The effect of Kirkuk Oil Refinery on Air pollution of Kirkuk City-Iraq

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Abstract

The total suspended particles (TSP) concentrations in air at Kirkuk Oil Refinery and the areas around was determined by using low volume air sampler (Sniffer) at selected locations in two periods October 2010 and March 2011. The results of average concentration of suspended particles (TSP) are higher than the permissible limits of the Iraqi National determinants of (350 µg/m^3) and the world limits of (60-90 µg/m^3) at the two periods: October 2010 (818.94µg/m^3) and March 2011(956.8µg/m^3). The little difference between the two periods reflects the little effect of the seasonal changes. Comparison of the averages of the heavy metals (Pb, Ni, Cr, and Cd) with the national and world limits, noticed that they are higher than these limits. Except for the concentration of Copper (Cu), at the two periods were lower than the world limits. These results represent the effect of meteorological factors on the air quality of the studied area. Consequently, the TSP and heavy metals pollutants concentrations for both sampling periods October 2010 and March 2011and the cumulative effects of both periods shown an increase at the direction away from the refinery mostly at the south east direction.

Keyword: air quality ,TSP, heavy metals, Kirkuk oil refinery .

تاثير مصفى كركوك على التلوث الهوائي في مدينة كركوك – العراق

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الخلاصة:

ان تراكيز الدقائق العالقة الكلية في نماذج الهواء الماخوذة من مصفى كركوك والمناطق المحيطة بة قد تم تعينها باستخدام جهاز جمع نماذج الهواء ذو الحجم الواطئ لفترتين هي تشرين اول ٢٠١٠ و اذار ٢٠١١. ان نتائج معدل تراكيز الدقائق العالقة الكلية كانت اعلى من الحدود المسموح بها للمحددات العراقي (٣٥٠مايكروغرام/م^٣) والمحددات العالمية (٦٠-٩٠ مايكروغرام/م^٣). للفترتين المدروستين حيث كانت في تشرين ٢٠١٠ هي (٩٤ر ٨١٨ مايكروغرام/م^٣) وفي اذار ٢٠١١ كانت (٨ر ٩٥٦ مايكروغرام/م^٣) ان الاختلافات الطفيفة بين الفترتين تعزى الى تاثير المناخي الفصلي المحدود. ان مقارنة معدلات الفلزات الثقيلة (الرصاص و النيكل و الكروم والكادميوم) في نماذج الهواء المدروسة مع تلك للمحددات الوطنية والعالمية اوضحت بان النتائج كانت اعلى ماعدا تركيز النحاس وللفترتين. ان نتائج تراكيز الدقائق العالقة الكلية و الفلزات الثقيلة كانت تمثل تاثيرات العوامل المناخية على نوعية الهواء في المنطقة المدروسة ولذلك كانت تراكيزها تزداد باتجاه الرياح السائدة وباتجاه الجنوب الشرقي مبتعدة عن المصفى

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Introduction

Air pollution is considered as one of the severe problems the worlds facing today. It deteriorates ecological condition. The air we breathe is a mixture of different gasses and small (solids and liquid) particles. Some substances come from natural sources while others are caused by human activities such as our use of motor vehicles, domestic activities, industry and different business. Air pollution occurs when the air contains substances in quantities that could be harmful to the comfort or health of humans and animals, or could damage plants and materials. These substances are called air pollutants and can be either in the form of particles, liquids or gaseous in nature [1, 2].

In general, air pollution is caused by both natural and man-made sources. Major man-made sources include automobiles, power generation and the industrial activities, which represent the main source of air pollution, especially oil industry activities using huge amount of consumable fuel like power plants and oil refineries; due the high rate emission of fume, solid particulates and toxic gases in quantity more than every other industry. These industries will be more hazardous upon its existence inside the limits of the cities, or its existence inside urban area [1, 2], such as Kirkuk oil refinery.

Suspended solids particle, which are air pollutants stuck in the air with a small volume ranges between (200-0.01) Micron [3]**.** Particulate matter is a mixture of liquid droplets and small particles either organic or inorganic substances. Particulate is a molecule that is bigger than 0.0002 μm but smaller than 500 μm which is formed as airborne solids or liquids [4]**.** Those partials have the ability to suspend in the air for periods varying from few seconds to several months, depending on their size and can eventually exist everywhere either on air, water and solid surfaces, [5,6]**.**

The particles, with a diameter bounded by the range of (1-10 μm), can constitute a significant health risk because they are small enough to penetrate the lungs and cause acute respiratory diseases. The impact of suspended particles is significant to human health because exposure to these particles for a long time increases the respiratory diseases, especially asthma, and may lead to lung tissue damage [7]**.** Studying those particles is important because of their long survival periods in the atmosphere, unlike the other big particles which will settle down more rapidly. In addition to that smaller particles seem to interact with other air pollutants, leading to severe damages.

