



Petroleum hydrocarbon contamination assessment and characterization of three quagmire soils in the Gassi El Agreb oil field (Hassi Messaoud, Algeria)

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Abstract: The aims of the current study are the physicochemical characterization, spatial assessment and monitoring of hydrocarbon contamination in quagmire of three sites (Agreb, Gassi and Zotti) in the Hassi Messaoud region (Algerian Sahara), as a result of the presence of an important oil industry rejecting industrial wastewater. Samples were obtained from three different depths for each site. Total Hydrocarbons (THC) were determined by a gravimetric method, and the four (F1:C6-C10), (F2:C10-C16), (F3:C16-C34) and F4>C34 hydrocarbon fractions and BTEX (Benzene, Toluene, Ethyl-benzene and Xylene) were determined by using gas chromatography (FID). The results obtained show a high contamination with hydrocarbons in different sites and depths. The concentrations of THC, four hydrocarbon fraction and BTEX recorded on Agreb site in different depth were in this order: 51200–120000 mg/kg d.w.; <LOD – 59500 mg/kg d.w.; 2.4–90.8 mg/kg d.w. respectively; and for Gassi site, in this order: 59600–70300 mg/kg d.w.; < LOD – 43000 mg/kg d.w.; 8.5–112 mg/kg d.w. Finely they were in the following order: 18100–19200 mg/kg d.w.; <LOD – 9130 mg/kg d.w.; 2.75–65 mg/kg d.w. for Zotti site. Statistical analysis demonstrated an important site effect of THC and the three hydrocarbon fractions except for F4. However, there is no site and depth effect for BTEX. On the other hand the depth effect is significant just for THC, F1 and F2 of hydrocarbons. This variation can be attributed to the difference of physicochemical parameters between studied sites.

Introduction

Petroleum is the main source of energy required for industry and daily life. Nowadays, the contamination resulting from the activities related to the petrochemical industry has become a serious environmental problem because their wastewaters commonly contain substances considered as persistent organic pollutants (POPs), e.g. hydrocarbons with high molecular weight like Polycyclic Aromatic Hydrocarbons (PAHs) and with low molecular weight like Benzene, Toluene, Ethylbenzene and Xylene (BTEX), which are considered harmful and highly toxic (Mozo et al. 2011, Paliulis 2021) The pollution of soils and subsoils with hydrocarbons results from the cumulative consequences of various human activities. This contamination, neglected until recently, is worrying because of its environmental, health and socioeconomic consequences (Colin 2000).

The Hassi Messaoud region belongs to the eastern Algerian Sahara characterized by a strong oil industry, mainly oil

drilling, quagmires, exploration of production units, refining, etc. For its surface area and these reserves, Hassi Messaoud represents a strategic area; it has the largest oil field in Algeria and occupies the central part of the Saharan platform.

The discharge of petroleum products into the environment causes an immense environmental damage that may directly or indirectly affect the human health and the ecological systems, both marine and continental (Jiang et al. 2010). In addition, the petroleum spillage causes explosion risks and the contamination of ecosystems (water, air and soil), which may affect both soil structure and its agricultural fertility (Mauricio-Gutiérrez et al. 2020). Petroleum products are generally toxic compounds and some of them have presented carcinogenic, genotoxic and/or mutagenic potential for several organisms; they can be transported over long distances and bioaccumulate in the food chain where they can reach high concentrations in living organisms (Ozcan and Aydin 2009, Ping et al. 2011, Moscoso et al. 2012, Khairy 2014, Weinstein and Lohmann 2014, Rota et al. 2014). Aside from carcinogenicity,

mutagenicity and genotoxicity, they also have been reported to cause asthma and other respiratory diseases (Jung et al. 2012, Rosa et al. 2011), cardiovascular diseases (Xu 2010, Clark 2012) and birth defects (Langlois et al. 2013). The evaluation of oil pollution by means of quantitative and qualitative analyzes proves to be very expensive although it is essential in providing quantified physicochemical data. In addition, these analyzes do not allow us to know the impact of these pollutants on the living environment. Nevertheless, these measurements make it possible to know the pollution type and measure different concentrations of the pollutants present and their effects (Greene et al. 2000). It is in this context that our study is placed, which consists of diagnosing the soil tested from three samples taken from a quagmire at the level of the three deposits of the Gassi El Agreb oil field and try to comprehend site and sampling depth effects on physicochemical parameters and petroleum hydrocarbons distribution.

Experimental

Description of the sampling sites

Presentation of the study site

The study was carried out in the region of Gassi El Agreb field (referred to "GEA complex"). It is located about 100 kilometers southwest of Hassi Messaoud in the Wilaya of Ouargla in southern Algeria (30°48'0" N and 5°30'0" E) (Fig. 1). The dominant climate on sampling site is the desert climate (dry, very high heat), with a maximum temperature of 49.6°C and minimum of -3.3°C. The average rainfall ranges from 5 mm to almost zero.

The study site is composed of three oil fields: El Agreb, Zotti and El Gassi.

- El-Gassi, with an area of 207 km², is divided into two main entities: Gassi-Nord and Gassi-Core, and consists of 24 oil production wells;
- Zotti, with an area of 77 km², contains five oil production wells;
- El-Agreb, covering an area of 162 km², is made up of 34 wells.

However, the solid wastes or swamps produced were stored in 90 swamps spread over the 3 oil fields, of which 49 are located at the El-Gassi field, 3 are located in the Zotti field and 38 at the El-Agreb field.

