

Distribution of hydrocarbons and heavy metals pollutants in groundwater and sediments from northwestern Libya

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Received 21 January 2014; revised 24 February 2014

Concentrations of TPH, Zn, Pb, Ni, Cu, Mn, Cd and Mo were determined in groundwater and sediments collected from three sites (Sobratah, Al Ajaylat and Al Jmayl) in northwestern Libya. Present study show that Al Jmayl site is suffered from existence hydrocarbons and heavy metals pollutants. Al Jmayl groundwater has TPH, Cd, Pb, Ni, Mo and Mn content exceed than permissible levels of WHO by (11.6, 27.6, 15, 5.5, 2.85 and 2.3 times) respectively. Also, Al Jmayl sediments recorded the highest levels of TPH, Cd, Pb, Ni and Mn than other two sites. On the other hand, Al Ajaylat groundwater is not polluted by hydrocarbons, and it shows relatively less polluted by some heavy metals. Procured data show strong relationship between the distribution of hydrocarbons in both groundwater and sediments, and also with some heavy metals. Al Jmayl well may be exposed to indirect pollution by petroleum leakage from fuel station tanks near to well.

[Keywords: Groundwater, Heavy metals, Petroleum hydrocarbons, Pollutants, Sediments.]

Introduction

Environmental pollution has been the subject of considerable interest in recent years because of serious concern that high levels of pollutants may have detrimental effects on human health⁽¹⁻⁷⁾. Petroleum hydrocarbons and heavy metals pollution become a worldwide problem and took the attention of the different scientific authorities⁽⁸⁻¹²⁾. Libya has great area about 1,760,000km² and was characterized by fewer pollutants. Now, It is a major oil producer in African. Libya produces petroleum from five major sedimentary basins: Sirt basin, Murzuq basin, Kufra basin, Ghadames basin and marine Sobratah basin. Ghadames, Murzuq and Kufra basins are of Paleozoic age. Sirt and Sobratah basins are of Mesozoic-Ceozoic age⁽¹³⁾.

In the last few years, Libya beginning exposed to some environmental problem because of petroleum explorations processes and industrial activities, in addition to less environmental cultural, few environmental laws and weak in its applications. Also, there is relatively little available information on the distribution of petroleum hydrocarbons and heavy metals in groundwater, sediments and marine environments. Present work is focused on the determination of the total petroleum hydrocarbons (TPH) and heavy metals distribution in three important groundwater wells and the surrounding sediments area in northwestern Libya. This groundwater wells are the main sources of purifying drinking water

stations, farmers and animal husbandry in this region.

Material and Methods

Sobratah, Al Ajaylat and Al Jmayl (Fig. 1) are the major cities in the northwestern Libya. They covered about 300km² (between 32° 47' to 32° 55' N and 12° 04' to 12° 26' E) and were chosen for the present study. This area located in Jifarah plain. This plain is triangle shape extending in northwestern-southwestern Libya, which lie about 20-50m above sea level and rises up towards south⁽¹⁴⁾. Jifarah plain is characterized by land flat especially in north part. Also, it has groundwater aquifers and fertile soil, so there are many of agricultural lands. Quaternary deposits lie on Eocene and Miocene rocks in north part of the plain, while it lie on Triassic and Jurassic rocks in western side. In eastern side Quaternary deposits lies on Cretaceous rocks. The land of Jifarah plain consists of thin bed of sand which lies on sandyclay bed. Pleistocene rocks (siliceous sands and clastic sands) distributed along shore line, while sabkhat deposits appear in some localities as at Zuwarah city⁽¹⁵⁾. The study area characterized by good climate along year because of nearly to the sea, the average temperature is 19.7° c, wind average is 6.3 held/h and quaternary rain with average 220mm/y.

The groundwater in Jifarah plain present in three aquifers, the first is "Surface aquifer", which the saturation part reach to 10-100m, but it subjected to water crisis which appear in decreases of groundwater level that due to seawater intrusion. Also, this aquifer is prone to contamination due to its limited depth. Second aquifer is "Middle aquifer", which encountered between 100-350m below sea level and under artesian pressure especially in north part of the plain. Third aquifer is "Lower aquifer", which located at an elevation of approximately 1000m below sea level near Tripoli and between 300-400m in western side of the plain⁽¹⁶⁾.

