Original Research Article

Assessment of the Total Petroleum Hydrocarbons and Heavy Metal Concentrations in Soils around Car Washing Stations in Misurata, Libya

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ABSTRACT

Car washing generates a lot of wastewater which flows into our environment through a wastewater network or drains directly into the soil carrying with it contaminants. This study assessed the heavy metal and total petroleum hydrocarbon concentrations in wastewater from car washing stations and the surrounding soils in Misurata city, Libya. Pollution indices, such as the contamination factor (CF) and geoaccumulation index (Igeo), were used to assess the heavy metal and total petroleum hydrocarbon contamination status and ecological risk in the wastewater and soil from car washing stations. The results obtained in this study show that the average pH of the soil samples inside the stations ranged between 6.6 -8.53, while outside the stations the pH ranged from 5.97-8.63 and in sediments 6.8-8.44. The results for the heavy metal contamination studied indicate that the average cadmium concentration in soil samples inside and outside the washing stations ranged from 0.013-0.018 ppm and 0.013-0.25 ppm, respectively, and the average cadmium concentration in sediment samples ranged between 0.05-0.23 ppm. Also, the concentration of lead in soil samples inside and outside the stations and in the sediments ranged from 0.21-0.85, 0.19-1.06 and 0.21- 1.06 ppm, respectively. The total petroleum hydrocarbon concentration levels obtained in this study were between 389-7000 mg/kg for the soil samples inside the stations, whereas in soil samples outside the stations the concentration ranged from 27000-55000 mg/kg. Some environmental indicators were used to determine the environmental status of the particular washing stations studied.

Keywords: Total Petroleum Hydrocarbons, Car Washing Stations, Heavy Metals, Misurata- Libya, Index of Geoaccumulation.

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Introduction

Professional car wash stations are an easy way for consumers to remove dirt and grime from their vehicles. However, car washing is a highly water-consuming process and involves the use of chemicals, generating potentially toxic wastewater effluents [1]. Effluents from these professional car washes are, by law, supposed to drain into an oil/water separator or clarifier for pre-treatment before they are discharged into municipal wastewater treatment works.

It is realised that storm water contains a large variety of contaminants including oil and grease which have long been recognized as pollutants which can cause significant environmental damage [2]. There is, however, an under - appreciation of the ecotoxicological potential of effluents from the car wash industry possibly caused by a perception that wastewater from the car wash industry is not as severely contaminated as effluents from other industries [3] which may originate from previous research work carried out in three regions of the USA[4].

Pollutants of concern in car wash effluents include diesel range organics (DROs) such as oil and grease, carbon, asphalt, surfactants, salts, detergents, phosphates, ammonium compounds, heavy metals, acids, organic matter and microorganisms among others [3,5,6]. Some of these pollutants such as oil, grease, detergents, heavy metals and ammonium compounds can be directly toxic to aquatic organisms like fish, while others like nutrients can cause a shift in ecological balance should they be improperly managed and discharged [7]. Oily wastewater contains toxic components such as phenols, petroleum hydrocarbons and polyaromatic hydrocarbons (PAHs) which are inhibitory to plant and animal growth and is mutagenic and carcinogenic to humans [8]. Soils contaminated with petroleum products create widespread environmental problems due to their adverse effects [9]. It is becoming urgent to assess contamination in some sites in question, to remediate and monitor these cleaning processes and to evaluate the final quality of the soil. Total Petroleum Hydrocarbons (TPH) are an important group of environmental contaminants that are toxic to human and environmental receptors [10]. In 1999 the United States Environmental Protection Agency (USEPA) Site Program began its evaluation of field methods for the determination of TPH in soils. This was an ambitious project that involved the establishment of a TPH definition and the development of a reference method for its quantification. One of the methods selected for this evaluation was SW-846 Method 9074 [11,12].

