

# Application of Geographical Information Systems and Chromatographic Analysis for Monitoring of Organic Derivatives Near the Petroleum Settlements in Alexandria

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**Abstract**— This research was objected to assess the potential of petroleum contamination in the surface soil near the industrial and municipal activities at the Iking Maryout regions, and to find out the origin sources of hydrocarbon contamination using n-alkane profiles and indices. During the year September. 2014; thirty-two surface soil sampling were collected along the Iking Maryout region in the southwestern parts of Alexandria and analyzed using gas-chromatography with flame ionization detector (FID) detector. Geo-statistical analysis of n-alkanes in soil samples, using Spline interpolation was conducted. The obtained results are summarized as a following: The total petroleum hydrocarbons (TPHs) in soil samples ranged from 5 to 3,525 µg/g d.wt. It accumulates on the side of the road indicating hydrocarbons from the petrogenic sources. The most frequently occurring n-alkanes were C27 suggests biological input. The ratio of (L/H) was varied, indicating that vascular plant sources and low concentration of mixed biogenic and petrogenic contaminants in the east and north of the study area. The ratio of pristane/phytane (pr/ph) ranged from 0.22 to 8.75 indicates a higher concentration of biogenic contaminants along the study area, while the minimum levels of mixed petrogenic and biogenic pollutants were accumulated in the north of the study area which might be due to the close location to the road and refinery activities. The obtained CPI values accumulate at the west of the study area due to the existence of a gas station in this area and at the northern east due to wind direction. While accumulates in the western region as the result of high urban densities. The contamination levels of n-alkanes have been then reclassified. The areas with high hazard risk which accumulated at the north of the study area represents accumulation of petrogenic pollutants due to the close location to refinery activities and of medium potential risk levels resulting from human activities including industries and urbanization which accumulate on the side of the road due to high traffic densities. An assessment of the low hazards was determined as a result of the existence of wide areas of gardens.

**Keywords**— case study; soil contamination; n-alkanes; TPHs ;PAHs ; hydrocarbon indices; GIS mapping; analysis; interpolation;

## I. INTRODUCTION

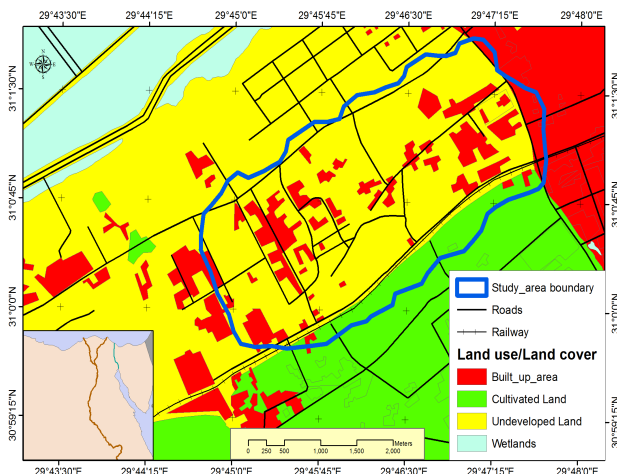
Due to a rapid growth in the population during the last few decades, the banks of the Nile River and its delta have reached upper limit capacity. As a result of this increase, the Egyptian government has constructed a new urban region and industrial cities outside the Nile river delta. Iking Maryout is one of these urban cities. This city is located around 60 km southwestern region of Alexandria City. It is characterized by petroleum refinery and other industries activities that release substantial amounts of crude oil and refined products into the natural environment as a result of events such as storage tank leakage or oil spills during routine transporting and shipping operations and therefore causes contamination of soil and lead to failure of foundation land subsidence, landslides, ground water pollution, etc. [1] Crude oil or petroleum contains thousands of compounds of which straight chain hydrocarbons (sometimes isoprenoids) predominate. Hydrocarbons are present in both dissolved, and particle phase. As a result of their low solubility level and their hydrophobic nature, they readily get together with inorganic and organic suspended particles and may accumulate in soil at high concentration levels. The highest hydrocarbon levels in soil were detected in the areas that have high anthropogenic impact and activities. Petroleum hydrocarbons (PHCs) are common contaminants. Aliphatic hydrocarbons (n-alkane) can arise from anthropogenic and natural sources. Anthropogenic hydrocarbons come from human activities which incorporate industries, urbanization, shipping, fishing and oil activities while natural hydrocarbon can come from biogenic sources which incorporate bacteria, insects, microorganisms, algae bacteria and terrestrial plants. [3] Generally, non-polluted areas demonstrate hydrocarbon concentrations of less than 10 ng/mg d.wt. [4]. N-Alkanes consist of odd and even carbon numbers ranging up to 64

