appropriate remedial measure that will achieve success within a reasonable time frame. Since denitrification took place in situ, it is worthwhile to examine this phenomenon carefully in order to determine if the occurrence of nitrate and hydrocarbon reduction can be generalized and adopted as a way to clean the aquifer from the oil contamination. A further detail study of this phenomenon could lead to a low cost solution for the problem of hydrocarbon contamination and can be achieved locally

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