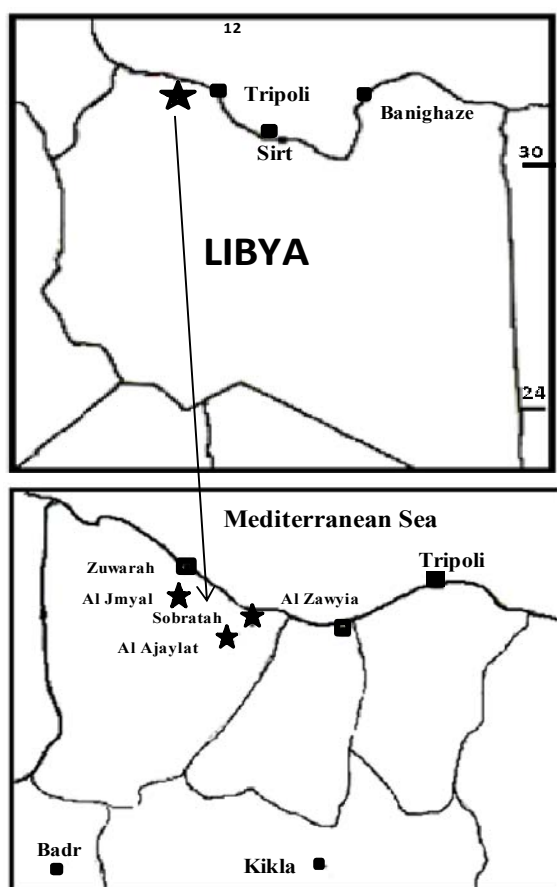


Fig. 1- Location map of the studied area

A total 45 samples were collected in January 2013 from three sites as (10 sediments about 250m away from borehole and 5 groundwater samples) from each site. For TPH in groundwater analysis, fifteen samples are directly take from three wells: Sobratah well (WS), Al Ajaylat well (WA) and Al Jmayl well (WG) in vacuum glassy bottles and send to analysis using Horiba instrument system. Also, used InfraCal TOG/TPH analyzer to measure TPH in sediment samples. Zinc (Zn), lead (Pb), nickel (Ni), copper (Cu), manganese (Mn), cadmium (Cd) and molybdenum (Mo) were measured in forty-five samples by using atomic absorption spectrophotometer after total digestion in a mixture of HF-HCl₄-HNO₃⁽¹⁷⁾, in the laboratory of Libyan Petroleum Research Center (LPRC).

Results and Discussion

Hydrocarbons are common and naturally occurred in the environment with varying concentrations. They are organic compounds composed of carbon and hydrogen atoms. Typically, hydrocarbons are broken down into three main classes: aliphatic, alicyclic and aromatics. TPH concentrations of the studied samples are obtained in Table 1. Hydrocarbons in water can be found as free floating, emulsified, dissolved or adsorbed to suspended solids⁽¹⁸⁾. The concentration distribution of TPH in groundwater samples shows that the maximum content (1.25ppm) is recorded in W4 from Al Jmayl well, while the minimum content (0.009ppm) is recorded in Al Ajaylat well. Also, the mean concentration of TPH in groundwater is (0.115, 0.011 and 1.22ppm) of Sobratah, Al Ajaylat and Al Jmayl wells, respectively.

The effect of petroleum leakage from one of hydrocarbons pipeline occurred in Al Zawia city are studied by⁽¹⁹⁾. The residual concentration of the TPH in groundwater was investigated between 2003 and 2006. Results