carbons with no alkyl branch or substitutes. The “Odd” carbon numbers come from the biogenic sources while “Even” carbon numbers are usually derived from the anthropogenic sources. In detail, n-C15, n-C17 and n-C19 are produced by marine biogenic sources, whereas nC25-nC33 hydrocarbons are produced from terrestrial vascular plants [5]. Some analytic parameters that have been utilized to distinguish and estimate the origins of n-alkane in the environment are Ratio of Low Molecular Weight alkane/High Molecular weight alkane (LMW/HMW), Carbon Preference Index (CPI) and the ratio of pristane/phytane (pr/ph). Environmental geochemistry of soil has been widely utilized as a part of the current year as a tool to assess the contamination level and assess their cause in an area. Spatial continuous data play a significant role in planning, risk assessment and decision making in environmental management (Li and Heap, 2008) [6]. This tool can combine data from various sources, present them spatially and analyze their relations and interactions. It supports the development of predictive models and provides support for decision-making. The main aims of this research are to assess the level of petroleum contamination in soil near the industrial and municipal activities, regions, and to find out the source of aliphatic hydrocarbons using n-alkane profiles. Accordingly, to develop Geo-database for the study area to make distribution maps for each measured parameter (mainly petrochemical contaminants). Interaction between the different environmental elements to assess the potential impact of petrochemical activities in the study area is also subject to assessment.

## II. MATERIALS AND METHOD

### A. Study area

The study area is about 10.9 Km<sup>2</sup>. It is subjected to regional development projects, including land reclamation, new factories and many economic, scientific and recreation center has been established. The study area is shown in figure II-1 located between latitudes 30° 59' 45.834" and 31° 1' 52.34" N and longitude 29° 44' 43.168" and 29° 47' 41.573" E. The area receives an annual average rainfall of 170 mm, but precipitation varies greatly from year to year. Rains are seasonal, almost all rain

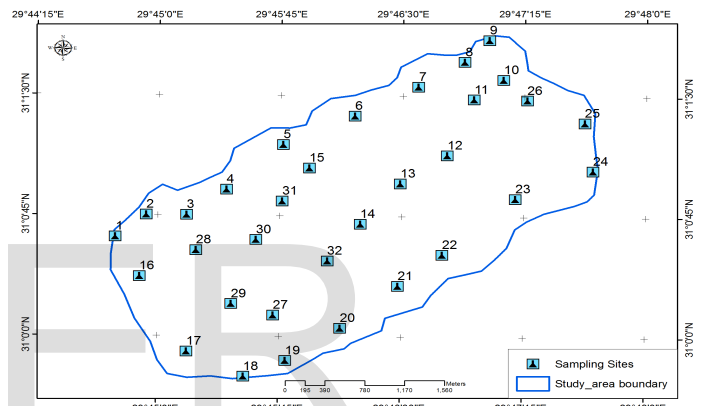


occurs between December through February, whereas between June and August it is essentially none [7]. Annual average wind roses showed that the dominant wind directions in the study area

were northwest [8]. The study area is dominated by a Mediterranean climate, which is characterized by an average relative humidity of 1.76%, the soil covering the study area have nature of very fine particles of medium and coarse sand.

Figure II-1: Description of the Study Area

### B. Sampling



Thirty-two surface soil samples were collected in an area of about 7.5 km lengths and 2.5 km width from near-surface soil with a hand trowel and the coordinates of each sampling point were measured using GPS so that the soil test results could be mapped figure II-2. At least 1,000 g of surface soil (10–15 cm of depth) were collected from each site. The samples were placed in a strong foil tray with cover. Then the sample was transferred directly into an appropriate, labeled sample container with a stainless steel lab spoon or equivalent and secures the cap tightly. The soil sample was mixed thoroughly to obtain a homogenous sample representative of the entire sampling interval and simply derived in the laboratory for carrying out drying, sieving and petroleum hydrocarbons analysis. All the analysis was carried out using the soil sample with a particle size of <150 um fraction.

