Study of the Pollution of Misurata Port by Heavy Metals and Hydrocarbons

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***Abstract**:*

The work aims to measure concentrations of heavy metals, assess of hydrocarbons and to measure some of physicochemical parameters for assessment of environmental quality in Misrata port, Libya. The sea water samples were collected from five sampling sites for two months and analyzed to determine levels of five metals, selected hydrocarbons (diesel) and some of physicochemical property. In September, mean value of concentrations of the metals are 0.142 mg/L, 0.078 mg/L, and 1.447mg/L for Cd, Pb and Zn, respectively, while in October it was 0.1478 mg/L for Cd, 0.0230 mg/L Pb and 1.3502 mg/L for Zn. Concentrations of Cr and Cu were less than the detection limit of the used instrument. To assess metal contamination in sea water, the mean concentration of Cd, Pb and Zn was compared to the USEPA guidelines and found that the concentrations exceeded the guidelines. In general, the presence of hydrocarbons is similar in the different sampling sites and the aliphatic hydrocarbons (alkane) was common in all sites. According to all results, the seawater of Misrata Port is moderately polluted by heavy metals and hydrocarbons.

Keywords: Misrata Port, Heavy Metals, Hydrocarbons, Environmental status, Libya.

Introduction:

Beaches and coastal areas worldwide have seen in the past few decades, continuously exposure to numerous environmental pollutants among which the most potentially hazardous are toxic chlorinated compounds, heavy metals, residual chemicals and nuclear wastes, radioactive compounds and hydrocarbons from oil spillage accidents, In addition, discharges from desalination, power generation, and sewage [1]. Heavy metals and trace elements are present in coastal seas in limited amounts as non-degradable and non-toxic naturally occurring free elements. They contaminate the marine and coastal environment in large quantities but not particularly toxic free elements through different sources [2, 3]. Their cationic forms are dangerous to living organisms because of their capacity to bind with short carbon chains [4]. Petroleum pollution results in co-contamination by different classes of marine sediment the occurrence of marine sediments difficult to remediate [5]. Mediterranean coasts and harbors, especially the industrial ones, are exposed to crude oil hydrocarbons (HC) deriving mainly from intense maritime traffic of oil tankers, wastes of refineries, chemical industries, and oil pipelines [6, 7]. The thousands of different oil molecules have a wide range of physico-chemical properties and toxicity. The individual molecules within the four main groups of oil HC, saturated HC, aromatic HC, resins and asphaltenes, are also classified according to their molecular weight into light fractions (low molecular weight) and heavy fractions (high molecular weight). The latter includes the most recalcitrant compounds to degradation that tend to accumulate in the sediments of harbors and coastal areas nearby oil related facilities [5]. These hydrocarbons may become dangerous especially if they come into the alimentary chain, they form DNA adducts which can induce mutations, because of their carcinogenic and mutagenic properties [8].

Background and sample collection:

Study region: study region is located on the far western edge of the gulf of Sirt on the Mediterranean coast, east of Misrata in Qasar Ahmed [9]. With the coordinates between longitude 15° 13' 0.00" E and latitude 32° 22' 0.00" N. The total area of 190 ha, total quay length of 4159 m, depths range from 6-13 m, open storage yards of 60 ha [10]. (Fig. 1).

Figure 1: Sample location of study area Misrata Port

Sampling: Samples had been collected by using a homemade sampler at a depth of 30 cm below water level from the five different sites monthly in Misrata Port, as shown on the map (Fig. 2). for heavy metals, and were transported to the laboratory for analysis, and for the determination of hydrocarbons, samples were taken from the same sites and at the same time from the surface of the water, and then transferred to the laboratory.

Figure 2: The map of five sampling stations in Misrata harbor

Table 1. Data of water sampling sites in Misrata harbor.

Station	Coordinates		Remarks
	Latitude (N*)	Longitude (E*)	
S_1	22.38' 32° 22	0.11' 15° 13	Near to roads
S_2	22.33' 32° 22	1.55' 15° 13	Near to roads
S_3	22.24' 32° 22	2.89' 15° 13	Near to roads
S_4	22.24' 32° 22	4.25' 15° 13	Near to roads
S_5	22.23 ' 32° 22	5.81' 15° 13	Near to roads

Analytical procedure: sample preparation methods for heavy metal is the digestion procedure by using liquid oxidizing agents (HNO_3 + HCL) [11], then analyzed by atomic absorption spectrometer. Secondly, sample preparation method for organic compounds is the liquid-liquid extraction procedure (LLE) as described in APHA [12], using a separatory funnel, where a suitable solvent is used, and then analyzed by using Fourier transform infrared spectroscopy (FTIR), vibration spectroscopy as IR, using dispersive or interferometric instruments, has been extensively used in the last two decades in different kinds of analytical applications, including the analysis of fuels [13].