Table 1: The concentrations of TPH in studied samples

W/S	groundwater					Sediments									
	G1	G2	G3	G4	G5	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
WS	0.120	0.099	0.119	0.119	0.118	0.41	0.43	0.41	0.46	0.42	0.41	0.48	0.41	0.40	0.42
WA	0.009	0.011	0.011	0.011	0.011	0.42	0.41	0.41	0.40	0.39	0.39	0.39	0.38	0.41	0.39
WG	1.220	1.190	1.230	1.250	1.210	0.76	0.73	0.73	0.75	0.74	0.73	0.75	0.73	0.73	0.73

showed TPH in 2003 was (656.7 ppm), in 2004 was (587.5 ppm), and in 2006 was (385.2 ppm). These data show reverse relationship between TPH content and time. The most of the natural attenuation occurring may be attributed to dilution due to rainfall and dispersion by the facilitated groundwater flow⁽¹²⁾. Also, studied the groundwater contamination with TPH from accidental damage of Nigerian petroleum pipeline. TPH content in groundwater in the area of oil spillage was (757.9ppm) after 12 months of accident. These studies show present direct effects of hydrocarbons leakage on groundwater. In comparison with the present obtained data, TPH content were very lower than reported in these studies. This observation may be point to the study sites subjected to indirect polluted by hydrocarbons. The total petroleum hydrocarbons mean concentrations which recorded in groundwater of Al Ajaylat was within the permissible level ($< 0.1\text{ppm}$) according to World Healthy Organization (WHO), and also relatively in Sobratah site. On otherwise, Al Jmayl groundwater is enrichment in TPH content, which recorded 11.6 times exceed than WHO. This suggests that natural attenuation has not successfully reduced the hydrocarbon level below WHO limit. Generally, there is relatively little information about the ability to remove petroleum products from water. Contaminated aquifers can be remediated by "pump and treat" or in situ methods⁽²⁰⁾. The first step is to pump out any floating petroleum products that can be recovered. "pump and treat" involves flushing clean water through contaminated zones, recovering the contaminated water, treating it in above ground reactors, then re-infiltrating the treated water. In situ remediation involves the utilization of microorganisms within the subsoil to degrade the contaminants⁽²¹⁾.

In sediments samples, the concentration distributions of TPH show that the highest content (0.76ppm) recorded in S1 from Al Jmayl site and the lowest content (0.38ppm) recorded in S8 from Al Ajaylat site. The mean concentration of TPH in sediment samples are (0.425, 0.398 and 0.738ppm) for Sobratah, Al Ajaylat and Al Jmayl respectively. There is apparently relationship between the distribution of TPH in both groundwater and surrounding sediments (Fig. 2).

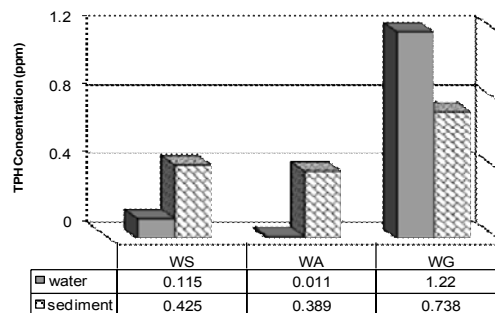


Fig. 2- The relationship between of TPH content in groundwater and sediments

The existence of hydrocarbons in groundwater and sediments may refer to indirect leakage hydrocarbons through sediments. It may be referring to partially damage in storage tanks of fuel stations nearly to Al Jmayl well. One of the most common sources of aromatic contamination in soil and groundwater is the release of petroleum products from leaking oil tanks. In general, the lower molecular weight aromatic compounds are the most water soluble components. Such incidents may lead to high concentrations of TPH in which case the probability of unacceptable taste and odour being detected by consumers will be significantly increased⁽²¹⁾. Some of the TPH compounds can affect on human central nervous system causes headaches and nerve disorder and also, have negative effects on blood, lungs, skin and eyes⁽²²⁾. The major anthropogenic sources of TPH in the environment are petroleum products in industrial applications, petroleum transportation pipeline leakage, petroleum removed trash, released and leakage in fuel stations, change car oil, storage fuel washing, oil exploration activities and seepage crude oil.