Those small particles can also have other chemical reactions to form secondary pollutants hazardous, which will be more damaging to the environment such as the case of the increase darkness of the atmosphere caused by suspended particles due to the blocking of the sun's rays and will help in the formation of clouds, as well as chemical corrosion of materials and minerals [8]**.** Heavy metals are of one type of pollutants that have a big potential harm to ecological environment which cannot be biodegraded when releasing into environment [9]**.** Metals are associated with a variety of health effects. For example, in experimental animals, cadmium can produce acute toxic effects on various organs such as the kidney, liver, pancreas, and lung (by inhalation); chromium (VI) compounds can cause chrome ulcers, corrosive reactions on the nasal septum, and allergic eczematous dermatitis among subjects who have been exposed; and the toxicity of lead may largely be explained by its interference with different enzyme systems; lead inactivates these enzymes by binding to SH-groups of its proteins or by displacing other essential metal ions [10]**.**

The literature surveys have indicated that the air pollution studies and researches in Iraq are very limited particularly those on the air pollution from oil industries activities. Several studies had been carried out by Iraqi scientists and researchers on environmental air pollution in Iraqi governorates especially in some industrial areas, [11, 12, 13, 14, 15]**.**

In this study the work conducted on analyzing the pollution levels in the air, of the area in and around Kirkuk Refinery due to its emissions to environment. The study applied the Arc view program- one of GIS programs, the study area is located around the oil refinery of Kirkuk city to the north-east of Baghdad between latitudes (35° 24" – 35° 29") to the north and longitude (44° 20" – 44° 26") to the east (Fig.1). The following steps were achieved:

1. Assess the air, contamination due to the Kirkuk refinery systems.
2. Establish detailed air, maps to set standards for safe environment.

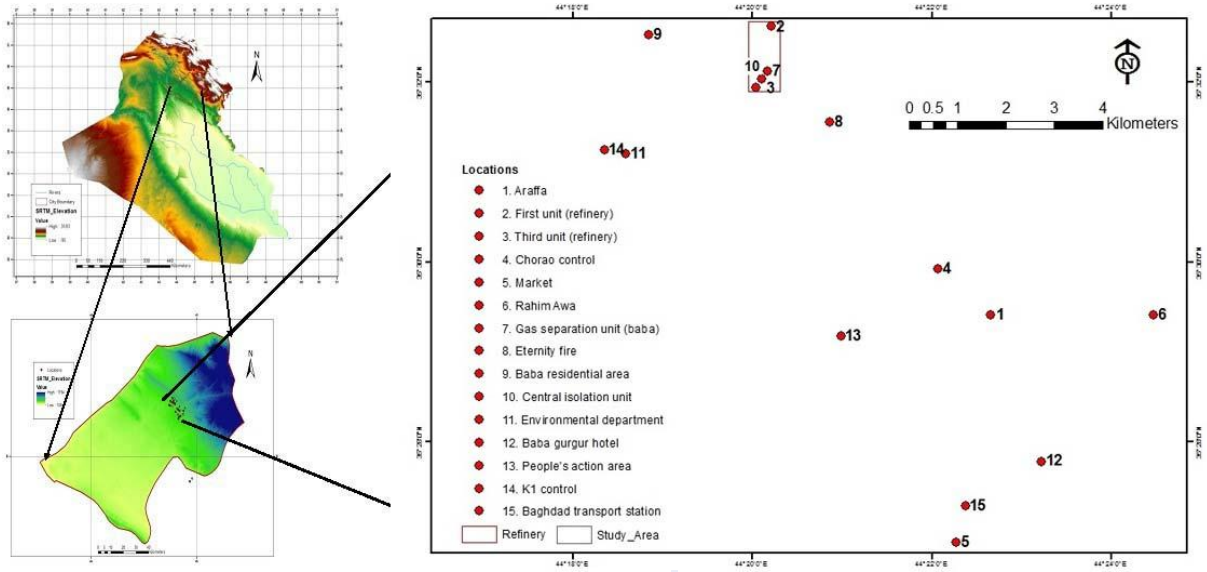

Figure 1-The topographic map of Iraq showing the location of Kirkuk governorate and the sampling sites.

Materials and Methods

1-Climate

Data of Kirkuk meteorological station records of the climatic elements were studied for the years 1980 - 2012 , such as maximum and minimum of temperature, wind speed and direction, rainfall, and relative humidity % for the years 1980–2012 [16]**.**

2- To examine samples for total suspended solids concentrations and heavy metals of the air samples in Kirkuk oil refinery, and give an indication of the environmental impacts on the residential areas near and around it, fifteen different sites inside and outside the refinery had been selected for ambient air sampling collection. The TSP concentration in air at Kirkuk refinery and the areas around was determined by using Low volume air sampler (Sniffer), (Fig. 2), at selected locations in two periods October 2010 and March 2011.