Samples collection

Three soil samples were collected from different sites and depths and then we proceed to homogenization to have an average sample for each site and depth. The choice of sampling sites takes into account their position vis-à-vis the petrochemical field, accessibility, soil quality and the age of the sloughs. Three quagmires were sampled with the dimensions recorded in Table 1.

For each quagmire, three samples were taken along a vertical plane at the following depths:

- Sample n ° 1 (S1): between 20 cm and 70 cm;
- Sample n ° 2 (S2): between 70 cm and 1.20 m;
- Sample n ° 3 (S3): > 1.20 m.

After receipt of the samples at the laboratory, secondary sampling was carried out by quartering approximately 10 Kg of the aggregate sample. The soil samples were air-dried at

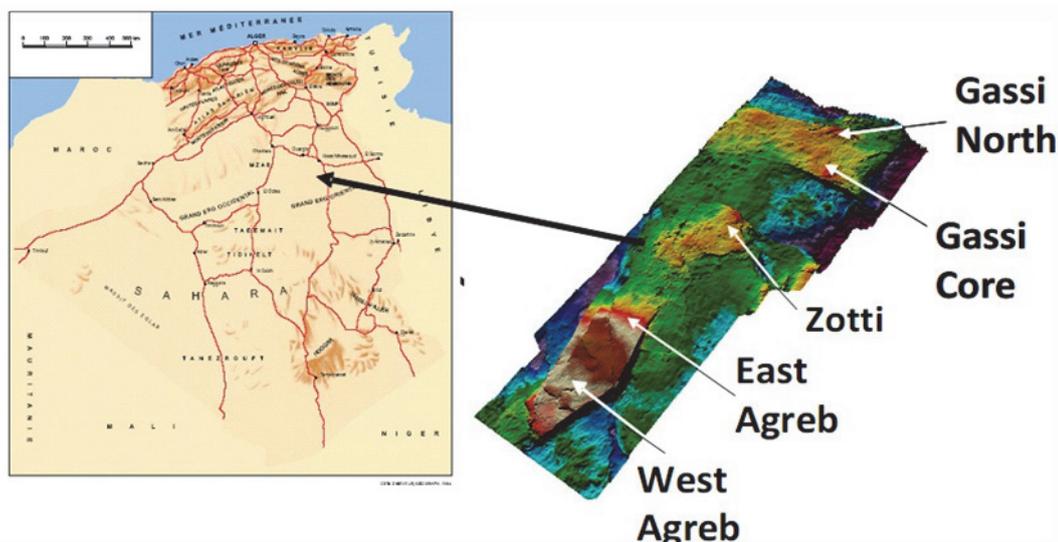


Fig. 1. Location of Gassi El Agreb complex with the three oil fields: El Agreb, Zotti and El Gassi

Table 1. Specifications of the quagmires used in the study

Quagmire name	Length [m]	Width [m]	Area [m ²]	Depth [m]
Agreb	17	12	204	2–4
Gassi	33	19	627	2–4
Zotti	38	22	836	2–4

room temperature then sieved through a mesh smaller than 2 mm. The samples were stored in polyethylene bags at 4°C before analyses.

Physicochemical characterization

The physicochemical analyses were carried out in accordance to the following French standards for grinding (NF ISO 11464). Residual humidity (NF ISO 11465), pH water + KCl (NF ISO 10390), granulometry (5 fractions – NFX 31-107), dry matter (NF ISO 11465), gravimetry (NF ISO 11465), temperature (NF ISO 11265), conductivity (NF ISO 11265), sodium (NF ISO 9964-3), potassium, calcium, magnesium (French Norm X 31-108), total nitrogen (NF ISO 13878), and density (ASTM C 128-97) (Zappellini et al. 2018).

Total HydroCarbons (THC) determination

Total hydrocarbons were determined using the Gravimetric method as described by Fusey et al. (1973, 1976, 1981). This method can be simply done by evaporating the extraction solvent and the residue weighing. The abiotic (evaporation process) loss was previously estimated in the marked sterile vials. For the extraction from the soil, the technique was slightly modified. According to this technique, we could determine the quantity of hydrocarbons present in the sample to be analyzed. The principle of the method consists of the following points:

(1) The sample to be analyzed was poured into a separating funnel. (2) A few drops of Methyl Orange and 0.2 mL of 50% HCl were added in order to acidify the sample. (3) Chloroform (best solvent for extraction of organic phases) was added for a volume equal to half of the sample volume. (4) The mixture was well shaken with opening from time to time to let the gas escape and then it was settled for some minutes. Finally, the upper phase was filtered through Na_2SO_4 to eliminate all traces of humidity. The solvent containing the organic phase was recuperated in a beaker previously weighed and placed in a stove until total evaporation. The final sample was weighed and the obtained quantity of the residue was calculated using the formula below:

$$Q_{\text{Total}} \text{ (ppm)} = \frac{W_f - W_i}{V_s}$$

where:

Q_{Total} – is the quantity of the total hydrocarbon, W_f – the final weight of the sample, W_i – the initial weight of the sample, and V_s – the volume of the sample (Belahmadi et al. 2021).