Statistical analysis: the data statistically analyzed using the STATISTICA software [14]. The means, standard deviations, minimum, maximum, range and Pearson's correlation were calculated of the metal concentrations in water samples.

Result and discussion

Descriptive statistics of the concentrations of heavy metals in Misrata Port are listed in table (**2**), also physico-chemical parameter. The metals concentrations decrease in the order Zn > Cd > Pb > Cu > Cr. The concentration of both Cr and Cu was less than the detection limit of the device. The mean concentration of Cd exceeded the USEPA saltwater guidelines [15], as well as the mean concentration of Pb, also exceeds the USEPA guidelines. Results of the comparison with the saltwater guidelines suggests that the seawater in Misrata Port are polluted by Zn, Cd and Pb. The anthropogenic activities are the main sources of these elements into the seawater. These sources include traffic emissions, atmospheric deposition, fossil fuel combustion, iron and steel production, and also may be natural sources. The high value of the (coefficient of variance) indicates a spatial change in the concentration values of metals, Pb showed a significant change in concentration in different samples, possibly due to local sources of Pb, as for Cd, it showed little change and Zn showed no apparent change.

The results of the Pearson's correlation coefficients and their significant levels ($P < 0.05$) are shown in table (3). Which are calculated between physicochemical parameters and heavy metals in seawater of the study area. The pH showed significant negative relationship with Pb (- 0.933). Correlation analysis provides an effective way to reveal the relationships between multiple variable and thus have been helpful for understanding the influencing factors as well as the sources of chemical components [16]. The EC has significant positive correlation relationships with T.D.S and also showed significant negative relationship with T (-0.948).

Table 2. Descriptive statistics of Heavy Metals conc.(mg/L) in sea water of the study area.

Month	Metals	Mean	Minimum	Maximum	Range	Standard Deviation	Coefficient of Variance
Sep.	pH	7.946	7.70000	8.03000	0.330000	0.139392	1.7542
	EC	38.660	36.70000	40.00000	3.300000	1.556599	4.0264
	TDS	19.416	18.50000	20.10000	1.600000	0.782835	4.0319
	T	26.100	25.80000	26.60000	0.800000	0.308221	1.1809
	Cd	0.142	0.10200	0.17000	0.068000	0.030295	21.2449
	Pb	0.078	0.00100	0.28100	0.280000	0.135667	172.8248
	Zn	1.447	1.24300	1.65500	0.412000	0.145904	10.0832
Oct.	pH	8.18000	8.00000	8.30000	0.300000	0.109545	1.33917
	EC	39.88000	39.10000	40.30000	1.200000	0.584808	1.46642
	TDS	20.24000	20.10000	20.80000	0.700000	0.313050	1.54669
	T	22.34000	22.10000	22.50000	0.400000	0.151658	0.67886
	Cd	0.14780	0.07000	0.23700	0.167000	0.059272	40.10301
	Pb	0.02300	0.01800	0.03200	0.014000	0.007810	33.95761
	Zn	1.35020	1.11300	1.47600	0.363000	0.146876	10.87813

Note: USEPA saltwater guideline for Pb → 0.008 ppm, Zn →0.08 ppm, Cd →0.0079 ppm, Cu →0.0031 ppm, Cr (VI) → .05 ppm.