Trace amount of metals are common in water and sediments, and these are normally not harmful to our health. In fact, some metals are essential to sustain life. Calcium, magnesium, potassium and sodium must be present for normal body functions⁽⁴⁾. But when the concentrations of these essential metals or toxic metals exceed than the permissible levels, may be hazardous to our health. Toxic effect of metal depends on its characteristics. They become toxic when complexes are form with organic compound⁽²³⁾. The most important heavy metals from the point of view of water pollution are Zn, Cu, Pb, Cd, Hg, Ni, Cr⁽⁹⁾. Groundwater also may contain elevated concentrations of elements resulting from weathering processes of rocks⁽²⁴⁾.

Mean concentrations of heavy metals in studied samples are summarized in Table 2. Quality of the groundwater and status of metal pollution were evaluated on the basis of the quality standards suggested by the guidelines of WHO. The concentration distribution of heavy metals show that the three studied wells are enrichment in Pb, Ni, Cd, and Mo excesses than the permissible levels according to world healthy organization. Al Jmayl site recorded the highest contents for all studied heavy metals in both groundwater and sediments samples. On otherwise, Zn and Cu are likely to be derived from the natural water rock reaction processes in the aquifers since none of these metals exhibited concentrations values outside the WHO limits. This confirm with⁽²⁵⁾, who reported that the existence of Cu in groundwater is a result of minerals dissolving naturally from weathered rocks and soils. Also, this results show positive relationship between the distribution of heavy metals in groundwater and sediments (Fig. 3).

Table 2- The mean concentrations (ppm, nw=5 & ns=10) of heavy metals in studied samples.

Groundwater	nw= 5						
	Zn	Pb	Ni	Cu	Mn	Cd	Mo
WS	0.86	0.072	0.09	0.10	0.27	0.029	0.13
WA	0.89	0.056	0.07	0.101	0.31	0.021	0.11
WG	1.16	0.150	0.11	0.301	0.92	0.083	0.21
DWS	3.00	0.010	0.02	2.00	0.40	0.003	0.07
Sediments	ns= 10						
	Zn	Pb	Ni	Cu	Mn	Cd	Mo
WS	76	15	13	12	135	0.13	nd
WA	43	18	11	10	120	0.12	nd
WG	93	28	19	16	188	0.22	nd
USEPA ⁽²⁶⁾	50	10	40		600		
DWS	Drinking water standard (WHO, 2004)						
nd							
USEPA, 1983							

To identify the pollution magnitude by heavy metals in the studied sites, enrichment factor (EF) was calculated according to $EF = C_s / C_b$, where C_s is the concentration of element in sample and C_b is the content of element in standard permissible limits as background values.

Cadmium is generally classified as toxic elements. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with Zn⁽⁴⁾. Geologic deposits of Cd can serve as sources to groundwater and surface water, especially when in contact with soft acidic water⁽³⁾. Cd may enter water as a result of corrosion of galvanized pipe

or by petroleum pollutants. Mean concentration of Cd is (0.029 – 0.021 and 0.083 ppm) for WS, WA and WG respectively. Enrichment factor of Cd in groundwater recorded (27.6, 9.6 and 7) for Al Jmayl, Sobratah and Al Ajaylat sites respectively. The obtained data show Al Jmayl groundwater high polluted by Cd when comparison with the groundwater of northeastern Thailand which recorded (0.15µg/l)⁽⁷⁾. Cadmium has dangerous effects on human health where it accumulates with age, causes headaches, vomiting and cancer diseases⁽⁴⁾.

Lead is a dangerous element; it is harmful even in small amounts. Mean concentration of Pb is (0.072 – 0.056 – 0.15 ppm) in WS, WA and WG respectively. EF of Pb in groundwater was (15, 7.2 and 5.6) for Al Jmayl, Sobratah and Al Ajaylat sites respectively. In comparison this result with Pb content in groundwater of Kapas Island (Malaysia) was 0.84µg/l⁽²⁷⁾, and it was 16.7 µg/l in groundwater of northeastern Thailand⁽⁷⁾. This means that the groundwater in the three studied sites is highly polluted with Pb. Mean content of Pb in sediments was (15, 18 and 28ppm) in WS, WA and WG respectively. The enrichment factor of Pb in sediments was (2.8, 1.8 and 1.5) for WG, WA and WS respectively. This results show that Al Jmail site has high level of Pb than other sites. Pb content in both groundwater and sediments recorded the highest values in Al Jmail site.