Petroleum Hydrocarbons Analyses

Chromatographic analyses of petroleum hydrocarbons were conducted according to the CCME Tier 1 Method – Reference method for the Canada-wide standard of petroleum hydrocarbons (CWS – PHC) in Soil (CCME 2001). The four fractions of hydrocarbons tested were F1 through F4. Volatile hydrocarbons are the F1 fraction (C6 to C10 hydrocarbon range) and benzene, toluene, ethylbenzene and xylene (BTEX). Extractable hydrocarbons are the F2 to F4 fractions (F2 is the C10 to C16 hydrocarbon range, F3 is the C16 to C34 range and F4 is the C34 to C50 range). The complete method description is provided in CCME (2001a). (CCME 2001). Briefly, volatile hydrocarbons (F1 fraction) were extracted from a 10 g soil sample with methanol (separating methanol

from the soil and then adding methanol to a purging vessel used for determination of volatile organics). For F2, F3 and F4 fractions, a mixture of acetone/hexane solvents (50:50) in a Soxhlet apparatus was used for the extraction. The solvent recovered from the extracted sample was dried using sodium sulphate and then treated in column chromatography with silica gel to remove polar material. A 1.0 μL aliquot was injected into an Agilent Technology gas chromatography system 7890A equipped with an Auto Sampler 7693 (Agilent Technology) and Flame Ionization Detector (FID). Data were acquired and processed using Agilent OpenLAB Chromatography Data System (CDS) Chemstation Edition for integrated peak areas, peak heights, and elution and analysis times. The GC used a MXT®-1 columns (nonpolarphase, Crossbond® dimethyl polysiloxane) with a maximum temperature capacity of 450°C, 15 m \times 250 μm \times 0.1 μm dimension. Splitless injection was used for all the experiments. The carrier gas used was helium, the make-up gas was nitrogen, and hydrogen was used as the fuel gas. The injector and detector temperature was set at 350°C.

Quality assurance and quality control (QA/QC) consisted of the analysis of field and laboratory blanks, field and analytical duplicates and spiked controls. In our study, the method blank and blank spike used clean sand. The blank spike and matrix spike were extracted after adding the commercial standards. For the standard mixture of F1-BTEX, BTEX, the stock solution had 2000 mg L^{-1} of n-decane, n-hexane, toluene, benzene, ethylbenzene, o-xylene, m-xylene, and p-xylene. The stock F2 and F3 standard contained 5000 mg L^{-1} of phytane, pristane, n-octadecane, n-heptadecane, n-decane, n-hexadecane, n-tetratriacontane, and o-terphenyl. All chemical standards were purchased from Sigma-Aldrich. The following criteria were met: blanks were below detection limit, duplicate values were within 30% of one another and spiked controls were returned within 10% of target value. The CWS method prescribes comprehensive QA/QC procedures that were met (CCME 2001). A chromatogram of an extracted soil sample is shown in Fig. 2.

Statistical analysis

Statistical analyses were performed using XLSTAT (Inc. Corporation. 2014) software. Data normality was checked using the Shapiro-Wilk test. Since data sets were normally distributed, they were analyzed using variance analysis (ANOVA) and comparison of means was done by Honestly Significant Difference (HSD) Tukey's test for investigating site variations of physicochemical characteristics and hydrocarbons concentrations. In addition, Principal Component Analysis (PCA) was applied to highlight the main factors that influence the hydrocarbons distribution, investigate the relationship dependency between them and physicochemical parameters. The critical level of significance was set at ($p < 0.05$) for all tests.

Results and discussion

Physicochemical parameters

The granulometry analysis of the soils of the three sloughs taken at different depths shows the dominance of the sand fraction, with low levels of clay and silt. The soil of Gassi is the

richest in clay at 2 m depth with 12.67% and the poorest at 1 m depth with 0.82%. Silt is frequent in all soils at all depths with percentages varying between 3.28% (minimum value recorded at the Zotti site on the surface) and 27.41% (maximum value recorded at the Agreb site on the surface) (Table 2).

Despite the differences observed in the different particle size parameters (between the different sites studied and the different sampling depths), the statistical analyses do not show any significant effects on the site. However, from the depth point of view, there is a very highly significant effect ($p = 0.0001$) for clay and very fine sand, an effect also highly significant for silt ($p = 0.006$) and a significant effect for coarse sand. Whereas for fine sand there is no depth effect (Table 2).

For the temperature, we can observe that values vary depending on the depth of the sample and the site studied (Table 3). The maximum value was recorded at the Agreb site of 21.7°C in sample E1 (taken between 20 cm and 70 cm) and a minimum of

20.2°C was noted in E2. The temperature values of the Gassi site are between 20.2, 20.4 and 20.5°C. The Zotti site recorded values, which decrease with depth: 21.4, 20.9 and 20.3°C.

The slough soil at the three sites was also found to have an alkaline pH, with a maximum value of 11.2 in El Agreb's E2 sample (Table 3). For the other two sites, the alkalinity increases with the depth of the sample.

For electrical conductivity, the results were highly variable between sites (Table 3). The Zotti site recorded a very high maximum value of 57600 $\mu\text{cm}/\text{cm}$ in sample E3 and a minimum value of 956 $\mu\text{cm}/\text{cm}$ was noted in E2 from the Gassi site.

From table 3 also we can see that the Zotti site was the richest one in dry matter compared to the other two sites. The maximum and minimum values of dry matter were observed in the Agreb site with 88.8% in E3 and 32.1% in E1 (Table 3).