Figure 2- Front and back view of Low Air Sampler (Sniffer) devise features.

The practical steps included an operation to measure the TSP concentrations and measuring the concentrations of some heavy metals (Pb, Cu, Ni, Cr, Cd).

The field work included sampling of air, using field sampling and measuring equipment's. The accurate selection of site location for environmental sampling can help in determining the impact of the pollutants and their sources. The site selection of the air sampling in Kirkuk oil refinery takes into consideration the prevailing wind direction that is an important factor in pollutants distribution. Site location selected in the different processing units inside the refinery and areas near or around the refinery as well as the nearby populated sectors within Kirkuk city, the whole sites were fifteen locations, (fig. 1). Laboratory works include chemical analysis of the environmental samples (air) that collected during the field work for the measurements of the concentrations of heavy metals, and their

distribution to determine the amount of these pollutants in the studied area, using Atomic Absorption Spectrometry equipment to determine heavy metals concentrations. To ensure the accuracy and validity analysis obtained calculation of accuracy and precision were done, [17,18] .

Table 1- The mean Monthly values of the climatic parameters of Kirkuk Meteorological station for years 1980 - 2011

Months	*Min Temp °C*	*Max Temp °C*	RH%	Wind Speed m/sec	Rainfall mm
October	١٨,٧	٣١,٦	٣٨,٥	١,٥	١٤,٢
November	١١,٦	٢٢,٣	٥٨,٩	١,٢	٥٠
December	٦,٤	١٥,٨	٧١,٣	١,١	٦٢,٦
January	٤,٨	١٤,٠	٧٣,٥	١,١	٧٠,٩
February	٥,٦	١٥,٥	٦٧,٨	١,٤	٦٣,٤
March	٩,١	١٩,٩	٥٩,٧	١,٦	٥٤,١
April	١٤,٢	٢٦,٥	٥١,٦	١,٨	٤١
May	٢٠,٢	٣٣,٩	٣٤,٩	٢,١	١٣,٤
June	٢٥,٣	٣٩,٩	٢٤,٩	١,٩	٠,٢
July	٢٨,٥	٤٣,٥	٢٣,١	١,٨	٠,٤
August	٢٧,٧	٤٢,٧	٢٤,٦	١,٨	٠,١
September	٢٣,٩	٣٨,٧	٢٧,٢	١,٤	١,٢

Results and discussion

1-Climate

Data of Kirkuk meteorological station records of the climatic elements were studied for the years 1980 - 2011, such as maximum and minimum temperature, rainfall, relative humidity wind speed and direction,(Table 1 and Figures 3) [16].

The results reflect that the high value of mean monthly maximum temperature was (43.5) ^{o}C during July, and the low value of minimum value was (14.0) ^{o}C during January. While, the high value of minimum temperature was (28.5) ^{o}C during July, and the low value of minimum temperature was (4.8) ^{o}C during January (Figures 3 – A and B).

The maximum Rainfall was (70.9) mm during January, while the Minimum was (0.1) mm during August, such a results are in accordance with the results of Relative Humidity% , the Maximum RH% was (73.75%) mm during January, while the Minimum was (23.07%) mm during July (Figures 3 – C and D).

The Maximum wind speed was (2.1) m/sec during June, while the Minimum was (1.1) m/sec during December and January. While, the prevailing annual wind direction for Kirkuk meteorological station for the period (2002-2012), reflect mainly northwesterly winds direction (Figures 3 – E and F).

The climatic parameters such as the temperature, relative humidity, wind speed and rainfall have an important effect on the concentration of pollutants in the air and lead a key role in controlling the spread of various air pollutants [6].

The high temperature lead to air movements and the dissemination of pollutants vertically to the greatest extent possible, while the low temperature lead to downward air movements, [6].Rain works to purify the air of a lot of solid and gaseous pollutants. Also, a large part of the particles attached to the outstanding during the rain drops fall like dust particles.

The relative humidity% is depending on temperature, the humidity decrease in the summer due to high temperature and low rainfall, while the humidity increase in winter due to low temperatures and frequent rainfall, so the inverse relationship between humidity and temperature, while the direct correlation between the humidity and rain [6].The importance effect of relative humidity is shown by reducing the concentration of pollutants in the air.

The wind direction plays an important role in the distribution of pollutants in air, moving the pollutants with the general direction of the prevailing winds. When the wind speed increase the movement and spread of contaminants increase and therefore lack of concentration in the air.