Pb is mainly attributed to gasoline fuels containing high ratio of Pb tetrachloride⁽²⁸⁾. Groundwater may be contaminated by Pb due to enlistment either natural or enriched from anthropogenic activates in sediments and in some cases mineral weathering⁽²⁹⁾. High concentration of lead in human body can causes death or permanent damage to the central nervous system, the brain and kidneys⁽³⁾. Most of Pb we take is removed from our bodies in urine, however, there is still risk of buildup, particularly in children⁽⁴⁾.

Nickel is regarded as an essential element but toxic in large amount to human health. It is considered as carcinogenic to human⁽⁴⁾. The mean concentration of Ni in groundwater was (0.09, 0.07 and 0.11 ppm) for WS, WA and WG respectively. EF of nickel in groundwater was (5.5, 4.5 and 3.5) for WG, WS and WA respectively. This result shows the groundwater in the three studied sites was enrichment in Ni with nearly levels. Also, the

studied area has Ni content higher than recorded in groundwater of northeastern Thailand ($6.13\mu\text{g/l}$)⁽⁷⁾. Pollution of water with Ni may be causes hair loss and human eczema⁽⁴⁾. The mean concentration of Ni in sediments in studied sites was (13, 11 and 19ppm) for WS, WA and WG respectively. EF for these samples was (0.3, 0.27 and 0.47) for WS, WA and WG respectively. This results point to that, the study area has lower content of Ni and within the permissible levels for sediments.

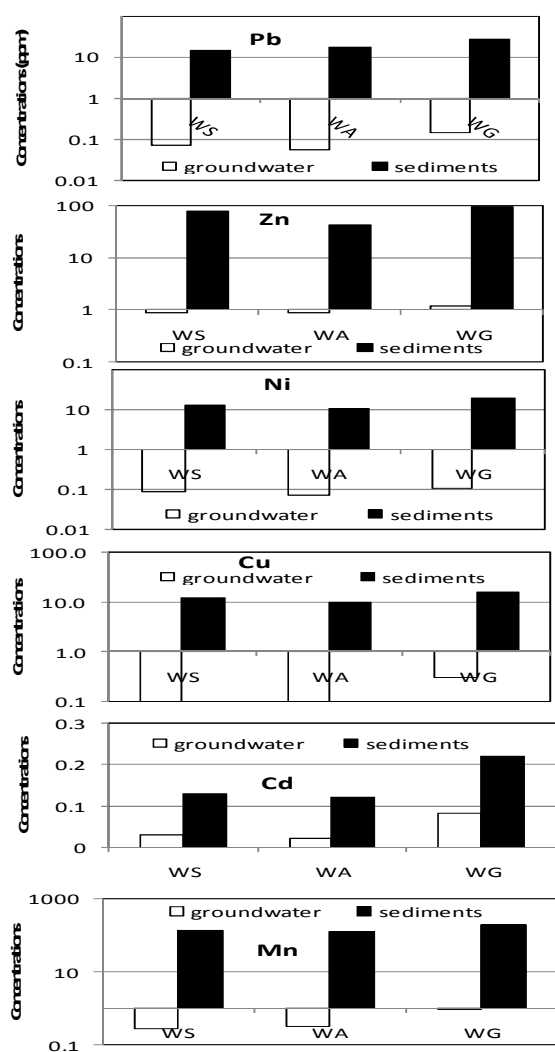


Fig. 3- The relationship between distribution of heavy metals in both groundwater and sediments

Molybdenum is an essential mineral and dietary nutrient which is a constituent of several mammalian enzymes⁽³⁰⁾. Mean concentration of Mo is (0.13, 0.11 and 0.2 ppm) in WS, WA and WG respectively. Enrichment factor of Mo in groundwater was (2.8, 1.85 and 1.57ppm) for WG, WS and WA respectively. This result shows no strong different significant

between three sites in Mo. Al Jmayl groundwater has the highest values than other sites. Molybdenum is present in very small amounts in human body⁽¹⁾. Human exposed to excess Mo from drinking water showed some elevation of blood and liver cirrhosis⁽⁴⁾.