Since the soil was sandy, our results show that the soil of Agreb's E1 was clearly moist (67.9%) (Table 3). The humidity

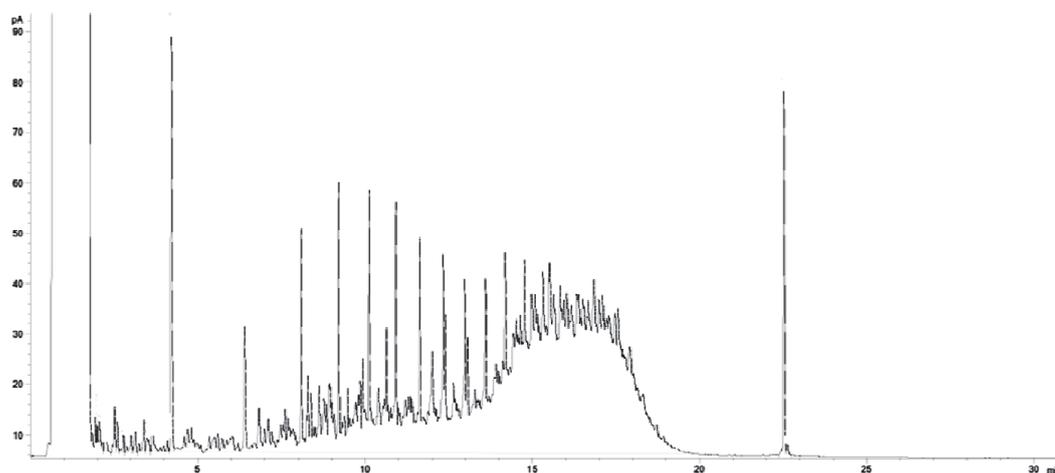


Fig. 2. GC-FID chromatogram of Petroleum Hydrocarbons extracted from a soil sample

Table 2. Soils granulometric parameters

Site	Depth [m]	Clay [%]	Silt [%]	Very fine sand [%]	Fine sand [%]	Coarse sand [%]
Agreb	0	1.170	27.410	20.090	21	30.330
	1	10.650	16.790	25.890	22.790	23.880
	2	7.820	15.560	31.070	23.780	21.770
	average	6.546	19.920	25.683	22.523	25.326
Gassi	0	2.830	4.960	2.220	67.530	22.460
	1	0.820	20.520	21.290	40.280	17.090
	2	12.670	18.470	26.590	22.460	19.810
	average	5.440	14.650	16.7	43.423	19.786
Zotti	0	1.4	3.280	1.390	65.310	28.620
	1	8.360	5.710	15	42.520	28.410
	2	11.210	23.180	36.990	16.580	12.040
	average	6.990	10.723	17.793	41.470	23.023
Control	average	0.9	4.320	2.490	64.310	27.980
Site effect (p)		0.424	0.161	0.170	0.086	0.359
Depth effect (p)		0.000	0.006	< 0.0001	0.146	0.042

of the other sites was between 17% and 23%. On the other hand, the soil density in the three sites was not very variable with a minimum value of 2.25 in E2 from Gassi and a maximum of 2.55 in E3 from Zotti (Table 3).

The exchangeable cation analysis reveals that the soil of the Zotti site was rich in sodium with a maximum value of 72500 mg/kg d.w. recorded in E3 and a minimum value of 1450 mg/kg d.w. present in E2 of the Gassi site. We noted also that Zotti site was rich in calcium with a maximum value of 221000 mg/kg d.w. recorded in E2, the minimum value was 6880 mg/kg d.w. present in E3 of El Agreb site.

It was also noted that the soil of the El Gassi site was rich in potassium with a maximum value of 5780 mg/kg d.w. recorded in E1, the minimum value was 667 mg/kg d.w. present in E1 of the Zotti site. The same observation for magnesium was noted, with a maximum value of 18200 mg/kg d.w. recorded in E3 (Zotti). The minimum value was 1460 mg/kg d.w. present in E3 of the El Agreb site (Table 3).

For total nitrogen, the soil of the three studied sites shows a richness with a maximum value of 781 mg/kg d.w. recorded in E2 and a minimum value of 435 mg/kg d.w. present in E3 in the Zotti site (Table 3).

Despite the differences observed in various physicochemical parameters and the sites studied or the sampling depths, the statistical analyzes show no significant effect (Table 3).

THC and PHC (F1, F2, F3 and F4)

Total hydrocarbons (THC)

Total hydrocarbons (THC) concentration in soil sampling sites at different depth levels vary from one site to another and from one depth to another on the same site. The highest average was recorded at Agreb with 76633 mg/Kg d.w. and the lowest average was that of Zotti soils with 19266 mg/Kg d.w. These results indicate that the soils of Gassi were the most polluted at the surface, while the soils of Agreb were the most polluted at depth. Zotti soils were the least polluted, with concentration average of 19266 mg/Kg d.w. (Table 4 and Figure 3).

Petroleum HydroCarbon fractions (PHC)

> F1 (C6-C10)

The concentrations of Petroleum HydroCarbons (PHC) F1 (C6-C10) in sampling site soils vary from one site to another and from one depth to another on the same site also. The highest average was recorded in Gassi with 608 mg/Kg d.w. and the lowest average was that of the soils of Agreb with 429 mg/Kg d.w. These results indicate that the most polluted soil at the surface is the Agreb soil, while the most polluted soils at 1 m and 2 m depth are the Zotti and the Gassi soils respectively. (Table 4 and Figure 3).