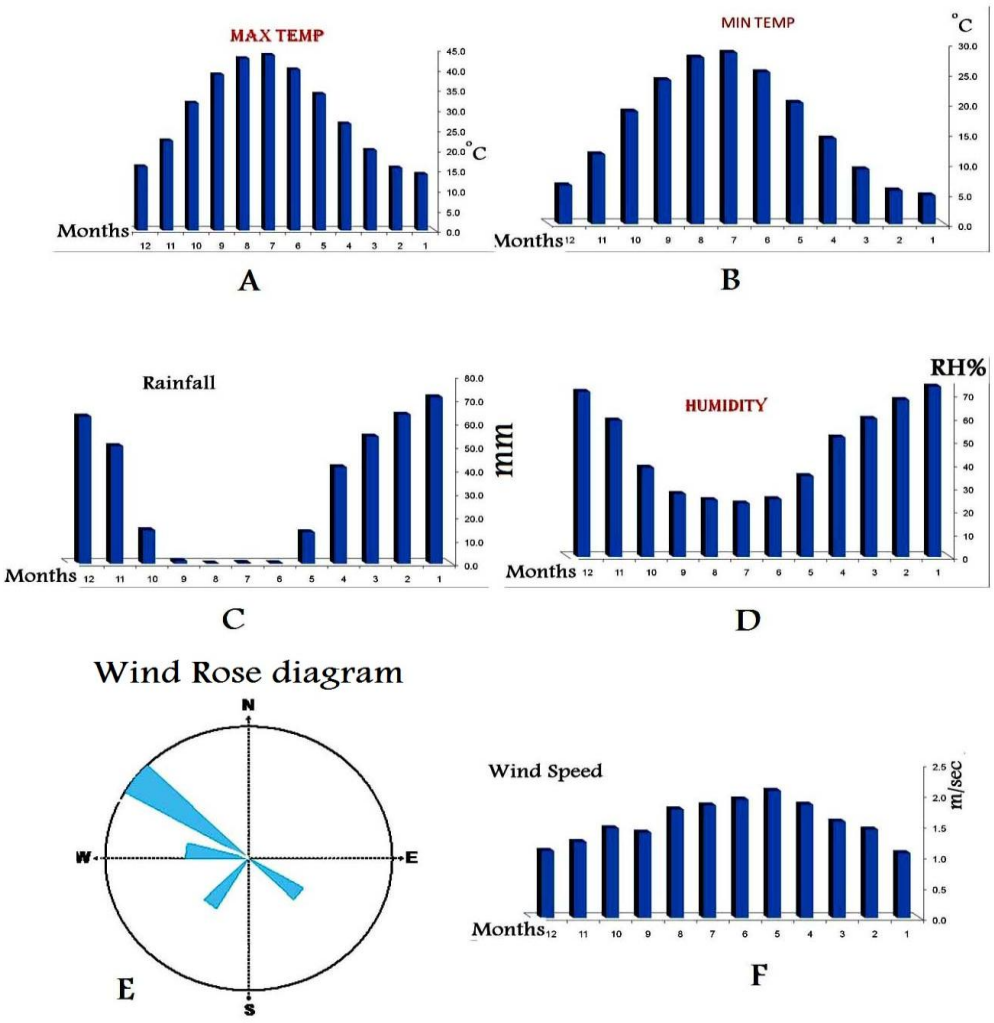

Figure 3- The mean monthly meteorological parameters of Kirkuk station for the years 1980 – 2011. A- mean monthly maximum temperature (^{o}C), B- mean monthly minimum temperature (^{o}C), C- mean monthly rainfall (mm), D- mean monthly Relative Humidity %, E-The rose diagram of annual wind directions for Kirkuk Meteorological Station for years (2002-2011), F- Mean monthly wind speed (m/sec)

2- Total suspended particles (TSP):

The results of the average suspended particles concentration (TSP) (Tables 2), reflect that the highest value recorded for TSP was during October 2010, for sample No. 8 that represents the Eternity fire (2371.8µg/m^3) which is due the presence of the gas flares of the refinery nearby. On the other hand the lowest value was for sample No. 4 that represents the Chorao Control site (192.3µg/m^3) as shown in table (2) and figure (4). In March 2011, the highest recorded value was for sample No. 15 that represents Baghdad transport station (3555.6 µg/m^3) due to traffic intensity at this site, while the lowest value was for samples No. 10 and 11 that represent the Central Isolation Unit at the refinery and the Environmental Department of the Northern Oil Company respectively with value of (229.9 µg/m^3) as shown in table (2) and figure (4). The average concentration of suspended particles (TSP) were significantly higher than the permissible allowable limits of the Iraqi National standards (350) µg/m^3 [3,19]. and the worlds international allowable limits (60-90) µg/m^3 (Table 2) for both periods of this study : October 2010 and March 2011 , the averages were 818.94µg/m^3 and 956.8 µg/m^3, respectively. It was also observed that the TSP concentrations increased at the direction away from the

refinery (fig. 4) mostly at the south east direction that coincides with the wind direction at the studied area.