The chemical composition of soil, particularly its metal content, is environmentally important because toxic metal concentrations can reduce soil fertility and can increase their input to the food

chain, which leads to the accumulation of toxic metals in foodstuffs and ultimately can endanger human health. Metals occur naturally in the earth's crust and their environmental presence can vary between different regions, resulting in spatial variations of background concentrations. The distribution of metals in the environment is governed by the properties of the metal and the local influences of environmental factors [13].

There is a dearth of information with regards to the contribution of car wash effluents in soil and water pollution in Libya. The fast growth of car wash service centres, as is the case in Misurata city, results in increased contribution of pollution into environmental water and soil. To the best of our knowledge, no studies have previously been carried out to investigate the contribution of car wash effluents to soil pollution in Misurata - Libya. The purpose of this study was to evaluate the Total Petroleum Hydrocarbons and Heavy Metal Concentrations in soils around professional car wash stations in the Misurata area.

Experimental

Material and Methods

Sampling techniques

Soil samples were taken from nine (09) car washing and service stations in Misurata city. At the sampling sites, about 50 g of soil sample were collected from inside and outside (20m) the stations by sweeping, using soft touch brush, scoop, trowel and plastic containers. Three samples were collected from each car washing or service station. The car washing and service station soil samples were stored in sealed plastic containers, carefully labelled and taken to the Chemistry Labs in the Department of Chemistry, Faculty of Science, Misurata University and the Libyan Petroleum Institute (LPI) Tripoli for analysis.

Physicochemical analysis

Soil moisture, electrical conductivity (EC) and pH were determined according to the methods enumerated by Adeniyi *et al.* [14].

Digestion of soil samples and heavy metals analysis:

The soil samples collected were air dried to a constant weight in the laboratory under room temperature for 24 hours and then sieved using a 200 μm mesh. A sample of 0.5 g was weighed into a Teflon bucket ; 6 ml HNO_3 acid and 3 ml HCl with 5 drops of H_2O_2 were added to the samples on a hot plate in a fume hood. The Teflon bucket was affixed to a rotor, placed in the microwave oven and programmed to commence the digestion process required for each sample. The digested samples were then diluted to 50 ml and transferred into the appropriate test tube. The concentrations of trace metals such as Cr, Cu, Zn, Mn, Fe, Pb, Ni, Co and Cd in the filtrate were determined using atomic absorption spectrometry.

Determination of Total Petroleum Hydrocarbons

Total Petroleum Hydrocarbons were determined by using an InfraCal TOG/TPH Analyser (model Hatr-T2 CH) as described in the user's manual [15].

Quality assurance

Strict QA/QC measures were adopted to ensure the reliability of the results. All chemicals and reagents used were of high purity. The glassware used was cleaned thoroughly with detergent and rinsed several times using deionised water. Deionised water was used for all dilution purposes. For the purposes of detection and determination of the quantification limits of the AAS instrument, a blank solution was analysed 25 times, and the standard deviations were calculated for the noise levels generated for each of the elements of interest. The detection limit (LOD) for each element was achieved as follows:

$$LOD = \frac{3 \times S}{m}$$

Where S is the standard deviation of the blank readings and m represents the gradient of the calibration curve for each element. The limit of quantification was calculated using 10s /m. The accuracy and reproducibility of the analytical procedure was determined by spiking and homogenizing three replicates of each of three samples selected at random. Triplicates of each sample were spiked with three different concentrations of the element of interest as follows: Cd (0.05, 0.1 and 0.2 mg/l), Cu (0.05, 0.5 and 1 mg/l), Fe (5.0, 10.0 and 15.0 mg/l), Zn (0.2, 0.5, and

1.5 mg/l) and Pb (0.5, 8.0, and 1.5 mg/l) and treated in a similar manner to the samples. The absorbances measured by the AAS instrument were converted to concentrations using standard calibration curves.

The car washing and service stations' soil contamination was assessed using two recognised indices namely the contamination factor (CF) (degree of contamination) and the index of geoaccumulation (I_{geo}).