> F2 (C10-C16)

A large variation in the F2 (C10-C16) fraction content was noted from one site to another and at the same site also. From Tables 4 and Figure 3, it can be seen that the lowest content was found at Zotti site in the surface, however the highest value was registered at the Agreb site at a depth of 1 m with a respective values of 7930 mg/Kg d.w. and 52300 mg/Kg d.w. The results showed that the soils of Agreb site were the most polluted ones followed by those of Gassi and Zotti sites (Table 4 and Figure 3).

> F3 (C16-C34)

In the case of F3 (C16-C34) fraction, the results showed that the concentrations in the different soil samples sites change from a site to another and also from one depth to another on the same site. The highest average concentration was recorded in Agreb site with 45866 mg/Kg d.w. and the lowest one was found in Zotti site soils with 11 mg/Kg d.w. Those results indicate that the soils from Gassi site were the most polluted at the surface and at 2 m depth, while the soils of Agreb site were the most polluted at 1 m depth. (Table 4 and Figure 3).

> F4 (>C34)

For the F4 (>C34) fraction, the concentrations were lower than the limit of detection (LOD= 0.6 mg/Kg d.w.) at the different sites despite the variation in depth (Table 4 and Figure 3).

Table 3. Soil physicochemical parameters

Sites	Depth [m]	T [°C]	pH	Electrical Conductivity [μS/cm]	Dry matter [%]	Humidity [%]	Density [g/cm ³]	Na ⁺ [mg/kg d.w.]	K ⁺ [mg/kg d.w.]	Ca ²⁺ [mg/kg d.w.]	Mg ²⁺ [mg/kg d.w.]	Nitrogen Kjeldahl [mg/kg d.w.]
Agreb	0	21.7	9.850	29200	32,1	27.9	2.530	34400	2660	70500	5220	586
	1	20.2	11.2	13600	70.9	29.1	2.5	14900	5780	66200	7180	649
	2	21	9.010	2210	88.8	11.2	2.450	13900	667	51800	1890	664
Gassi	0	20.5	8.520	5830	78.3	21.7	2.440	3310	1090	36100	2060	498
	1	20.2	9.41	1964	74.5	25,5	2.250	1450	895	160000	2300	660
	2	20.4	10.2	956	76.1	23.9	2.45	2880	850	221000	2650	781
Zotti	0	21.4	8.59	4110	82.2	17.8	2.38	4360	703	6880	1460	554
	1	20.9	8.840	4970	77.9	22.1	2.4	6900	908	91300	2240	676
	2	20.3	10.4	57600	81.1	18.9	2.550	72500	2860	95300	18200	435
Control	average	19.9	10.7	1019	80.1	22.8	2.750	5400	4750	24100	5300	537
	Site effect (p)	0.408	0.626	0.508	0.500	0.500	0.348	0.437	0.337	0.299	0.591	0.578
	Depth effect (p)	0.092	0.247	0.144	0.541	0.773	0.327	0.459	0.087	0.112	0.623	0.531

BTEX**➤ Benzene**

A large variation in benzene content was observed from one site to another and in the same site at different depths. It can be seen that the most polluted soils were in the Gassi site at 2 m depth and the Agreb site in surface with 112 mg/Kg d.w. and 45.3 mg/Kg d.w. values respectively (Table 4 and Figure 4).

➤ Toluene

For the toluene concentrations, we found that they change in the different sites and in different depths at the same

site also. The highest average was recorded in Gassi site with 44.63 mg/Kg d.w. and the lowest one was observed at Zotti site with 18.32 mg/Kg of d.w. These results showed that Agreb site soils were the most polluted at the surface, Zotti site soils at 1 m depth and finally Gassi site soils were the most polluted at 2 m depth (Table 4 and Figure 4).

➤ Ethyl-benzene

The results showed a large variation in the ethyl-benzene content between different sites and at different depths (Table 4). From Table 4 and Figure 4, it can be seen that the most polluted soil was from Gassi site at 2 m depth and from Agreb site at