Figure II-2: Land Use Map Represent the Sampling Sites along the Study Area in Iking Maryout Region

## III. SOIL ANALYSIS

Moisture percentages were determined according to Loring and Rantala, (1992) [9] and are useful when contaminant

Layer Name	Feature Type	Description
Sampling point	Point	Represent the location of samples in the study area
Agriculture land	Polygon	Covering all green zones in the study area
Space area	Polygon	Covering the zone with no residential densities
Building	Polygon	Covering the building in the study area
Road	Polyline	Covering all roads in the study area

The base map of study area consists of four layers representing the various physicals as well as, man-made features of the study area Table IV-1.

Table IV-1: Layer Developed in Geo-database

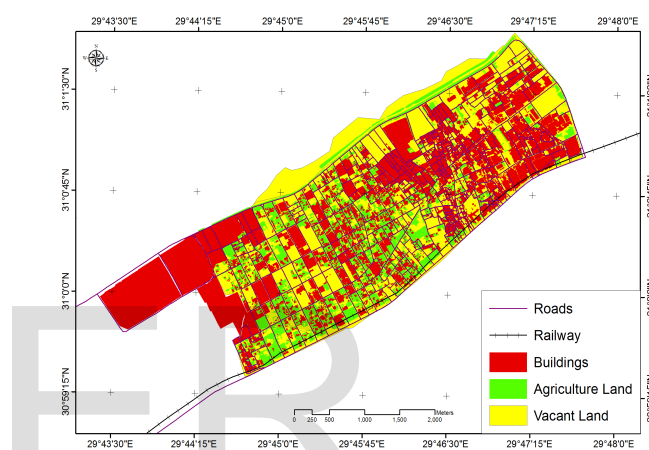
These features were delineated from a topographic map scale 1:50000. The topographic map was firstly scanned and rectified using Geo-referencing tool. The process of Geo-referencing relies on the coordination of points on the scanned image (data to be Geo-referenced) with points on a geographically referenced data (data to which the image will be Geo-referenced). By connecting coordinate points on the image with those same locations in the geographically referenced information you will

concentration is to be reported on a dry weight basis. The total organic matter is carried out according to the method of ASTM D 2974 [10] and ranged from 25.1 to 212.6 mg/g d.wt. . All samples were extracted using the Soxhlet extraction according to the methods EPA 1664 [11] and EPA 3550 [12]. About 10 g dry soil (particle size of <150um fraction) was weighed into a pre-cleaned 100 ml Erlenmeyer flask. Soil sample was extracted with 30 ml of n-hexane by sonication for 10 minutes; n-hexane (100%) was proved to be the most suitable solvent over a mixture of hexane and dichloromethane (1:1) and dichloromethane (100%) due to n-hexane gives a better value in TPHs. This might be due to the polarity of the solvent since n-hexane employed as non polar solvent while dichloromethane moderately polar (Specht, 1994) [13]. Individual analysis of aliphatic hydrocarbons (AHCs) as n-alkanes (C14 - C36) obtained in the final extract of the soil samples using gas chromatography method according to EPA 1663 [14]. Gas chromatograph (Thermo 2009) equipped with flame ionization detector (FID) and nitrogen carrier gas (1ml/min), TG-1 MS column (100% dimethyl polysiloxane; 30 m, 0.32mm I.D., 0.25 film thickness) was used. The instrument was calibrated by injection of the standard component mixture at three different concentrations (5, 10, 20 ng/μl) of AHCs prior to analysis of the samples. The chromatographic conditions for analysis: Injection port temperature was 250°C with splitless injection mode (3 min) then split mode with a split ratio 1:10. Column temperature was programmed from 80 to 240 at 7°C min<sup>-1</sup>, and then to 300°C at 3°C min<sup>-1</sup>, held for 5 min at 300°C. FID temperature was 300°C. FID gases were, air at 350 ml/min and hydrogen at 35 ml/min.