Contamination factor

To assess the extent of the contamination of heavy metals and TPH in car washing and service station soils the contamination factor was used (Rastmanesh et al., 2010). The C^i f is the single element index which is determined by the relation:

$$C^i f = C^i_o - 1 / C^i_n$$

Where $C^i f$ is the contamination factor of the element of interest, $C^i_o - 1$ is the concentration of the element in the sample, C^i_n is the background concentration and for this study the continental crustal average was used [16]. $C^i f$ is defined according to four categories: <1 a low contamination factor, 1-3 a moderate contamination factor, 3-6 a considerable contamination factor and >6 a very high contamination factor.

Index of geoaccumulation

The index of geoaccumulation (I_{geo}) is widely used in the assessment of contamination by comparing the levels of heavy metal and TPH obtained with the background levels originally used with bottom sediments [17]. It can also be applied for the assessment of the contamination of the car washing and service station soil samples . It is calculated using the equation:

$I_{geo} = \log_2 (C_n / 1.5B_n)$

Where C_n is the measured concentration of the heavy metal and TPH in car washing and service station soil and B_n is the geochemical background concentration of the heavy metal or TPH (crustal average) [16]. The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithological variations in the sediments [18].

The following classification is given for the geoaccumulation index [19,20]: < 0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely strongly polluted and > 5 = extremely strongly polluted.

Statistical analysis

The statistical package for social sciences (IBM SPSS Statistics 22) was used for data analysis. Analysis of variance (ANOVA) was used to determine the statistically significant differences in the concentration of pollutants in effluents collected from different carwash stations at a 0.05 level of significance using the least significant difference (LSD) as the post hoc test. Descriptive statistics were used to generate the means and standard deviation for the data sets.

Results and discussion

1- pH

The results of the soil and sediment pH determinations are shown in Table 1. There was no significant difference (P>0.05) in the soil pH between the soil samples from the different stations. However, the pH ranged between 7.6 to 8.63 for soil samples outside the stations, 6. 6 to 8.53 for soil samples inside the stations and 7.6 to 8.44 for the sediments.

Soil pH is a major factor influencing the availability of elements in the soil [21]. Many metal cations are more soluble and available in the soil solution at low pH (below 5.5) including Cd, Cu, Hg, Ni, Pb, and Zn [22].

Table 1. Mean of pH in soils and sediments

Soil inside station	Soil outside station	Sediments	Stations code
7.06	8.26	8.44	**As1**
7.66	8.5	8.21	**As2**
8.3	8.58	7.6	**As3**
8.3	8.42	8.19	**As4**
6.6	8.1	6.8	**As5**
8.53	8.63	7.95	**As6**
8.45	7.97	8.22	**As7**
7.57	7.6	7.9	**As8**

Electrical Conductivity

The results of the soil and sediment electrical conductivity (EC) determinations are shown in Table 2. There was no significant difference ($P>0.05$) in the soil pH between the soil samples at different stations However, the EC measurements ranged between 505-1760 µS/cm for soil samples taken outside the stations with a mean of 1016 µS/cm, range 617-1730 µS/cm , for soil samples taken inside the stations with a mean 1098 µS/cm and range of 517-1748 µS/cm for sediments with an average of 1193 µS/cm.

From the correlation coefficient we have observed a weak correlation between the soil samples inside the stations and the aquatic layer inside the stations, while the weak reverse correlation was observed between soil samples and the aquatic layer inside the stations with soil samples taken from outside the stations.