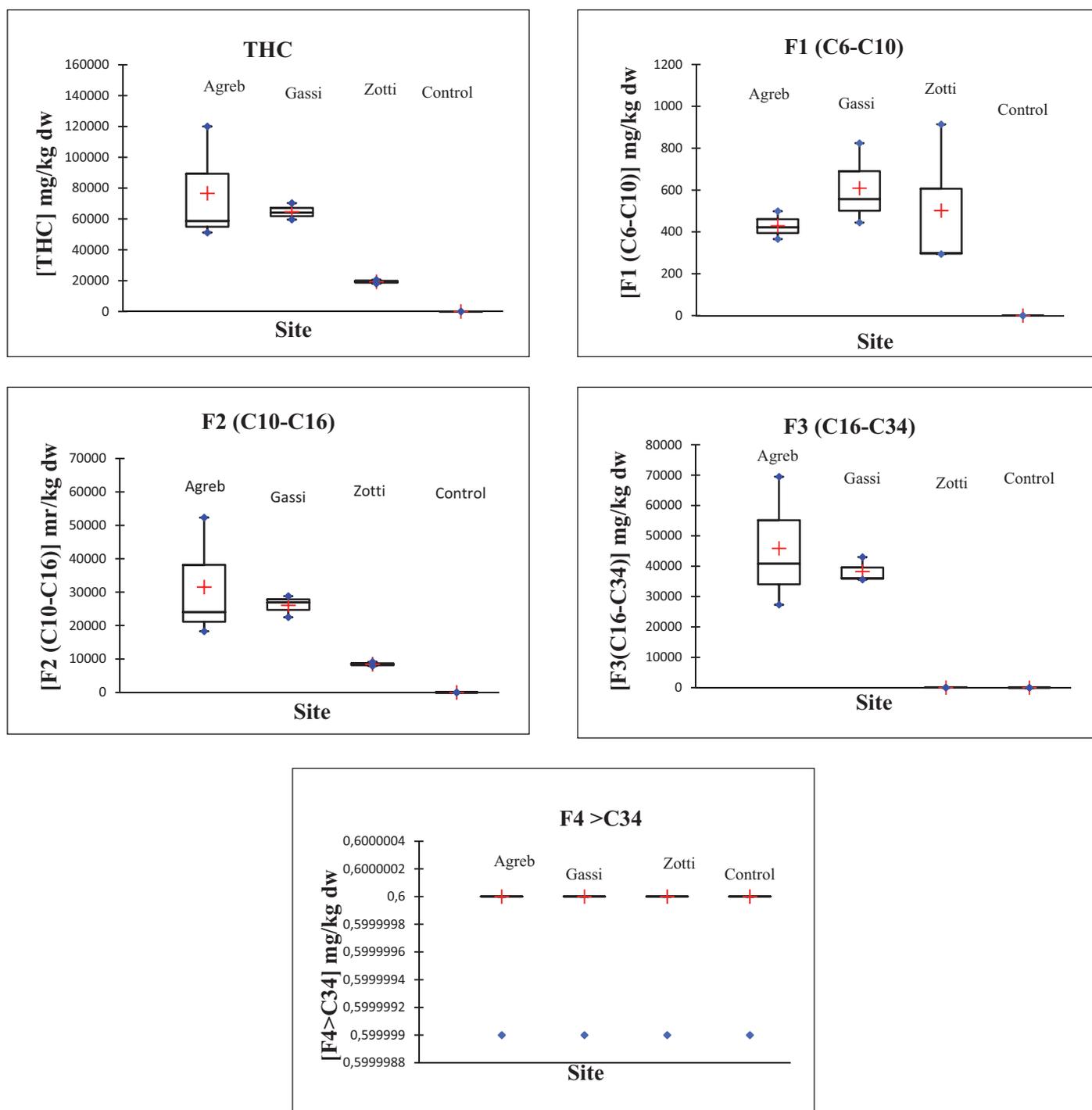


Fig. 3. THC and different petroleum fractions concentrations in the three sampling sites

the surface with the respective values of 116 mg/Kg dw and 79.2 mg/Kg dw, while the soil of Zotti was the most polluted at a depth of 1 m with concentration of 27.6 mg/Kg dw.

➤ O-Xylene

In the case of the O-Xylene, a large variation was also noted at the different sites and depths. It can be seen that the most polluted soils were in the Gassi site at 2 m depth and Agreb site at the surface with 129 mg/Kg d.w. and 90.8 mg/Kg d.w. values respectively. For Zotti site the highest concentration (40 mg/Kg d.w.) was registered at 1 m depth. (Table 4, Figure 4).

➤ m+p-Xylene

m + p xylene concentrations vary from one site to another and in different depths studied. The highest average was recorded in Gassi site with 58.03 mg/Kg d.w. and the lowest one at Agreb soil site with 35.88 mg/Kg d.w. These results indicate that the soils of Agreb were the most polluted at the surface and the Gassi soil was the most polluted at 1 m and 2 m depth. (Table 4 and Figure 4).

According to Baumard et al. (1998), contamination in soil can be classified into four different levels: low (<0.1 mg/Kg d.w.), moderate (0.1–1 mg/Kg d.w.), high (1–5 mg/Kg d.w.) and very high (> 5 mg/Kg d.w.). The results obtained in