#### IV. APPLYING GIS IN ASSESSING HYDROCARBON CONTAMINANTS

The present study focuses on the environmental monitoring of hydrocarbon pollutants in the surface soils of an industrial area in Alexandria City, Egypt. It is a valuable feature to carrying out mapping, spatial variations of various contaminants within the study area and evaluating their levels compared to the threshold limits in the literature. This evaluation can also support of prediction models and provides clear evidences to the decision makers. For this purpose, a Geo-database for the study area was developed using GIS, and the developed Geo-database was employed in:

- Integrating sampling data into Geo-database.
- Visualizing the dispersion of various considered pollutants.
- Assessing risk through a composite index.



convert the location of the entire image to the correct geographic location [15]. Their after various features were delineated through on screen digitizing. Digitizing is the process of making features editable on the image. This is followed by an attribute data entry figure IV-1. It should be noted that the topography of the study area was not put into consideration in this study because of the volatile nature of the organic compounds analyzed. These compounds have a high vapor pressure at room temperature conditions. Their high vapor pressure results from their low boiling point which causes large numbers of molecules to evaporate and enter any surrounding medium.

Figure IV-1: Land use in the study area (Iking Maryout, Alexandria)

#### V. INTEGRATING SAMPLING DATA

The coordinates of sampling data were utilized in integrating these data into the developed Geo-database and creating a point feature class (layer) representing the location of sampling station

## A. Identification of Best Interpolation technique

For the purpose of this study, Interpolation of all soil sampling points and their contamination levels were conducted using the Spline interpolation method in ArcGIS software. Spline was applied because it is better when dealing with unevenness in the distribution of sample points like the soil points; it is best for generating gently varying soil table contamination levels. Generally, the raster surfaces continuously represent the spatial variations in each contaminant within the study area [8].

## B. ASSESSMENT OF LEVEL OF CONTAMINATION

The main aims of this research are to assess the level of petroleum contamination in soil near the industrial and municipal activities regions, and to find out the source of aliphatic hydrocarbons using n-alkane profiles. Accordingly, to develop Geo-database for the study area to make distribution maps for each measured parameter (mainly petrochemical contaminants). Interaction between the different environmental elements to assess the potential impact of petrochemical activities in the study area is also subjected to assessment.

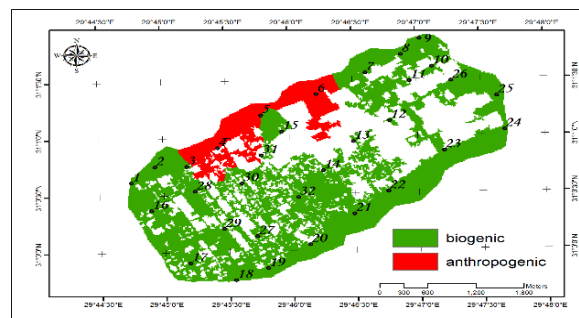
## C. CREATING RISK MAP

The raster surfaces created in previous step were reclassified by replacing input cell values with new output cell values. This is necessary in order to group certain values together, and classify them to a common scale. In this study, each data layer was reclassified to a common scale showing potential areas of hydrocarbon contaminant source, classifying into biogenic, petrogenic and anthropogenic origin contaminants [16]. Overlaid identify the different levels of risk based on various contaminates in an integrated manner [17].

## VI. RESULTS AND DISCUSSION

### VI.1. LEVELS OF TOTAL OF PETROLEUM HYDROCARBON (TPHs) IN SOIL SAMPLES

The concentrations of the total petroleum hydrocarbon (TPH) of each sample depth at the site are presented in TableVI-1. The overall level of TPH recorded here in the petroleum contaminated site ranges from  $5 \pm 0.9$  to  $3525 \pm 0.7 \mu\text{g/g d.wt}$ , where the lowest value was recorded at sites S12, S16 and S17 with the levels of 10, 10 and  $5 \mu\text{g/g d.wt}$ , while the highest recorded at sites S 4, S 5 and S 6 with the levels of 3525, 440 and  $620 \mu\text{g/g d.wt}$ , respectively it was noted as in figure VI-1, that most various sites of the study area (IKing Maryout, 2015) are dominated by hydrocarbon contaminants originated from the biogenic sources.



FigureVI-1: Types of Petroleum Hydrocarbons (TPHs) in Soil Of the Study Area

This can be attributed to the existence of wide areas of gardens associated with high-class residence in the study area. Meanwhile, hydrocarbon contaminants originated from the anthropogenic sources were distributed mainly in the northern parts of the study area, covering a total area of 8.34 % of all the study area. The anthropogenic source probably petrogenic hydrocarbons, but it can also be recycled, organic matter of different origins, such as sewage, soil organic matter washed by rains, and effluents from water treatment plants. The close location of these sites S 4, S 5 and S 6 to refinery activities existing to the north may increase the probability that these contaminants come from petroleum source and may indicate the significant impacts of such activities in determining the distribution pattern of this type of contaminants in the study area.