Table 2. Mean of Electrical Conductivity in soils and sediments

Electrical Conductivity (EC) µS/cm			Stations code
Soil inside station	Soil outside station	Sediments	
1111	505	969	**As1**
1077	735	1725	**As2**
786	869	1402	**As3**
1324	868	1748	**As4**
705	1515	1140	**As5**
617	1215	517	**As6**
775	1760	1095	**As7**
1730	1320	950	**As8**

2- Moisture

Table 3 and Figure 3 show the results of the moisture content values obtained for the study samples, which ranged from 6-21% in soil samples from inside the stations with an average of 15.31%, while the moisture content values for soil samples taken from outside the stations ranged between 1.6% and 8.2% , with an average of 3.4%. The highest value of the moisture content in soil samples inside the stations was 21% for station As4, while the lowest value of moisture content was 6% for station As8, whilst the highest moisture content outside the station was 8.2% for As4, and the lowest value was 1.6% for the stations As1 and As6. Through the correlation coefficient there is seen to be a moderate direct correlation between the soils inside the station with the soil outside the station.

Table 3. Mean of Moisture in soils

Content of Moisture%		Stations code
Soil inside station	Soil outside station	
11.6	1.6	As1
20.2	1.98	As2
20.7	6.77	As3
21	8.2	As4
17	1.8	As5
7.2	1.6	As6
18.8	3.2	As7
6	2.04	As8

3- Heavy metal concentration

Heavy metals enter the environment by natural and anthropogenic means , such as natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest and disease control agents applied to plants, air pollution fallout, oil leaking from underground storage tanks and corroded metallic storage tanks among others. Soil and sediment samples from all the sites under investigation revealed varying concentrations of all the five heavy metals analysed (Pb, Cd, , Cu, Zn and Fe). Metal concentrations in the following ranges were determined : 0.089–0.90 mg kg^{-1} Cu; 0.21–1.06 mg kg^{-1} Pb; 0.013–0.25 mg kg^{-1} Cd; 0.17–1.24 mg kg^{-1} Zn; and 4.32–24.21 mg kg^{-1} Fe in dry soils in the sampling sites close to the carwash stations. However, in the ssediments, the metal concentrations varied between 0.77 and 0.80 mg kg^{-1} Cu; 0.21–1.06 mg kg^{-1} Pb; 0.05–0.23 mg kg-1 Cd; 0.14–0.91 mg kg^{-1} Zn; and 4.74 -16.01 mg kg^{-1} Fe (Tables2,3). Tables 2 and 3 show that iron (Fe), copper (Cu) and zinc (Zn) were the most abundant of the heavy metals in the carwash effluent samples. Comparison of the metal

concentrations with Tables 3 and 4 indicates that all the metals are well above the target concentration values. For metals like cadmium and lead that have no biological function this calls for public concern [23,24]. The elevated levels of these metals in the soil profiles constitute a serious threat to both the surface and ground water. These results tally with the observations of Moores et al. [25] who reported that Zn and Cu are the highest metal contaminants found in carwash effluents, derived mainly from tyres and brakepads , respectively Oknich [26].

Table 3. Mean of Cadmium, Lead and Copper (mg/kg) in soils and sediments

| Cu | | | pb | | | Cd | | | |
Soil inside station	Soil outside station	Sediments	Soil inside station	Soil outside station	Sediments	Soil inside station	Soil outside station	Sediments	Stations
0.089	0.19	0.46	0.43	0.43	0.21	0.13	0.05	0.05	**As1**
0.90	0.18	0.77	0.43	0.85	0.43	0.03	0.13	0.1	**As2**
0.31	0.37	0.15	0.85	1.06	0.21	0.08	0.08	0.1	**As3**
0.53	0.77	0.22	0.64	0.85	0.21	0.013	0.013	0.05	**As4**
0.38	0.1	0.077	0.21	0.85	1.06	0.13	0.25	0.23	**As5**
0.17	0.14	0.19	0.21	0.19	0.23	0.18	0.08	0.17	**As6**
0.55	0.51	0.48	0.43	0.41	0.39	0.09	0.15	0.09	**As7**
0.71	0.77	0.80	0.22	0.21	0.22	0.11	0.1	0.16	**As8**

Concentrations of the total petroleum hydrocarbons (TPH) in soil samples from carwash stations ranged between 389 and 70000 mg.kg^{-1} for soil inside the stations with a mean (TPH) concentration value of 24438.88 mg.kg^{-1} (Table 4) , while the concentrations of total hydrocarbons in soil samples outside the stations ranged between 27000 and 550000 mg.kg^{-1} , with a mean value of 37333.33 mg.kg^{-1}.