The relationships of TPH with heavy metals and with each other in groundwater and sediments samples were determined by calculating the correlation matrix (Table 3).

The data obtained in table 3 show existing strong correlations among TPH in both groundwater and sediments, and among TPH in water and Cd in sediment, with ($r = \leq 0.01$). There is correlation between TPH and (Pb & Cd) in water and also between TPH and Cd in sediments. On other hand, the correlation coefficient of heavy metals with each other shows poorly existing between almost element except the following: Cu and (Mn & Pb), (Cd & Mo), (Zn & Mn) in water, also among (Pb^w & Mn^s, Cd^s), (Cd^w & Cd^s), (Mo^w & Ni^s, Mn^s), (Ni^s Mn^s), with ($r = \leq 0.05$). Also, there are reverse correlation Ni^w and Pb^s.

Conclusion

Total hydrocarbons level in groundwater in Al Jmayl well recorded 11.6 times exceed than the permissible levels of the world healthy organization. On other hand, Al Ajaylat and Sobratah wells were within the permissible levels. On otherwise, TPH content of the studied area recorded lower levels than other polluted sites exposed to accident petroleum pipelines damage. This observation may be point to the present studied area is exposed to indirect pollution by hydrocarbons. Al Jmayl sediments recorded the highest TPH content than other two sites. This results show a relationship between the distribution of TPH in groundwater and sediments. Human exposed to high levels of TPH from drinking water will be suffered from headaches, dizziness, nerve disorder and cancer diseases.

The groundwater of Al Jmayl, Sobratah and Al Ajaylat are partially polluted by Cd, Pb, Ni and Mo when comparison with world healthy organization. Also, they have high levels of these metals than recorded in other world groundwater sites. Al Jmayl groundwater has the highest levels of these metals than other

studied sites. Also, the highest content of Pb and Cd recorded in Al Jamyl sediments. While Zn and Cu are within permissible level of WHO that refer to the natural accumulation sources. Finally, the trend of hydrocarbons and heavy metals pollution in groundwater and sediments was: Al Jmayl > Sobratah > Al Ajaylat.

Table 3- Correlation matrix of studied heavy metals and TPH.

	TPH ^w	Zn ^w	Pb ^w	Ni ^w	Cu ^w	Mn ^w	Cd ^w	Mo ^w	TPH ^s	Zn ^s	Pb ^s	Ni ^s	Cu ^s	Mn ^s	Cd ^s
TPH ^w	1.000														
Zn ^w	0.985	1.000													
Pb ^w	0.997*	0.969	1.000												
Ni ^w	-0.947	-0.988	-0.919	1.000											
Cu ^w	0.996	0.996	0.987	-0.971	1.000										
Mn ^w	0.991	0.999*	0.977	-0.982	0.999*	1.000									
Cd ^w	0.999*	0.978	0.999*	-0.934	0.992	0.985	1.000								
Mo ^w	0.994	0.961	1.000	-0.906	0.981	0.970	0.997*	1.000							
TPH ^s	1.000**	0.987	0.996	-0.950	0.997*	0.962	0.999*	0.993	1.000						
Zn ^s	0.811	0.699	0.854	-0.580	0.758	0.724	0.832	0.870	0.805	1.000					
Pb ^s	0.954	0.991	0.928	-1.000	0.976	0.986	0.942	0.916	0.957	0.599	1.000				
Ni ^s	0.987	0.945	0.987	-0.883	0.970	0.956	0.992	0.999*	0.985	0.894	0.894	1.000			
Cu ^s	0.968	0.911	0.985	-0.837	0.943	0.926	0.977	0.990	0.966	0.931	0.850	0.996	1.000		
Mn ^s	0.992	0.955	0.999*	-0.897	0.977	0.965	0.996	1.000*	0.990	0.880	0.907	1.000*	0.993	1.000	
Cd ^s	1.000**	0.984	0.998*	-0.944	0.995	0.989	1.000*	0.995	1.000*	0.817	0.951	0.989	0.971	0.993	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

X^w element in water and X^s element in sediments.

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