### VI.2. RATIO OF LOW MOLECULAR WEIGHT ALKANE/HIGH MOLECULAR WEIGHT ALKANE (LMW/HMW) IN SOIL SAMPLES:

The low to high (L/H) molecular weight ratio of n-alkanes below 1 indicates natural input of hydrocarbons from terrestrial biogenic sources, while values above 1 show natural input from biogenic sources. A value around 1 is referring to petroleum sources (Fagbote and Olanipekun, 2013) [18]. The obtained results found that the ratio of (L/H) was ranged from 0.1 at site samples S 1, S 4 and S 17 and 0.78 at site S 8, indicating that vascular plant sources played a very important role in soil contaminated with hydrocarbons.

TableVI-1: Hydrocarbons Levels and its Source Indices In the Surface Soil of the Study Area

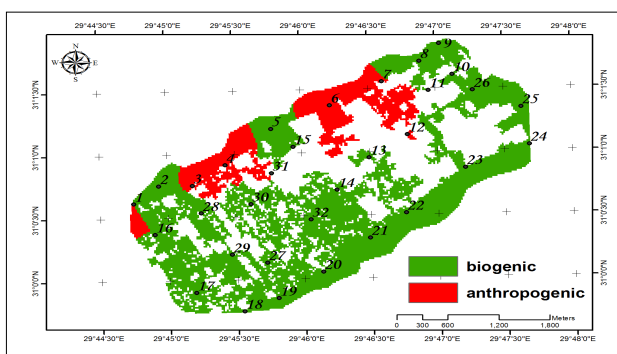


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Sampling Sites	CPI	(L/H)	TPHs $\mu\text{g} / \text{g} \cdot \text{d.wt}$	(Pr/Ph)
1	1.1	0.11	50	0.65
2	0.8	0.29	25	1.78
3	1.3	0.28	17	0.65
4	1.1	0.11	3525	0.22
5	1.1	0.74	440	1.17
6	1.9	0.22	620	0.67
7	1.9	0.22	210	0.67
8	1	0.78	30	8.75
9	1.3	0.32	80	3.72
10	2.4	0.33	20	6.15
11	2.4	0.33	80	6.15
12	1.6	0.31	10	0.71
13	1.6	0.31	20	1.42
14	1.6	0.31	20	1.42
15	1.6	0.31	30	1.42
16	1.4	0.29	10	1.45
17	0.4	0.12	5	1.41
18	1.4	0.29	70	1.45
19	1.4	0.29	60	1.45
20	1.2	0.29	70	1.52
21	1.2	0.29	100	1.52
22	1.2	0.29	30	1.52
23	1.2	0.29	80	1.52
24	1.1	0.29	90	1.52
25	1.2	0.29	70	1.54
26	0.7	0.4	60	1.42
27	0.7	0.4	80	1.41
28	0.7	0.4	50	1.41
29	0.7	0.4	60	1.42
30	0.7	0.4	280	1.4
31	0.7	0.4	20	1.38
32	0.7	0.4	30	1.42

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Figure VI-2 shows that most of the study area is dominated by hydrocarbon contaminates originated from the biogenic



sources. Meanwhile, hydrocarbon contaminants originated from the anthropogenic sources were distributed mainly in the north and north east parts of the study area, covering a total area of 1.53% of the study area. Accordingly, the variation in n-alkanes content may refer to the anthropogenic sources (sewage, industrial discharges, and vehicle emission) and natural inputs (El Nemr et al., 2013)[19] in the case of northern east part due to the close location of site S 8 to Borg

oad to the east, has a significant impact of vehicles emission in this area or leakage of petroleum tank and wind direction which is predominantly north to northwest lead to spread the hydrocarbon contaminants in the northern eastern part of the study area, while the close location of site S 5 to refinery activities may be a reason of contamination in the northern part of the study area.