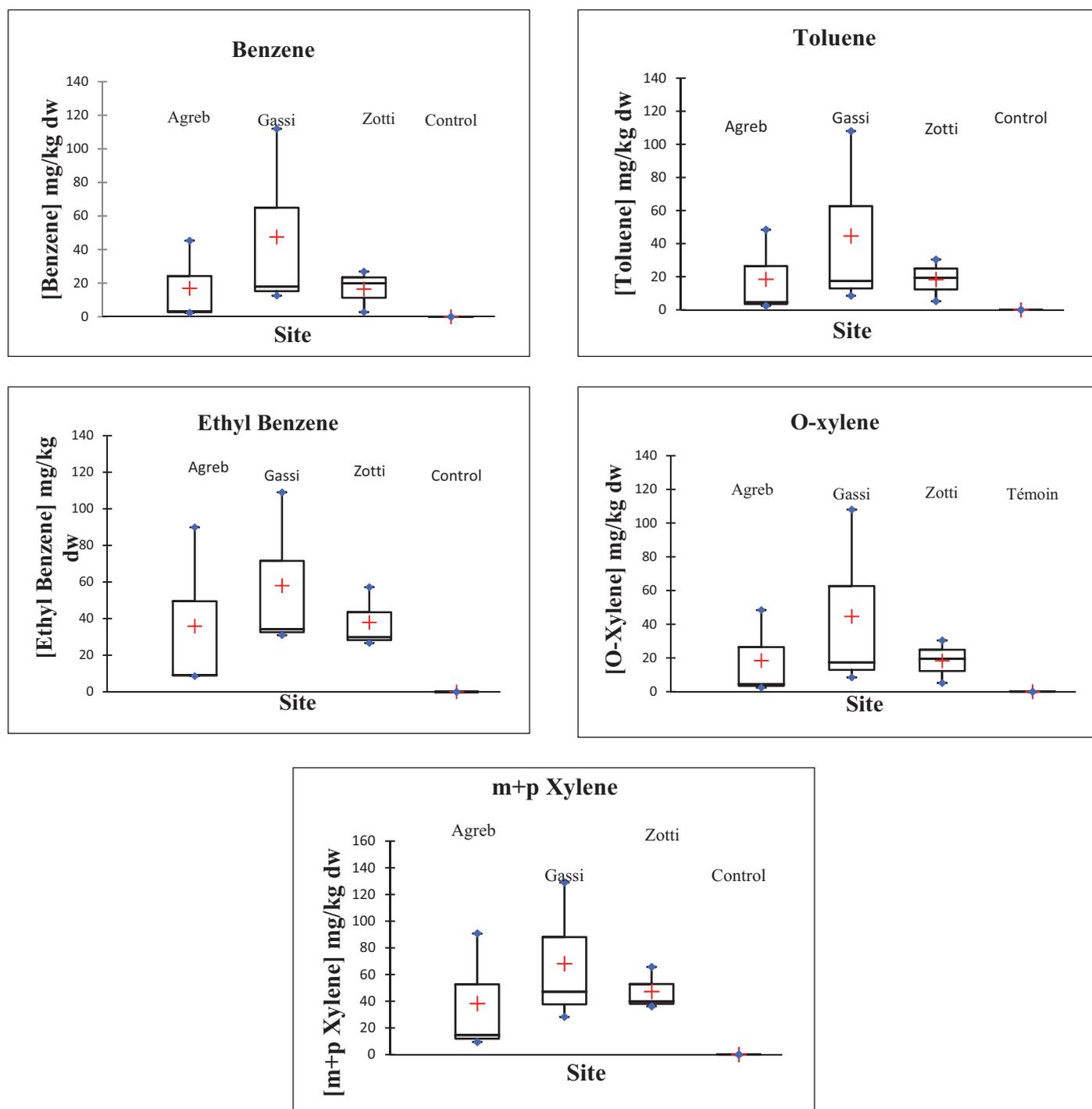


Fig. 4. BTEX concentrations in the three sampling sites

this study allowed for consideration that the hydrocarbon concentration in the studied soil sites were very high. This result was due to the intensive dump of pollutants resulting from a petroleum industry in these soil sites. On the other hand, and by comparing the contents of HCT and BTEX in the soils of the quagmires studied with the Algerian legislation, we find that the values were greatly higher than the norms fixed by Algerian legislation for industrial discharges, which are 10mg/l and 0.08 mg/l for HCT and BTEX respectively (Official Journal of the Algerian Republic OJAR 2006).

Site effect

For spatial point of view, the results and statistical analysis show that there was a very high significant site effect of THC and all measured hydrocarbon fractions (F1, F2, F3) (Table 4).

Tukey's test groups different sampling sites into three different groups for THC, alternatively, for the three fractions, the Tukey's test groups the sampling stations into two groups, where the Agreb and Gassi sites are grouped together and the Zotti site is separate.

Depth effect

With regard to the effect of the depth of sampling, the results and the statistical analyzes show that the effect of the depth was significant for THC and the first two fractions of hydrocarbons (F1 and F2), while the depth showed no significant effect on the distribution of the third and fourth fractions (F3) ($p = 0.092$). (Table 4).

Tukey's test determines the three depths in three different groups for THC and the first two fractions of hydrocarbons (F1 and F2), while for the third fraction of hydrocarbons (F3) it puts the three depths in one group and this which agrees with

the ANOVA, where the depth effect is not significant for this fraction of hydrocarbons.

With regard to BTEX, we noticed that their concentration was minimal compared to other fractions of hydrocarbons, in addition, there was no significant effect of site and depth. This can be explained by the fact that the disappearance of a pollutant is conditioned by their solubility, their volatility (emission into the atmosphere and photochemical destruction), or their adsorption on soil and sediment particles (humus and clays) (Neff et al. 2000, Park 2001, Zhao and Voice 2001). Strongly adsorbed products stay longer in sediment and soil, while very soluble products like BTEX are quickly carried to the groundwater (Alvarez and Illman 2005). This difference in concentration between different study sites and their different depth levels can be attributed, in the first place, to the difference in the granulometric aspect (clay, and sand) of the different depth levels (Table 2), in addition to physicochemical characteristics such as humidity (Table 3) (Vuruna et al. 2017)

Statistical results

Principal component analysis (PCA)

The principal component analysis was carried out to highlight the main factors influencing the distribution of physicochemical parameters and the concentrations of hydrocarbons in different soil sampling sites. It revealed the dependencies, relationships and similarities between these parameters (Figure 5). PC1 and PC2 together accounted for 55.52% (38.14% for PC1 and 17.39% for PC2) of the total variance. The results obtained showed three large groups of parameters studied according to the main factors f1 and f2. F1 represents petroleum hydrocarbon pollution, which was positively correlated with sampling sites and the concentration of calcium. We also notice

Table 4. THC, different petroleum fractions and BTEX concentrations in the three site samples