Total petroleum hydrocarbons (TPH) may move through the soil [27], especially TPH components like benzene, toluene, ethylbenzene, and xylene (BTEX) which exhibit particularly high mobility in soil [28]. This may result in TPH linked health concerns for people who depend on borehole water for domestic use since it is usually assumed safe and therefore not subject to frequent water quality monitoring as is the case with surface water. Spill prevention and implementation of management best practices remain the best remedy against any such occurrences. The findings of this research seem to concur with the observations of O'Sullivan et al. [29] that carwash wastewater is predominantly characterised by pollutants such as Pb, Fe, Zn, Cu and TPH.

Through the values of the correlation matrix for the soil from inside the station, we note that the highest value of the correlation coefficient in the matrix 0.856 strong direct correlation was between the two elements copper and iron, while the second highest value was the correlation coefficient of 0.549, which is an average direct correlation between the copper element and the moisture content.

Table 4. Mean of Zinc, Iron and TPH (mg/kg) in soils and sediments

TPH		Fe			Zn			
Soil inside station	Soil outside station	Soil inside station	Soil outside station	Sediments	Soil inside station	Soil outside station	Sediments	**Stations**
28740	-	4.32	7.03	15.79	0.24	0.17	0.62	**As1**
954	-	15.79	12.63	7.37	0.33	0.21	0.48	**As2**
2461	-	13.16	11.05	5.79	0.48	0.33	0.14	**As3**
1480	-	15.26	24.21	4.74	0.93	1.24	0.83	**As4**
389	-	10.53	5.79	6.84	1.19	0.36	0.31	**As5**
28487	27000	8.11	7.89	9.07	0.26	0.20	0.26	**As6**
63000	30000	11.28	11.31	11.2	0.31	0.28	0.25	**As7**
70000	55000	15.46	15.37	16.01	0.84	0.79	0.91	**As8**

Geo-accumulation index (i-GEO)

The calculation of environmental geochemical baselines is necessary to assess the current state of the environment and to provide guidelines and quality standards in environmental legislation and policymaking, especially in the evaluation of contaminated soils and in environmental risk assessment [30] The results of a recent study showed that the iGEO grades for the heavy metals studied here varies from metal to metal and site to site (table.5). According to the i-GEO values, Cd i-GEO states remain polluted in soil inside stations As2 ,As3 ,As4 ,As7, and as 8 This is because the geological accumulation coefficient is less than (0). However, in other stations it is indicated that the soil of these stations is slightly polluted by Cd , for example the soil inside stations As1, As5 and As6 where   i-GEO values range between 0.08-0.405. Furthermore, according to the i-GEO values, Cd i-GEO states remain unpolluted in soil outside stations As1, As3, As4, As, and As8. Slight pollution in soil is seen outside stations As2, As5, and As7) , where also there is slight pollution in the sediments of stations As5, As6, and As8.

Lead is the environmentally most toxic heavy metal of our group; it is significantly accumulated in the station soils, as indicated by their respective averages. According to our results, i-GEO values (2.245 -0.847), (0.747 - 2.466) and (0.847 - 2.466) of soil inside the stations, outside the stations and in the sediments, respectively, indicate a moderate to severely polluted category.