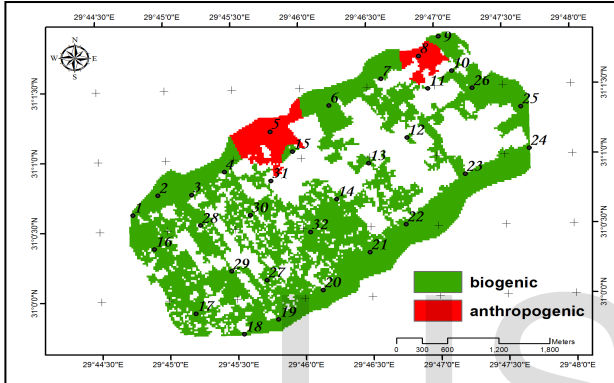
Figure VI-2: Spline Interpolation of (L/H) Ratio of the Hydrocarbons of the Study Area

### VI.3. RATIO OF Pr/Ph. IN SOIL SAMPLES

The ratio of (Pr/Ph) which ranged from 0.22 to 8.75 at sites S4 and S8 respectively. The low levels were obtained at sites S 1, S 3, S 4, S 6, S 7 and S 12 and ranged from 0.22 to 0.71 indicate that petroleum contamination has been occurred.

**Figure VI-3: Spline Interpolation of (Pr/Ph) of Study Area**

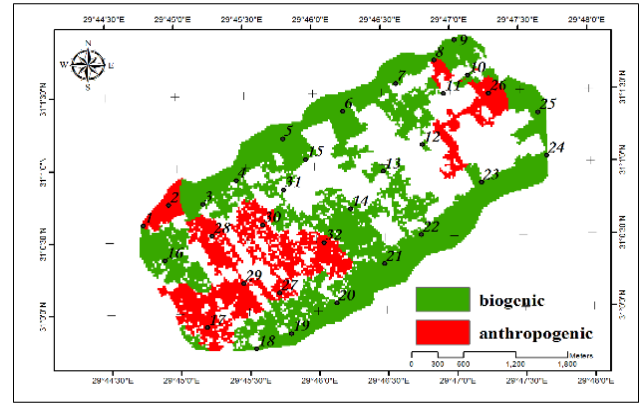
The low levels were obtained at sites S 1, S 3, S 4, S 6, S 7 and S 12 and ranged from 0.22 to 0.71 indicate that petroleum contamination has been occurred. Generally, it was noted in figure VI-3, that most of the study areas are dominated by hydrocarbon contaminants originated from the biogenic sources. This may be attributed to the decayed vegetation on the subsurface since the refinery plant and all the human activities sited on a land may be used for farming, thus, high concentrations of pristane may be indicative of high levels of microbial degradation by weathering. Meanwhile, hydrocarbon contaminants originated from the anthropogenic sources were distributed mainly in northern zones of the study area at the sites S 1, S 3, S 4, S 6, S 7, S 21 and S 31 covering a total area of 11.6 % of the study area. The close location of the road and refinery activities may highlight the significant impacts of such activities in determining the



distribution pattern of the type of contaminant in the study area. Since the identified ratio values reveals the effect of biodegradation did not alter the Pr/Ph ratio because cyclic and branched alkanes are known to resist microbial degradation more effectively than n-alkanes and thus have a greater tendency to remain in the environment after n-alkanes have degraded [20].

**VI.4. CARBON PREFRENE INDEX (CPI) IN SOIL SAMPLES:**

In the present study, the n-alkanes distribution of the surface soil samples; S 2, S 17, S 26, S 27, S 28, S 29, S 30, S 31 and S 32 found that the CPI values for the hydrocarbon sources of these soil samples were below to unity ranged from 0.4 to 0.8 signifying anthropogenic origin except for the sample of site the S 8 that has a value of 1 which indicating a petrogenic hydrocarbon source for this site and values more than 1 indicate significant impacts of biogenic contaminants ranged from 1.1 to 2.4 (Didyk et al., 2000) [21].