Table 2 -Comparison TSP concentrations in the studied area with national and world limits [3,17].

Sa. No.	TSP. in October (µg/m^3)	TSP. in March (µg/m^3)	The site name
1.	628.9	253.2	Araffa
2.	440.3	333.3	First unit (refinery)
3.	273.1	238.1	Third unit (refinery)
4.	192.3	238.1	Chorao control
5.	833.3	622.5	Market
6.	1635.2	2068,9	Rahim Awa
7.	740.7	919.5	Gas separation unit (baba)
8.	2371.8	493.8	Eternity fire
9.	1294.5	238.1	Baba residential area
10.	776.7	229.9	Central isolation unit
11.	1111.1	229.9	Environmental department
12.	566	2000	Baba Gurgur hotel
13.	433.1	1666.7	People's action area
14.	317.5	1264.4	K1 control
15.	1234.6	3555.6	Baghdad transport station
Mean	818.94	956.8	
Iraqi National standards[19]	350 µg/m^3	350 µg/m^3	
Intern. limits[3]	60-90 µg/ m^3	60-90 µg/ m^3	

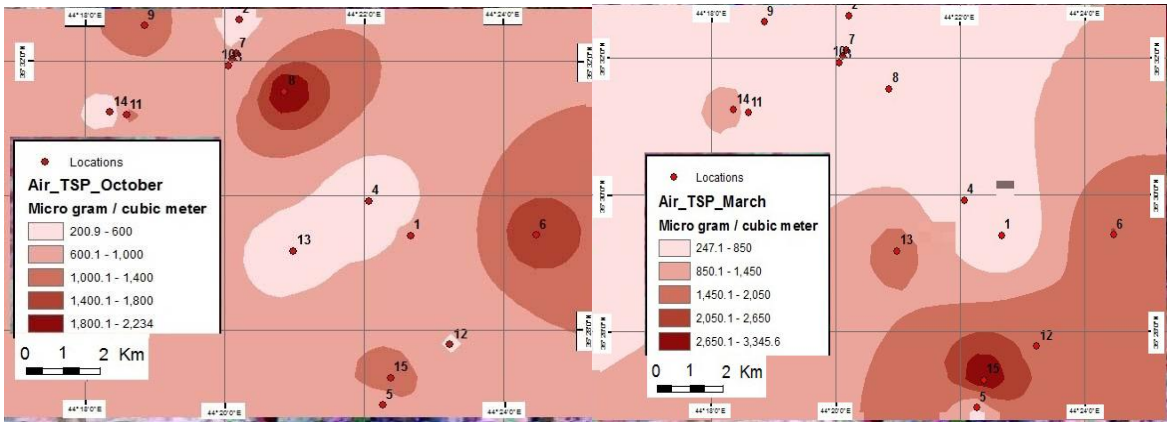

Figure 4- Total suspended particles distribution in air of the studied area at October 2010 and March 2011.

3-Heavy metals analyses and their effect

Suspended solids are important pollutions which consist of suspended minerals and Heavy metals. Inorganic trace elements are commonly present at low levels in nature and there is already a natural level of tolerance. There is, however, a fine division between natural tolerance and toxicity. It is

therefore essential to have good information on the concentration of trace elements in the air. These trace elements pose a threat to human health. Therefore, trace elements should be a priority for evaluation. The source of heavy elements can be divided into two sources, natural and artificial. The sources of heavy metals in air are mainly natural, including geologic sources such as rocks formation, soils, and transported sediments by winds, while the artificial sources include industrial sources that supply the heavy metals to the air and cause contamination of the atmosphere. The trace elements (Pb, Cu, Ni, Cr, and Cd) are designated as priority pollutants by many researchers [1,2,5,6].In the present research, the five heavy metals concentrations (Pb, Cu, Ni, Cr, and Cd), were analyzed by using atomic absorption, from 15 samples. It is expected that the heavy metals concentration varied considerably with the polluted, industrial, and contaminated areas, depending on the wind speed and directions. The results reflect that the mean concentrations of trace metals of all studied stations are shown in table (3) for October 2010 and March 2011 samples. The studied heavy metals mean, minimum, maximum, and health effects are discussed as follow:

Lead (Pb)

The concentration of lead in air of the studied area at October 2010 was 4.56 $\mu g/m^3$ in average, table (3). Comparison these values with the national and world limits noticed that they were higher than these limits. While, the concentration of lead at March 2011 was lower than the national and world limits ٣$\mu g/m^3$, 0.5$\mu g/m^3$ respectively, where the average was 0.045 $\mu g/m^3$, table (3). This decreasing in lead concentration reflects the effect of meteorological conditions at this period.