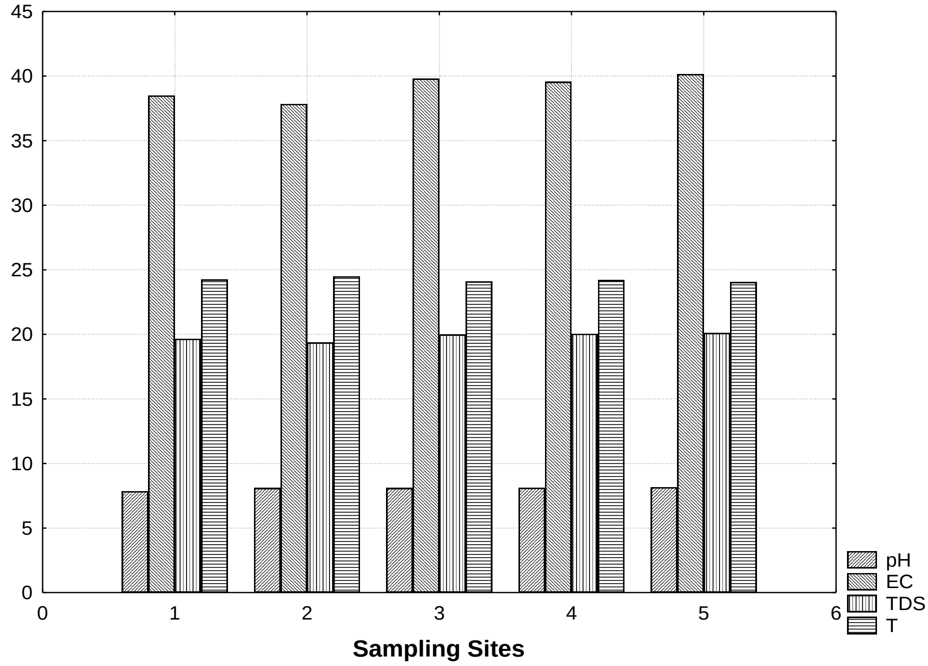

Fig 3. Spatial variation of the physicochemical parameters in sea water of the study area.

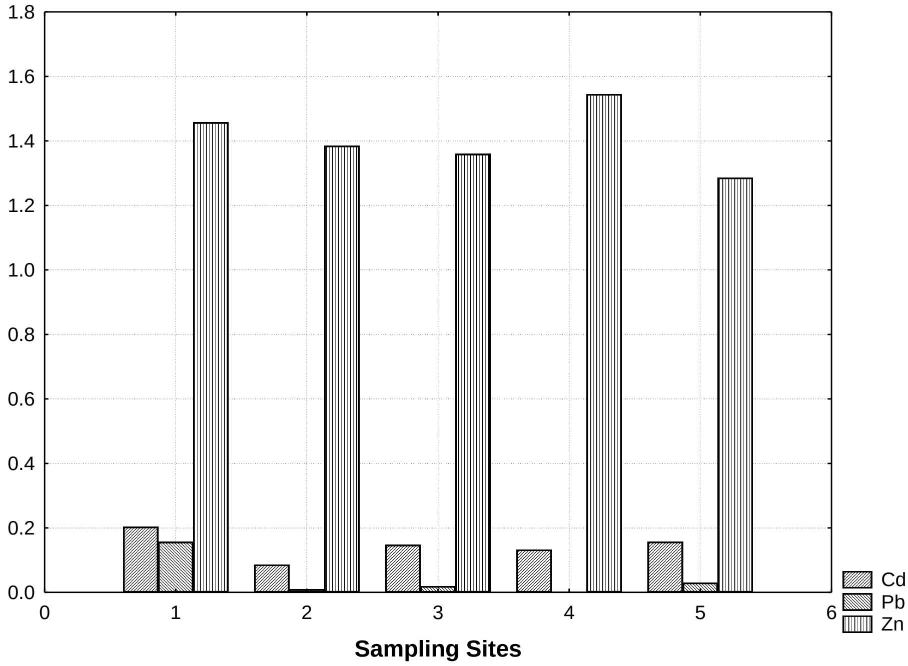

Fig 4. Spatial variation of the heavy metals conc. In sea water of the study area.

Table 3. Pearson's correlation coefficient of the physic-chemical parameters and heavy metals in sea water of the study area.

Variable	pH	EC	TDS	T	Cd	Pb	Zn
pH	1.000						
EC	0.502	1.000					
TDS	0.432	***0.978****	1.000				
T	-0.221	***-0.948****	-0.930	1.000			
Cd	-0.658	0.287	0.334	-0.564	1.000		
Pb	***-0.933****	-0.305	-0.259	-0.001	0.820	1.000	
Zn	-0.369	-0.265	-0.072	0.272	0.058	0.139	1.000

*Marked correlations are significant at $p < 0.05$.