Site	Depth [m]	THC [mg/kg _{d.w.}]	F1 (C6-C10) [mg/kg _{d.w.}]	F2 (C10-C16) [mg/kg _{d.w.}]	F3 (C16-C34) [mg/kg _{d.w.}]	F4>C34 [mg/kg _{d.w.}]	Benzene [mg/kg _{d.w.}]	Toluene [mg/kg _{d.w.}]	Ethylbenzene [mg/kg _{d.w.}]	O-Xylene [mg/kg _{d.w.}]	m+p Xylene [mg/kg _{d.w.}]
Agreb	0	58700	499	18300	40800	<0.6	45.3	48.4	89.9	48.4	90.8
	1	120000	423	52300	59500	<0.6	3.12	4.5	9.14	4.51	9.44
	2	51200	366	24000	27300	<0.6	2.36	2.4	8.6	2.4	14.5
Gassi	0	70300	445	28800	43000	<0.6	17.9	17.4	34.1	17.4	47.1
	1	64000	557	26900	36100	<0.6	12.6	8.5	31	8.5	28.3
	2	59600	824	22500	35600	<0.6	112	108	109	108	129
Zotti	0	18100	298	7930	10.4	<0.6	26.9	30.4	57.2	30.4	65.7
	1	19200	914	9130	10.5	<0.6	19.9	19.4	29.8	19.4	40
	2	20500	294	8300	12,3	<0.6	2.75	5.2	26.7	5.17	36.2
Control	0	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
	1	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
	2	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Site effect (p)		0.000	0.03	0.01	0.001	1	0.366	0.423	0.212	0.268	0.422
Depth effect (p)		0.045	0.015	0.04	0.092	1	0.099	0.103	0.09	0.103	0.068

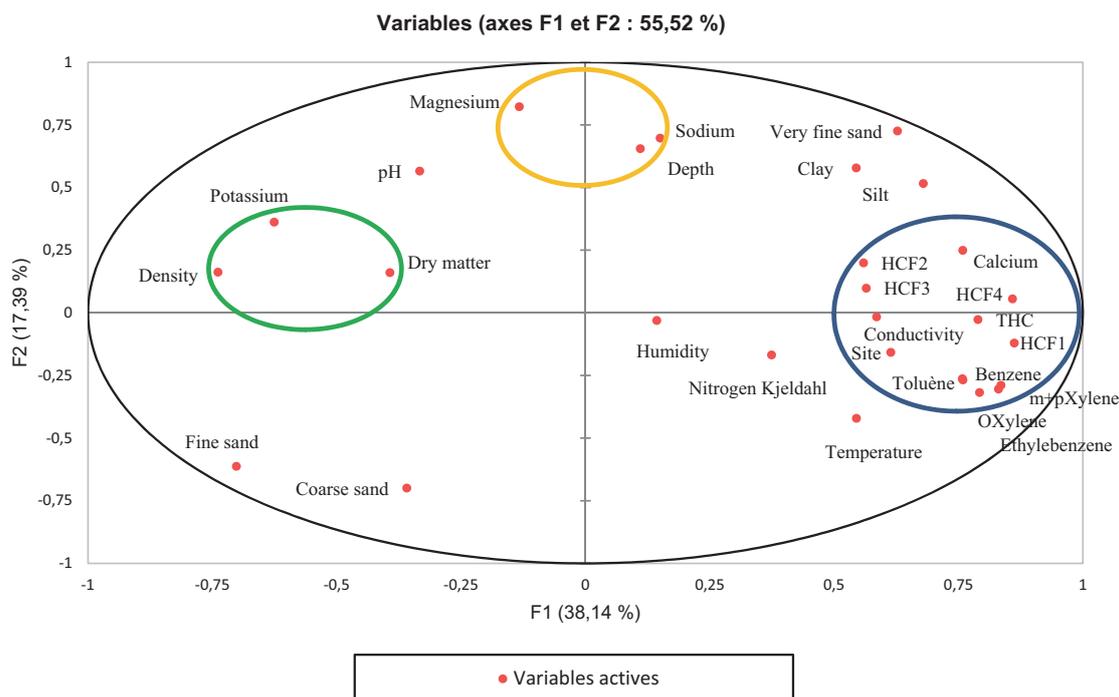


Fig. 5. Principal component analysis (PCA) of THC, PHC, BTEX concentrations and physicochemical properties

that oil pollution was positively correlated with conductivity, which makes sense because petroleum contamination has been shown to increase the electrical conductivity of soil (Adebiyi and Afedia 2011, Arocena and Rutherford 2005). Pollution by petroleum hydrocarbons correlates negatively with soil density and dry matter. F2 represents the depth of soil sampling, which was positively correlated with sodium and magnesium concentration.

Conclusion

The present study revealed valuable knowledge on the physicochemical characteristics of three sites contaminated with petroleum industrial waste, i.e., Agreb, Gassi and Zotti sites situated in Hassi Messaoud region (Algerian Sahara) and the spatial distribution of the total hydrocarbons (THC), the four hydrocarbons fractions: (F1 (C6-C10), F2 (C10-C16), F3 (C16-C34), (F4>C34) and the BTEX (benzene, toluene, ethyl-benzene and xylene) at different depths. According to the obtained results, we can say that there was a difference between the different studied sites and different sampling depths in terms of the physicochemical characteristics. On the other hand, a large difference of contamination with petroleum hydrocarbons was also noted between the different sites and at different levels of depths. This variation in the rate of contamination can be attributed to the difference of physicochemical parameters between the studied sites. This petroleum hydrocarbons contamination can be carried to the groundwater and can represent a great threat to human health in the future.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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