This element causes stimulation of bronchial mucosa of the respiratory system which results in allergy and asthma. Reaching the nervous system through food and drink will result to headache, fatigue, and cause bone weakness if its rate increases in the human body. The Pb vapors resulting from fuel compounds because of fuel burn evaporation will complex in the environment, the vapors produced had negative effects on living bodies [20].

Copper (Cu)

The concentration of copper in air at october 2010 was 0.031$\mu g/m^3$ in average that were very low than the world limits , table (3). While, copper concentration at march 2011 was (0.115) $\mu g/m^3$ in average. The concentration of copper at the two periods were lower than the world limits. Copper is one of the non-important elements to human body and will be poisonous if its rate increases. Usually, Cu damage effect will not always be present in food because it has high rates in sewage substances used for plants. Its increment through plants in the human blood and liver tissues will cause the Wilson disease which results in changes in tissues of brain and liver and ophthalmic cornea [20].

Nickel (Ni)

The averages of Nickle at two periods were higher than the world limits shown in table (3) , where the average at october period was 0.627 $\mu g/m^3$, While the average of Nickle at march 2011 was 0.474 $\mu g/m^3$. The decreasing of the concentration at march due to the meteorological conditions. Comparison these values with the national and world limits noticed that they were higher than these limits.

Nickel has negative effects on humans and cause bronchial- or nasal carcinoma due to nickel gases. The nickel carbonate (Ni) which results from interaction with carbon monoxide producing complex is carcinogenic to humans and animals resulting in rapid damage of the respiratory system. Its large doses cause many harmful effects like infection of the outer layer of the skin; besides, it affects the kidneys and causes vertigo, bronchitis, and asthma [20].

Chromium (Cr)

The average of Chromium in air of the studied area at october 2010 was 0.233 $\mu g/m^3$. While, the average at march was 0.745 $\mu g/m^3$ as showen in table (3) . Comparison these values with the national and world limits noticed that they were higher than these limits.

People can be exposed to chromium through breathing, and through skin contact with chromium or chromium compounds. The uptake of too much chromium (III) can cause health effects as well, for instance skin rashes. Chromium (VI) is known to cause various health effects. After breathing it in chromium (VI) can cause nose irritations and nosebleeds. Other health problems that are caused by chromium (VI) are: Skin rashes, Upset stomachs and ulcers, Respiratory problems, Kidney and liver damage, Lung cancer and Death. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch [20].

Cademium (Cd)

The averages of Cademium (Cd) in air of the studied area at october 2010 was 0.095 µg/m^3. While the average of March was 0.096 µg/m^3, (Table 3). The little difference between two averages reflect that the concentration of cademium was not effected by season changes. Comparison these values with the national and world limits noticed that they were higher than these limits.

Cadmium will be absorbed easily through respiratory and gastrointestinal systems in humans; when it reaches the blood, it will distribute quickly through human tissues like the liver and kidneys and will take the place of useful elements in human body which prevents their absorption through the intestine, increasing the effect of anemia [20]. Cadmium poisoning results in damage to the kidneys and hypertension and takes the place of calcium. It has an accumulative effect in the human body and cause bone damage. The highest level allowed for cadmium in air is 0.05 mg/m3 according to the WHO [3].

Table 3- Heavy metals concentrations in the air of the studied area in October 2010, and in March 2011, with air standard of the trace elements [3,19].

Heavy metals concentrations	Sample No.	Pb µg/m^3	Cu µg/m^3	Ni µg/m^3	Cr µg/m^3	Cd µg/m^3
October 2010	Min	0.86	0.002	0.46	0.01	0.023
	Max	9.08	0.072	0.86	0.37	0.18
	mean	4.56	0.031	0.627	0.233	0.095
March 2011	Min	0.01	0.04	0.27	0.01	0.072
	Max	0.109	0.217	0.61	2.49	0.16
	mean	0.045	0.115	0.474	0.745	0.096
Standard	Iraqi[19]	3µg/m^3				
	WHO [3]	0.5µg/m^3	0.257 µg/m^3	0.2 µg/m^3	0.04 µg/m^3	0.05 µg/m^3

Air pollution modeling

Air pollution modeling is a numerical tool used by researchers to describe the causal relationship between emissions, meteorology, atmospheric concentrations, deposition, and other factors [5, 6, 8, 13, and 21]. In this study, the Geographic Information Systems (GIS) was applied. Arc GIS 10 modeling of measurements of heavy metals pollutants in air was applied for both sampling periods October 2010 and March 2011,(fig. 5) [17].The cumulative effects of both periods shown in fig.6,that represent the cumulative air model of heavy metals of both periods . The result show that the concentrations of these pollutants increase away from the refinery toward the south west part of the studied area.