Table 5. Geoaccumulation index of the samples for heavy metals and TPH in the study sites

Heavy metals	Stations	Soil inside station	Soil outside station	Sediments
	As1	0.08	-0.875	-0.875
	As2	-1.386	0.08	-0.182
Cd	As3	-0.405	-0.405	-0.182
	As4	-2.223	-2.223	-0.875
	As5	0.08	0.734	0.651
	As6	0.405	-0.405	0.348

	As7	-0.288	0.223	-0.288
	As8	-0.087	-0.182	0.288
pb	As1	0.847	1.564	1.564
	As2	1.564	2.245	1.564
	As3	0.847	2.466	2.245
	As4	0.847	2.245	1.962
	As5	2.466	2.245	0.847
	As6	0.938	0.747	0.847
	As7	1.466	1.516	1.564
	As8	0.894	0.847	0.894
Fe	As1	0.102	0.589	1.398
	As2	1.398	1.175	0.636
	As3	1.216	1.041	0.395
	As4	1.364	1.826	0.195
	As5	0.993	0.395	0.562
	As6	0.732	0.705	0.844
	As7	1.062	1.065	1.055
	As8	1.377	1.371	1.412
Zn	As1	-2.381	-2.726	-1.432
	As2	-2.062	-2.514	-1.688

	As3	-1.688	-2.062	-2.92
	As4	-1.026	-0.738	-1.14
	As5	-0.78	-1.975	-2.125
	As6	-2.301	-2.563	-2.301
	As7	-2.125	-2.227	-2.34
	As8	-1.128	-1.189	-1.048
Cu	As1	-2.873	-2.115	-1.231
	As2	-0.56	-2.169	-0.716
	As3	-1.625	-1.449	-2.351
	As4	-1.089	-0.716	-1.968
	As5	-1.422	-2.757	-3.018
	As6	-2.226	-2.42	-2.115
	As7	-1.052	-1.128	-1.188
	As8	-0.797	-0.716	-0.677
TPH	As1	9.831	-	-
	As2	6.426	-	-
	As3	7.373	-	-
	As4	6.865	-	-
	As5	5.529	-	-
	As6	9.822	9.7686	-

As7	10.62	9.8739	-
As8	10.72	10.48	-

The values of the geological accumulation of iron in this study as shown in Table 5, ranged between 0.102 - 1.398 in the soil inside the washing stations, while the values of the geological accumulation index outside the studied stations ranged between 0.395 - 1.826, and the values of the geological accumulation of the sediment samples ranged between 0.195 - 1.412. It was evident through the values of the geological accumulation that there was moderate contamination in all the samples of the study sites as the values of the geological accumulation coefficient are higher than zero , which is indicative of a clean environment, and the highest value of the geological accumulation index was 1.826 determined in the soil outside station As4.

The values of the geological accumulation of the studied samples ranged from (-1.048) to (-2.92) in the soil inside the washing stations, while the values of the accumulation outside the study sites ranged between (-2.726) to (0.738), and the accumulation values in the sediment samples ranged from (-2.381) to (-0.78). From the values referred to above, we note that there is no pollution with zinc indicated at the sites of the study, as the values of the geological accumulation coefficient are less than zero, which indicates the absence of pollution and that the environment is clean [19,20].

It was evident through the values of the geological accumulation that there is no pollution with the copper element at the study sites as the values of the geological accumulation coefficient are less than zero, indicating the absence of pollution and that the environment is clean. According to the values of the geological accumulation index of (TPH) pollution in this study, which ranged between 5.529 - 10.72 in samples inside the washing station, while outside the study sites these ranged between 9.769 - 10.48. From the values of the geological accumulation coefficient, we note that the environment is categorised as being very polluted with petroleum hydrocarbons at the study sites, as the geological accumulation values are higher than (5).