**Figure VI-4: Spline Interpolation of CPI Ratio Along the Study Area**

Figure VI-4 elucidates that most various part of the study area is dominated by hydrocarbon contaminates originated from the biogenic sources. Since n-C27 n-alkane at the highest concentration which is defined as major hydrocarbon. It leads the total n-alkanes to the specific direction of hydrocarbon load. This index varies from one location to another. The n-C27 hydrocarbon is known to be an indicator for the terrestrial biogenic hydrocarbon existed. This can be attributed to the existence of wide areas of gardens associated with high-class residential and agricultural land to the south west part of the study area. Meanwhile, hydrocarbon contaminants originated from the petrogenic sources were distributed on site S8 and S26 might be due to the existence of gas station or parking for trucks in this area. The hydrocarbon contaminants originated from the anthropogenic sources (mixture of the petrogenic and biogenic sources) mainly distributed in the northwest and west of the study area, covering a total area of 15.1% of the total study area at site S 17, S 27, S 28, S 29, S 30 and S 32 in the western part as a result of landfills or other garbage disposal sites. Since it is not a residential area and surrounded by stadium Borg El Arab and king police office station and this may be a significant source of wastes in this area. The result shows the hydrocarbon contaminants distributed northern west of the study area at site S 1, S 2 may be from petrogenic source as a result of vehicle emission.

**VI.5. CONTAMINATION INDEX**

The contamination index maps for various hydrocarbon concentrations can classify according to risk levels as high (red area), medium (yellow area) and low (green area). The cumulative concentration of contamination map can be achieved by overlaying the four hydrocarbons contamination index maps respectively. Then, by adding the entire map and reclassifying one can get the contamination index, through which the level of contamination at various locations can be assessed easily as shown in figure IV-5. The figure shows that the accumulation of hydrocarbons originates from the petrogenic source have a significant high-risk impact at the northern zone of the study area which covering a total area of 0.81% of the total area. This may indicate that petrogenic sources are also passed from oil well blow outs, spills and disposal from an oil tanker. These contaminants have a significant high risk. The anthropogenic contaminants have an area of 8.2 % of the study area, which localized at the north and northeast zones indicating the medium risk level of

these contaminants in the study area. The anthropogenic contaminants may release from vehicles emission, rain fall, which moves contaminants from the place to other and as well as wind direction. Mostly various parts of the study area are dominated by hydrocarbon contaminants originated from the biogenic sources. This indicates a low risk level since all the contaminants originate from the plant.

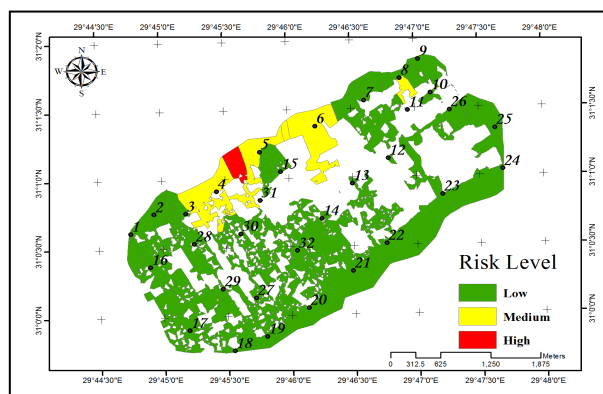


Figure VI-5: Risk Assessment Map for Organic Contaminants In Soil of the Study Area

## VII. Conclusions

- The levels of total organic matter in the surface soil samples along the study area of the Iking Maryout regions were ranged from 25.1 to 212.6 mg/g d.wt with an average value 68.1 mg/g d.wt. Levels of oil & grease ranged from 30 to 6600 µg/g d.wt. The similar trend was observed for the total petroleum hydrocarbons (TPHs) which ranged from 5 to 3525 µg/g d.wt soil, indicating terrestrial vascular plant sources. Levels of aliphatic hydrocarbons of n-alkanes (C14-C36) were detected in most of the soil samples analyzed with levels ranged between 25 and 3175 ng/g d.wt. Since n-C27 is abundant. This finding reflects the relative contributions of natural hydrocarbons to the soil.

- The relation between three main hydrocarbons indices and spline interpolations was determined to specify the origin and spatial distribution of hydrocarbons in the soil analyzed. The distribution of (L/H) of n-alkanes molecular weight indicates higher levels of biogenic and low of anthropogenic HCs along the study area, as a result of emission of hydrocarbons from vehicles. The indices of CPI and pristane/phytane ratio indicate higher levels of biogenic and anthropogenic contaminants accumulates, indicating a significant contribution of fossil fuel, while lower levels of petrogenic contaminants accumulated in the north might be due to the traffic densities.

- High hazards risk accumulated in the north of the study area represents accumulation of petrogenic pollutants due to traffic densities and wind direction which affecting the transporting the pollutants. An assessment of a low hazard was carried out along the study area, as a result of high densities of green land area.

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