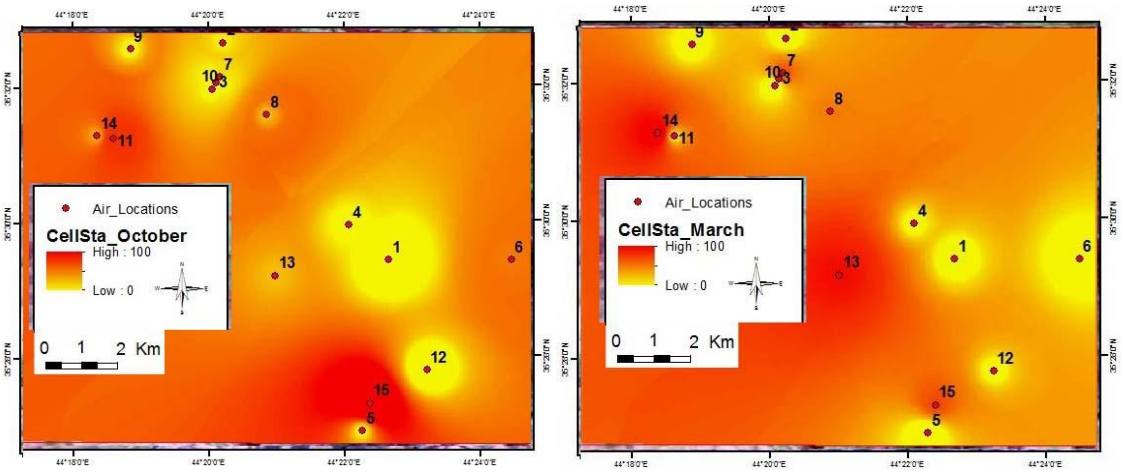

Figure 5- Arc GIS model for Air pollution (heavy metals) of the studied area in October 2010 and March 2011