Contamination factor

Contamination factors of various metals in the soils from the sampled sites are presented in Table 6. From these values, we note that there is no contamination detected with cadmium and copper at the study sites, as the values of the contamination factor were less than zero. In contrast, all sampling sites showed a moderate contamination of zinc, for which the sampling site As4 showed a maximum of (CF = 0.092) contamination. It was noted that the environment was clean in the other sites. Also, iron showed moderate contamination for sites As1 and As6 in the soil inside the washing stations and for the sites As1, As5 and As6 outside the washing stations, and very high iron contamination of site As4 outside the washing station. The results of the contamination factor showed a low contamination of lead in all study sites. Moreover, all sampling sites showed very high contamination of (TPH).

Table 6. Contamination factors of the samples for heavy metals and TPH in the study sites

Heavy metals	Stations	Soil inside station	Soil outside station	Sediments
	As1	-10.88	-11.88	-11.88
	As2	-12.13	-10.88	-11.25
	As3	-11.5	-11.5	-11.25
Cd	As4	-12.34	-12.34	-11.88
	As5	-10.88	-9.375	-9.625
	As6	-10.25	-11.5	-10.38
	As7	-11.38	-10.63	-11.38
	As8	-11.13	-11.25	-10.5
Pb	As1	-6.333	-6.333	-8.778

	As2	-6.333	-1.667	-6.333
	As3	-1.667	0.667	-8.778
	As4	-4	-1.667	-8.778
	As5	-8.778	-1.667	0.667
	As6	-8.778	-9	-8.556
	As7	-6.333	-6.556	-6.778
	As8	-8.667	-8.778	-8.667
	As1	1.277	2.319	5.688
	As2	5.688	4.473	2.45
	As3	4.677	3.865	1.842
Fe	As4	5.485	8.927	1.438
	As5	3.665	1.842	2.246
	As6	2.735	2.65	3.104
	As7	3.954	3.965	3.923
	As8	5.562	5.527	5.773
	As1	-0.293	-0.32	-0.146
	As2	-0.258	-0.304	-0.2
Zn	As3	-0.2	-0.258	-0.331
	As4	-0.027	0.092	-0.066
	As5	0.073	-0.247	-0.266

	As6	-0.285	-0.308	-0.285
	As7	-0.266	-0.277	-0.289
	As8	-0.062	-0.081	-0.035
Cu	As1	-0.578	-0.514	-0.343
	As2	-0.063	-0.521	-0.146
	As3	-0.438	-0.4	-0.54
	As4	-0.298	-0.146	-0.495
	As5	-0.394	-0.571	-0.586
	As6	-0.527	-0.546	-0.514
	As7	-0.286	-0.311	-0.33
	As8	-0.184	-0.146	-0.127
TPH	As1	27902	-	-
	As2	925.2	-	-
	As3	2388	-	-
	As4	1436	-	-
	As5	376.7	-	-
	As6	27656	26213	-
	As7	61164	29125	-
	As8	67960	53397	-

Contamination factors of various metals in the soils from the sample sites are presented in Table 6. From the above values, we note that there is no contamination with cadmium, and copper at the study sites, as the values of the contamination factor were less than zero, while all sampling sites showed a moderate contamination of zinc , where sampling site As4 showed a maximum of (CF = 0.092) contamination . It is to be noted that the environment was clean in the other sites. Also, iron showed moderate contamination for sites As1, As6 in the soil inside the washing stations, and sites As1, As5 and As6 outside the washing stations, and a very high contamination of site As4 outside the washing station. The contamination factor showed a low contamination of lead in all study sites. Moreover, all sampling sites showed a very high contamination of (TPH).

Conclusion

This analytical study demonstrates that carwash effluents are a potential public and environmental health hazard. Considering the dearth of information on monitoring and water quality discharge guidelines for the carwash waste water effluent in Libya, this study provides a basis for which the Department of Water Affairs can take on board serious considerations for legislating this industry to ensure public and environmental health protection. There is a need for municipal authorities to enforce environmental bylaws governing the operations of carwashes in Libya as a way of making sure that business operators adopt best management practices which are essential in addressing the root causes of surface water pollution.

Acknowledgments

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