In regard to the hydrocarbons assessment, we used Fourier Transform Infra-Red spectroscopy (FTIR). The FTIR spectra for the samples were collected using (PerkinElmer spectrum version 10. 4. 2). The samples were analyzed in the range of 4000-650 cm^{-1} under ambient conditions. In this study, we studied diesel fuels as marine pollutant. (Fig. 4) shows the FTIR spectrum of standard diesel sample, which

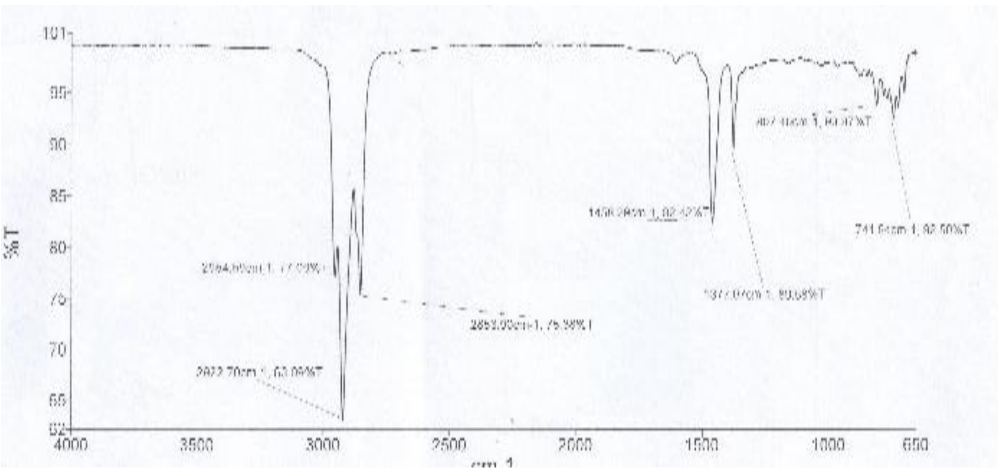

Fig. 4. FTIR spectrum of a diesel sample

is regarded as a reference for a comparison with the spectrum results (Fig. 5), that were collected from different stations, and were illustrated in (Fig. 2). In general, most of the results were similar to each other, and this is proved in the figures below:

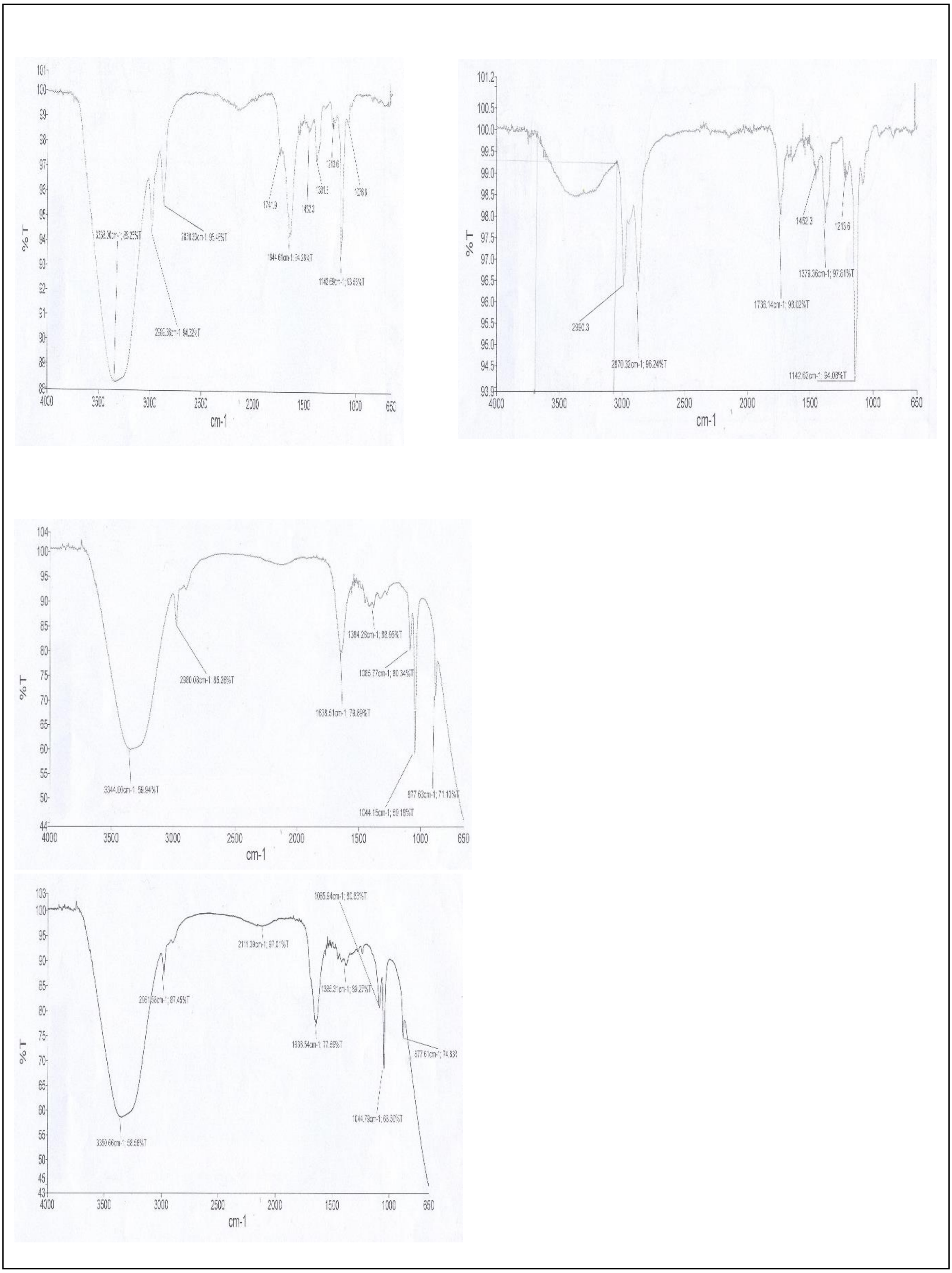

Fig. 5. FTIR spectrum results for the sample collection

The broad peak noted between 3000 and 3400 cm^{-1} is designated as the H-bonded O-H stretching vibrations. The peaks noted at the absorption values of 2989.36 and 2870 cm^{-1} indicate the C-H bending vibrations for the aliphatic hydrocarbon (alkane). (O-H stretching resulting from the residual water molecules). Because of the C-H stretching and bending from the collected sample, the peaks were seen to be corresponding to diesel standard e.g., a peak was noted at 2922.70 cm^{-1} (diesel C-H stretch), and 1377.07 cm^{-1} (diesel fingerprints).

Conclusions:

Heavy metals such as Pb, Zn, Cd, Cu, Cr concentration, were estimated in five sampling sites at the Misrata Port. The order of the mean concentration of tested heavy metals Pb, Zn, Cd, Cu, Cr concentration, were estimated in five sampling sites. The order of the mean concentration of tested heavy metals: Zn > Cd > Pb > Cu > Cr. International guidelines USEPA, applied for assessment of contamination. The mean concentration of Cd, Pb, and Zn exceeded the USEPA guidelines. About hydrocarbons assessment, most of the result were similar to each and showed the presence of aliphatic hydrocarbons (alkane) in all sites, so the seawater of Misrata harbor are moderately polluted by Heavy Metals and Hydrocarbons. All sampling sites suggest no overall pollution of site quality.

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الخلاصة:

يهدف هذا العمل إلى قياس تركيزات المعادن الثقيلة، تقيم الهيدروكربونات، وقياس بعض المعلمات الفيزوكيميائية، لتقيم الجودة البيئية في ميناء مصراتة، ليبيا. تم جمع عينات مياه البحر من خمسة مواقع، وأخذت العينات لمدة شهرين وتم تحليلها لتحديد مستويات خمسة معادن، وهيدروكريونات مختارة (الديزل)، وبعض الخصائص الفيزوكيميائية. في سبتمبر كان متوسط تركيزات المعادن 0.142 ملغم/ لتر، 0.078 ملغم/لتر، و 1.447ملغم/لتر لكل من الكادميوم، الرصاص والزنك على التوالى، بينما في شهر اكتوبر 0.1478 ملغم/لتر للكادميوم، 0.0230 ملغم/لتر للرصاص، و 1.3502 ملغم/لتر للزنك، وكانت تركيزات الكروم والنحاس أقل من حساسية الجهاز المستخدم. ولتقييم تلوث المعادن قى مياه البحر، تم مقارنة متوسط تركيز كل من الكروم، الرصاص، والزنك مع المعايير القياسية لوكالة حماية البيئة الامريكية، ووجد ان التراكيز تجاوزت الحدود المسموح بها، وبشكل عام كان تواجد الهيدروكربونات متشابه في مواقع أخذ العينات المختلفة، والهيدروكربونات الاليفاتية (ألكان) شائعه في جميع المواقع، ووفقا لجميع النتائج، فإن مياه البحر في مرفأ مصراتة ملوثة إلى حد ما بالمعادن الثقيلة والهيدروكربونات.

الكلمات المفتاحية: ميناء مصراته، المعادن الثقيلة، الهيدروكربونات، الحالة البيئية، ليبيا.