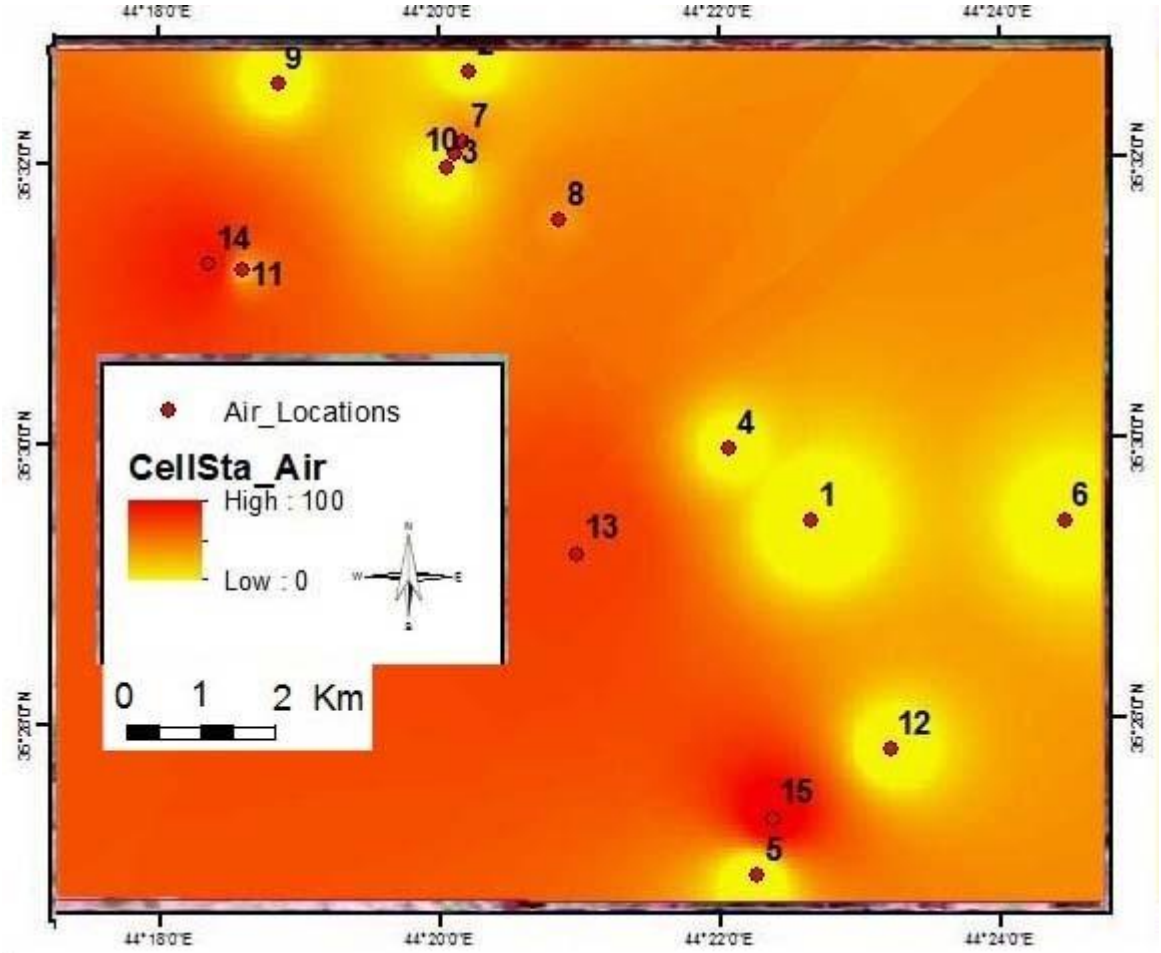

Figure 6-Arc GIS model for Air modeling of heavy metals (total) at the studied area.

Discussion

Comparison of the mean monthly averages of the studied climatic parameters of October and March for the years 1980-2011, indicated that the temperature values increased during October ,while the relative humidity % , wind speed and rainfall were decreased during October and increased during March ,(Table 1, and fig. 3). In spite of that the results of the averages of suspended particles concentration, and all studied heavy metals in air during October 2010 and March 2011, showed a general relative increase toward the wind direction (the south east direction) (Fig. 3). Therefore, the effect of climatic parameters such as temperature, relative humidity %, rainfall, wind speed is not clearly noticed except the wind direction effect that had clearly noticed.

The average concentration of suspended particles (TSP) recorded in this study (Tables 2), were significantly higher than the allowable limits of the Iraqi National standards (350) $\mu g/m^3$ and the worlds international allowable limits (60-90) $\mu g/m^3$ for both of the periods of this study: October 2010 and March 2011, (the averages were 818.94$\mu g/m^3$ and 929.89$\mu g/m^3$ respectively) [3, 19].

The average concentration of heavy minerals (Pb, Cu, Ni, Cr, and Cd) recorded in this study (Tables 3), were significantly higher than the allowable limits of the Iraqi National standards and the worlds international allowable limits for both of the periods of this study, October 2010 and March 2011, except for Pb during march 2011 [3, 19].

It was also observed that the TSP and heavy metals pollutants concentrations for both sampling periods October 2010 and March 2011and the cumulative effects of both periods shown an increase at the direction away from the refinery mostly at the south east direction (figs. 3,4, 5, 6).

Moreover, the study area is located around the Oil Refinery of Kirkuk city, and it covers a wide area of about 200Km^2, so that in addition to the effect of Kirkuk Oil Refinery as air pollutant source, there were many pollutants may be added from different sources within the Kirkuk Governorate such as the Eternity fire, fuel combustion operations, Baghdad transport station with high traffic intensity at this

site as well as K1 control station where many vehicles park waiting to complete their documents. Consequently, the results of the average suspended particles (TSP) and heavy metals concentration (Tables 1 and 2), reflect spatial variation of their recorded values for TSP and heavy metals concentration.

Conclusions

1. The concentration averages of suspended particles (TSP) in this study are higher than the permissible limits of the Iraqi National determinants of (350 $\mu g/m^3$) and the world limits of (60-90 $\mu g/m^3$) at the two periods: October 2010 (818.94$\mu g/m^3$) and March 2011(956.8$\mu g/m^3$). The little difference between the two periods reflects the little effect of the seasonal changes.

٢. Comparison of the averages of the Heavy metals (Pb, Ni, Cr, and Cd) with the national and world limits, noticed that they are higher than these limits. Except for the concentration of Copper (Cu), at the two periods were lower than the world limits.

3- It was also observed that the TSP and heavy metals pollutants concentrations for both sampling periods October 2010 and March 2011and the cumulative effects of both periods shown an increase at the direction away from the refinery mostly at the south east direction (figs. 3,4, 5, 6).

Recommendations

١. Increasing tests and environmental measurements periodically to determine the concentration of pollutants resulting from the refinery and other sources.

٢.Conduct detailed studies of each environmental elements and increase the number of sites studied to identify the most influential sources of environmental pollution.

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